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Corrosion issues of ethanol blends and the effect of water

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Composition of ethanol containing fuels

Code	E5	E10	E15	E25	E85	E100
Composition	max 5% anhydrous ethanol min 95% gasoline	max 10% anhydrous ethanol min 90% gasoline	max 15% anhydrous ethanol min 85% gasoline	max 25% anhydrous ethanol min 75% gasoline	max 85% anhydrous ethanol min 15% gasoline	~5.3% water 100% hydrous ethanol (contains on average 5.3 vol.% water)
Countries	Western Europe today	USA today (Western Europe in near future)	2010 USA EPA approval cars > 2000	Brazil	USA / Europe	Brazil

Gasoline blends for use in regular cars

Flex Fuel Vehicles

Two basic types of corrosion

- **Electrochemical corrosion "wet corrosion"**

  Facilitated by conductivity especially in case of phase separation and the formation of a water layer in low blends (<E10)

Corrosion at the bottom of a tank after phase separation of water
Source: METI, Japan

- **Alcoholate (alkoxide) corrosion "dry corrosion"**

"dry" alcoholate corrosion of a cast Al-alloy in an E10 gasoline blend

Source: TECHNISCHE UNIVERSITÄT DARMSTADT, MPA, IfW, Fraunhofer LBF, SzM

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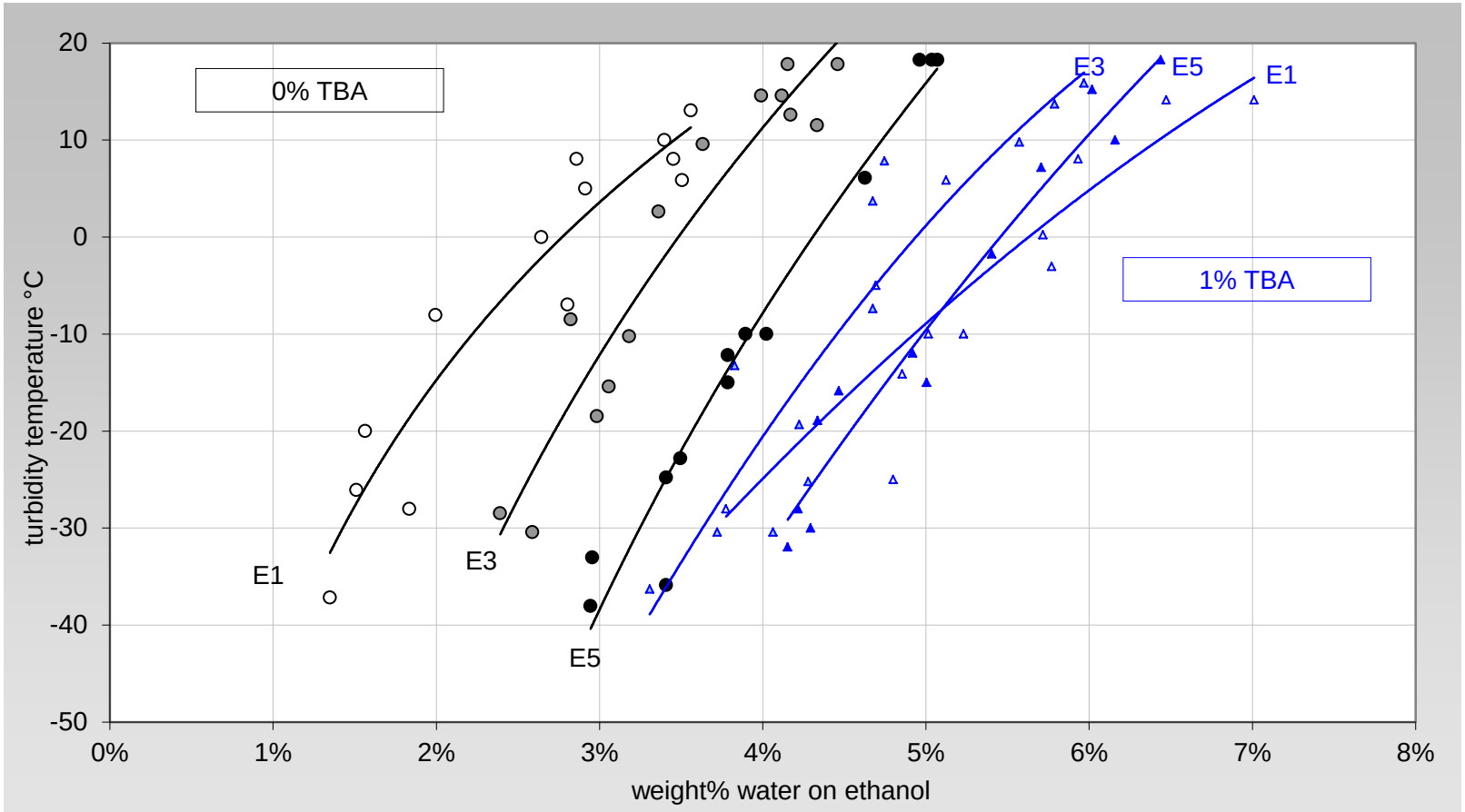
CONCAWE – 2008 Ethanol Report
Phase Stability Ethanol Blends



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

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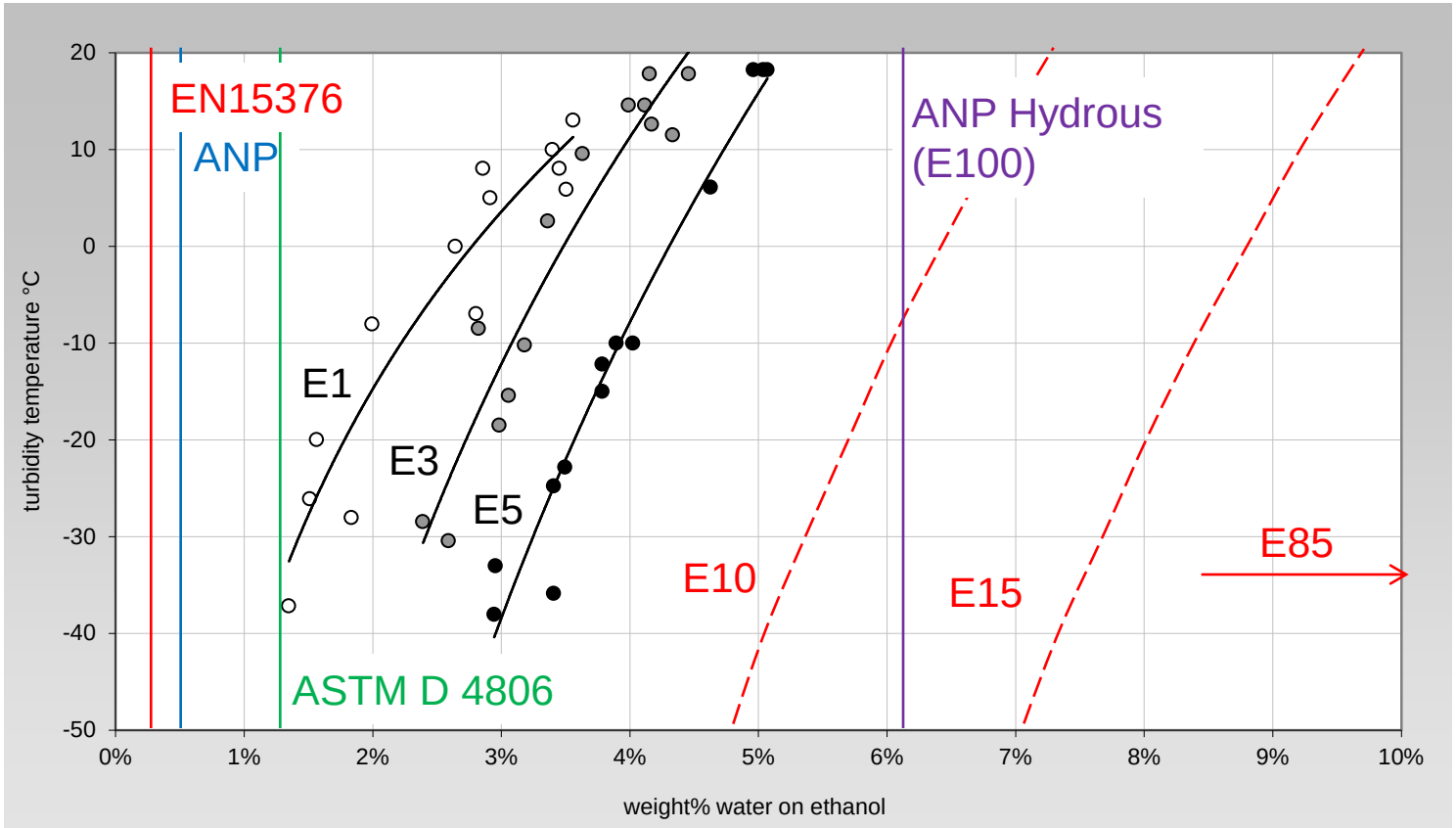
Phase Stability Ethanol Blends Continued



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

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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:**
  - Both the base gasolines as well as the ethanol containing fuels (at 2% ethanol content) were corrosive during the wet corrosion test.
  - These fuels required additisation in order to prevent wet corrosion.
  - At 10% ethanol (bioethanol and synthetic ethanol) none of the fuels were corrosive in the wet corrosion test.

Presented at the XVIII International Symposium on Alcohol Fuels

(Delhi – India ISAF 2010)

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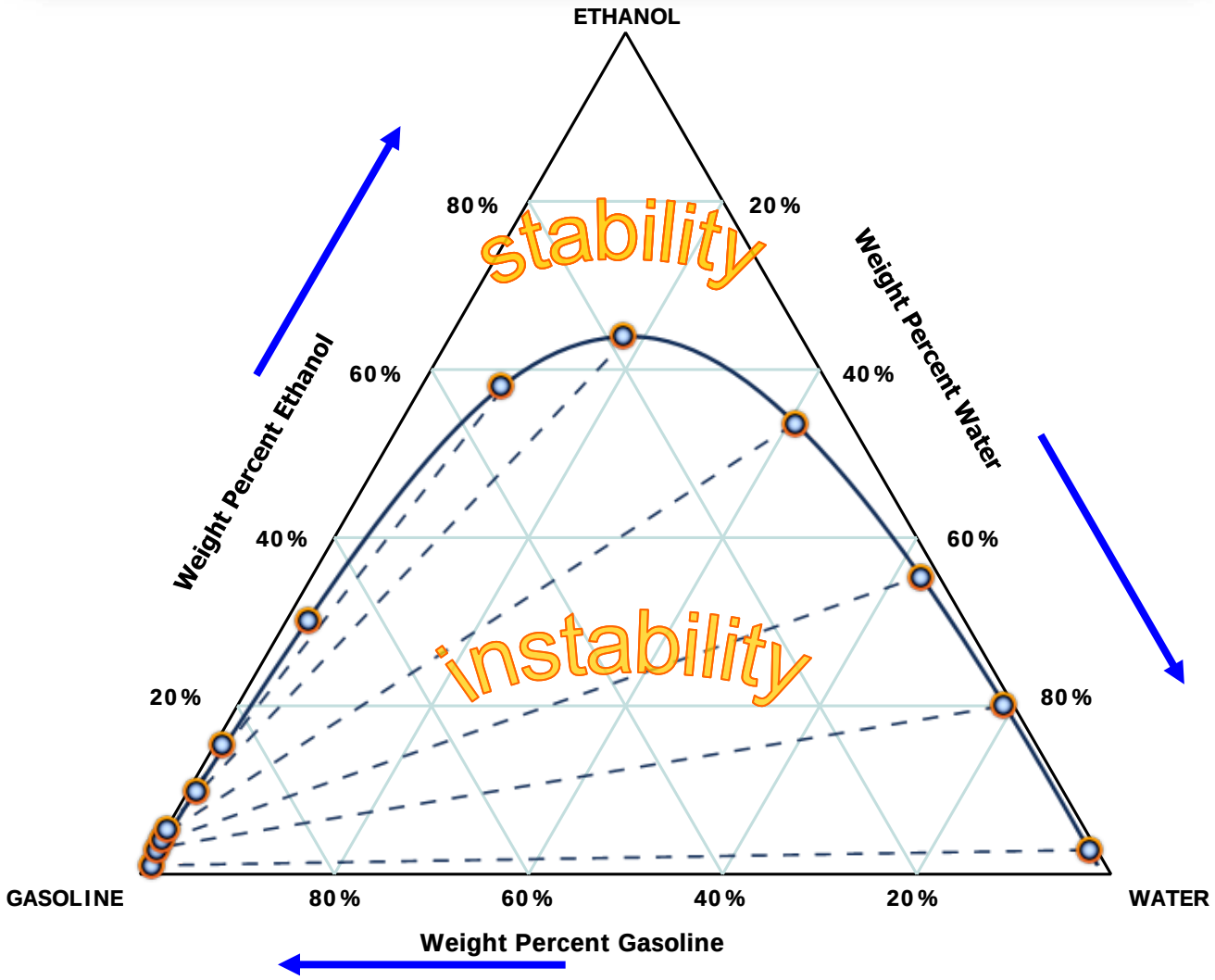
Wet Corrosion & Phase Separation



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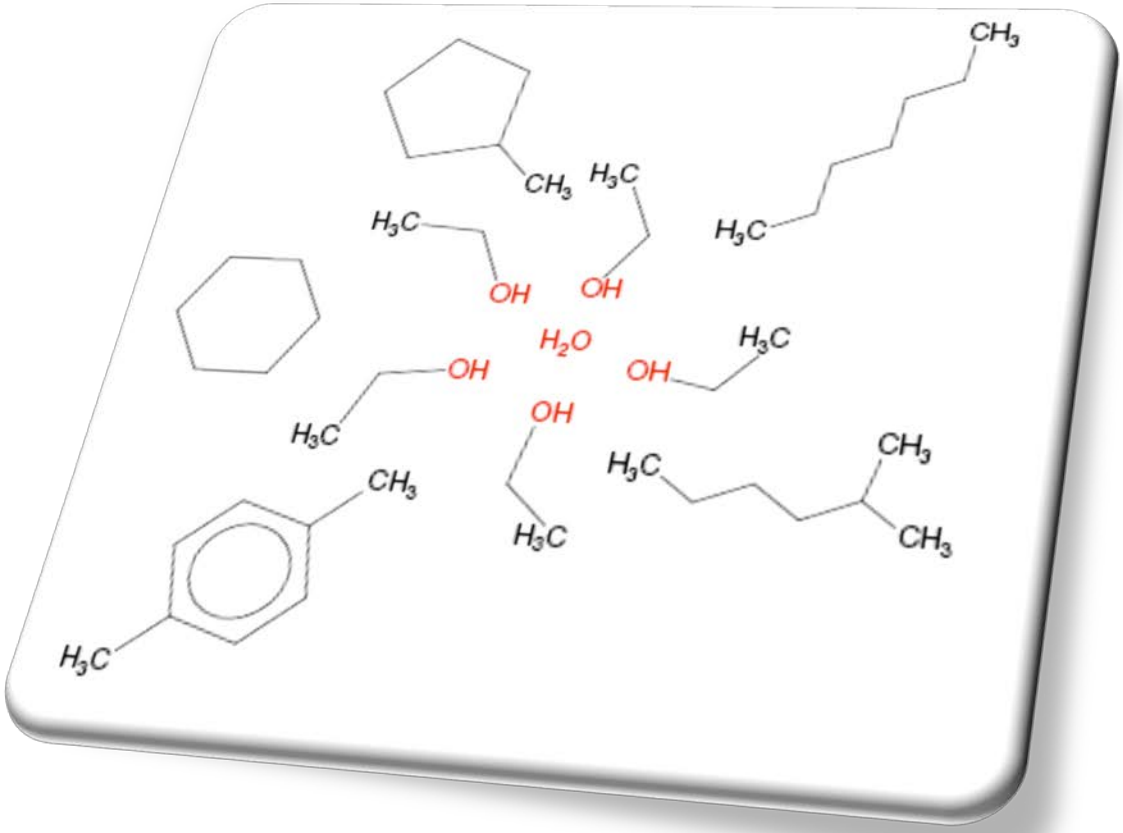
Capture H2O



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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 last week
to see if more hydrous E10
picks up more salts?

salt drops out

free water

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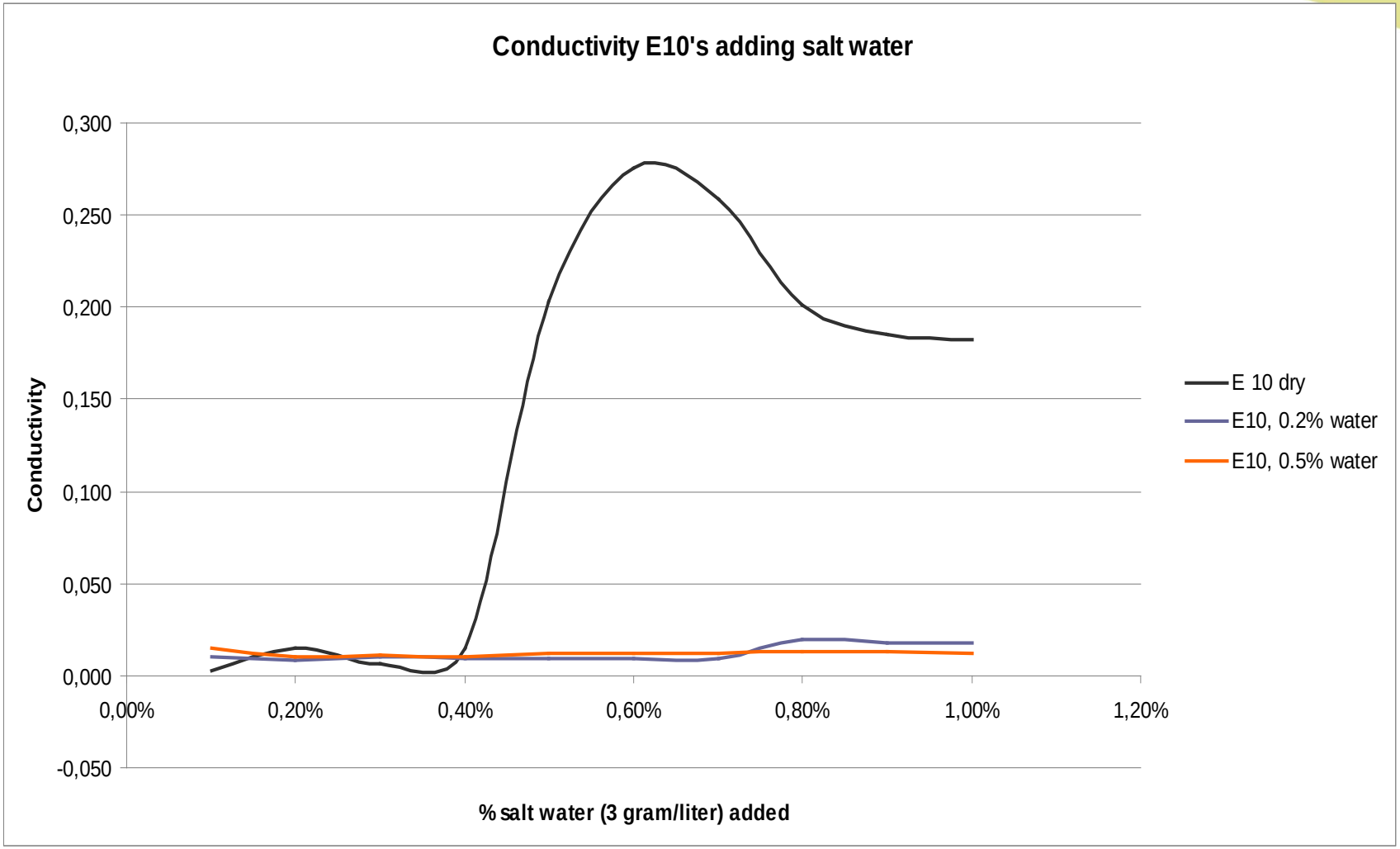
Conductivity E10's adding salt water



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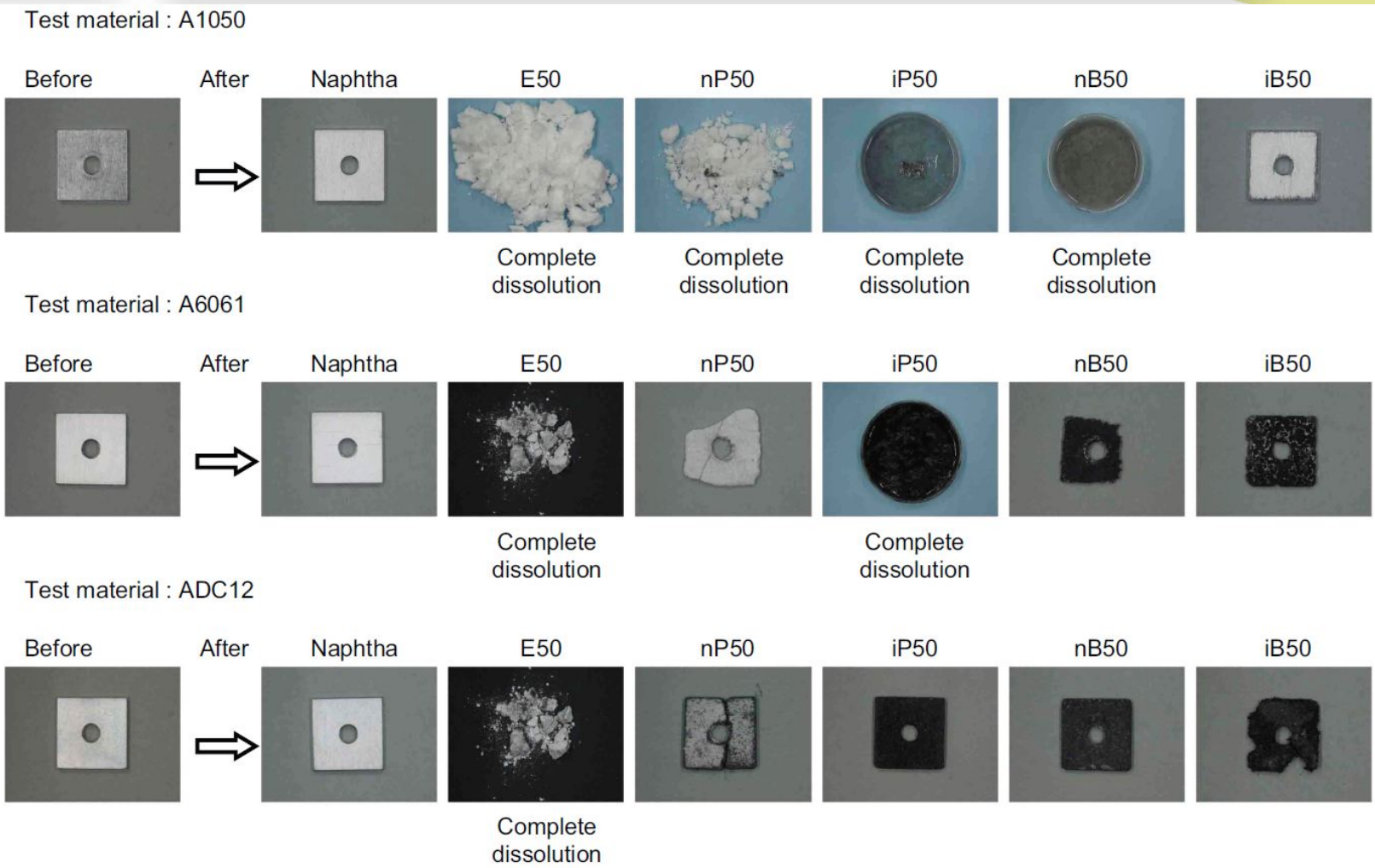
Dry Corrosion Research Japan (JARI)

SAE paper 2005-01-3708 Appendix 3.1 Copyright © 2005 SAE International



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)

SAE paper 2005-01-3708 Appendix 1.1 Copyright © 2005 SAE International

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 (dry) corrosion of aluminum

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)

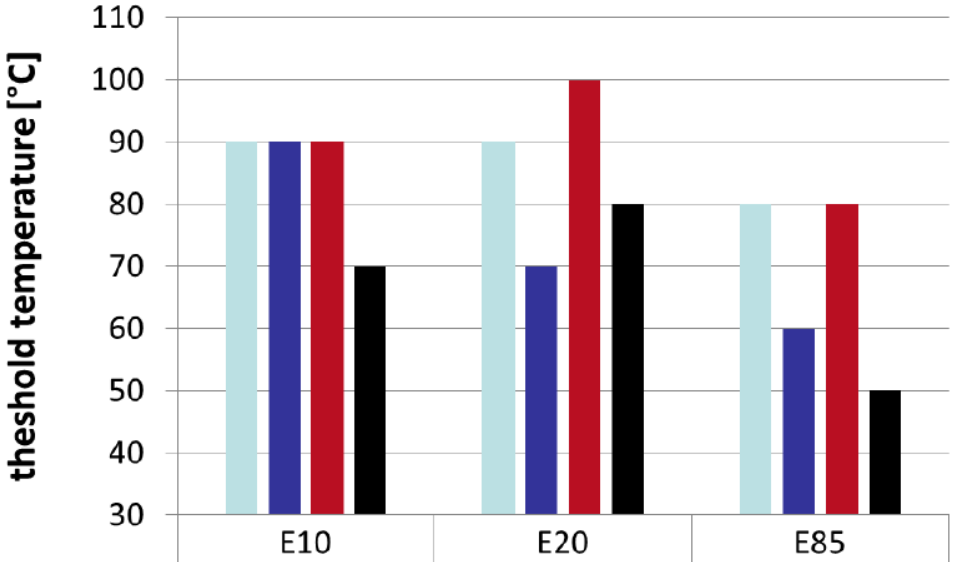
Damaging process may progress rapidly and is accompanied by an increase in pressure due to hydrogen formation

Alcoholate corrosion of Al

Alcoholate (dry) corrosion of aluminum

Technical temperature threshold

Influence of EtOH-content



	E10	E20	E85
Al99,5	90	90	80
AlSi9Cu3	90	70	60
AlMn1	90	100	80
Alusil	70	80	50

Observations:

- **Al99,5 / AlSi9Cu3** drop of threshold with increasing EtOH-content
- **AlMn1 / Alusil** highest threshold for E20, lowest E85
- Lowest overall threshold for cast **Alusil / E85**

Alcoholate (dry) corrosion of aluminum

Technical temperature threshold

Influence of water-content

TECHNISCHE UNIVERSITÄT DARMSTADT

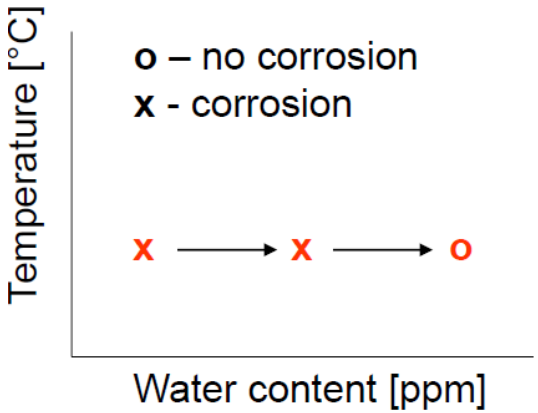
Starting temperature:

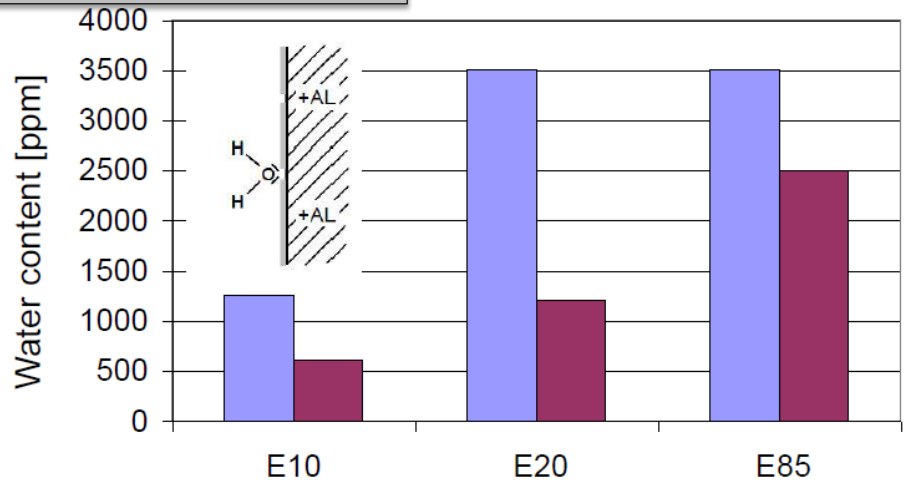
10 °C above the highest temperature level with **assured** alcoholate corrosion ➔ water addition, until no alcoholate corrosion occurs at this temperature level.

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….**





Effect of water on alcoholate corrosion

A little water works as fluoride in toothpaste and avoids corrosion

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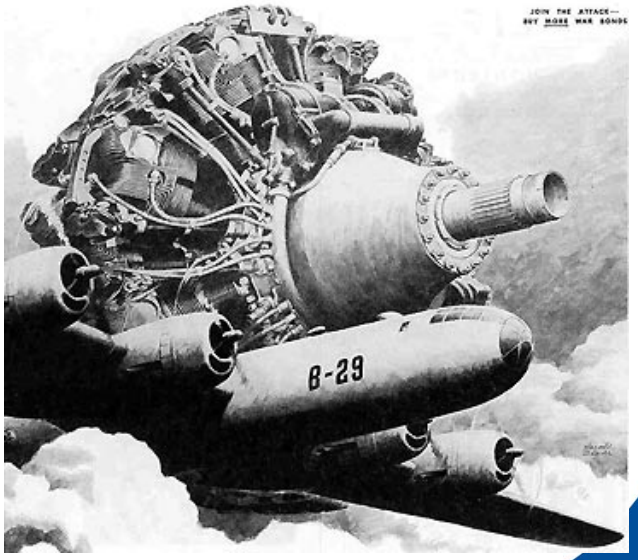
“Water Injection”
70 years proven technology!

2010

1983

1940’s



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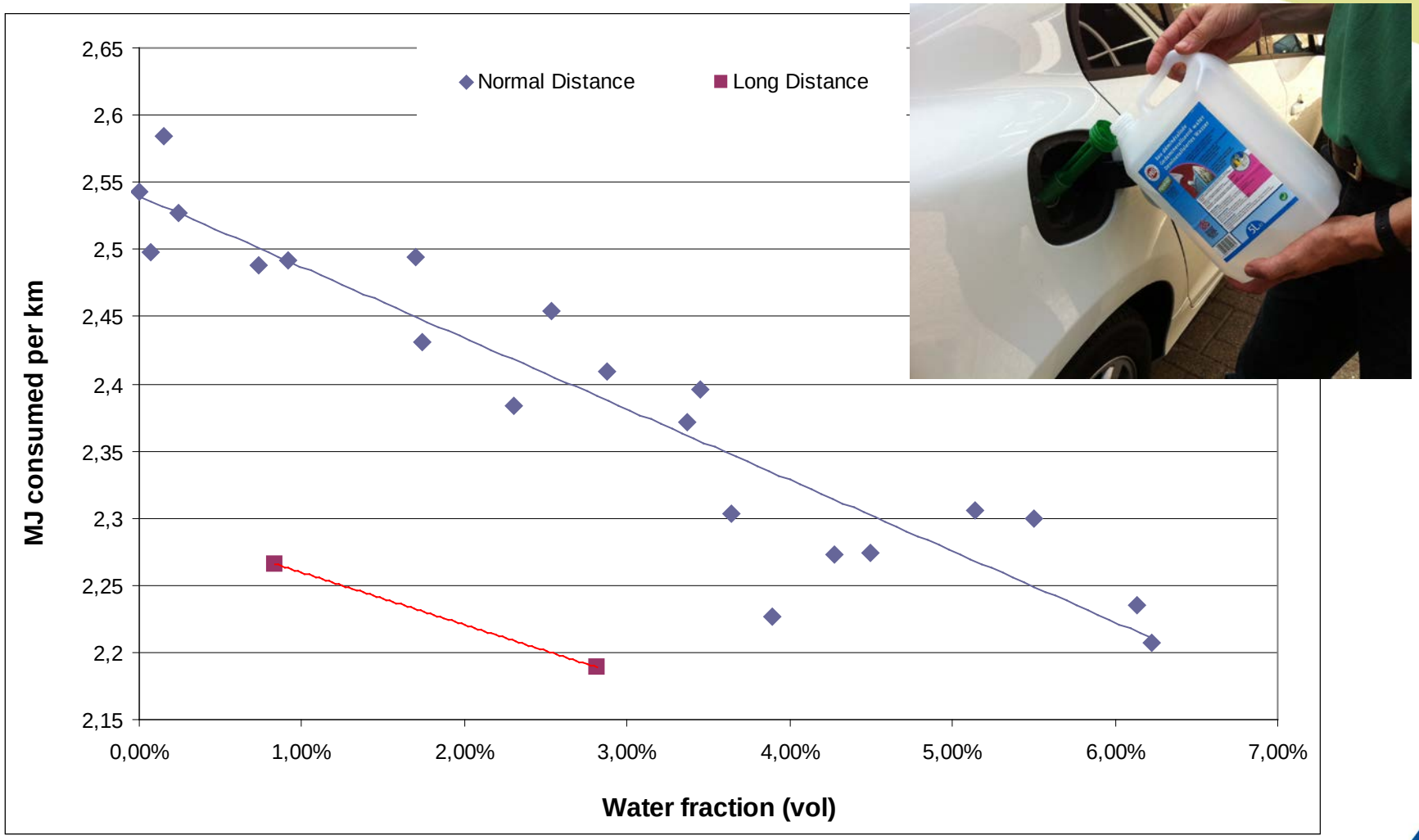
Energy efficiency in a modern down sized turbo charged Volvo S60 T4F (Flex Fuel Vehicle)



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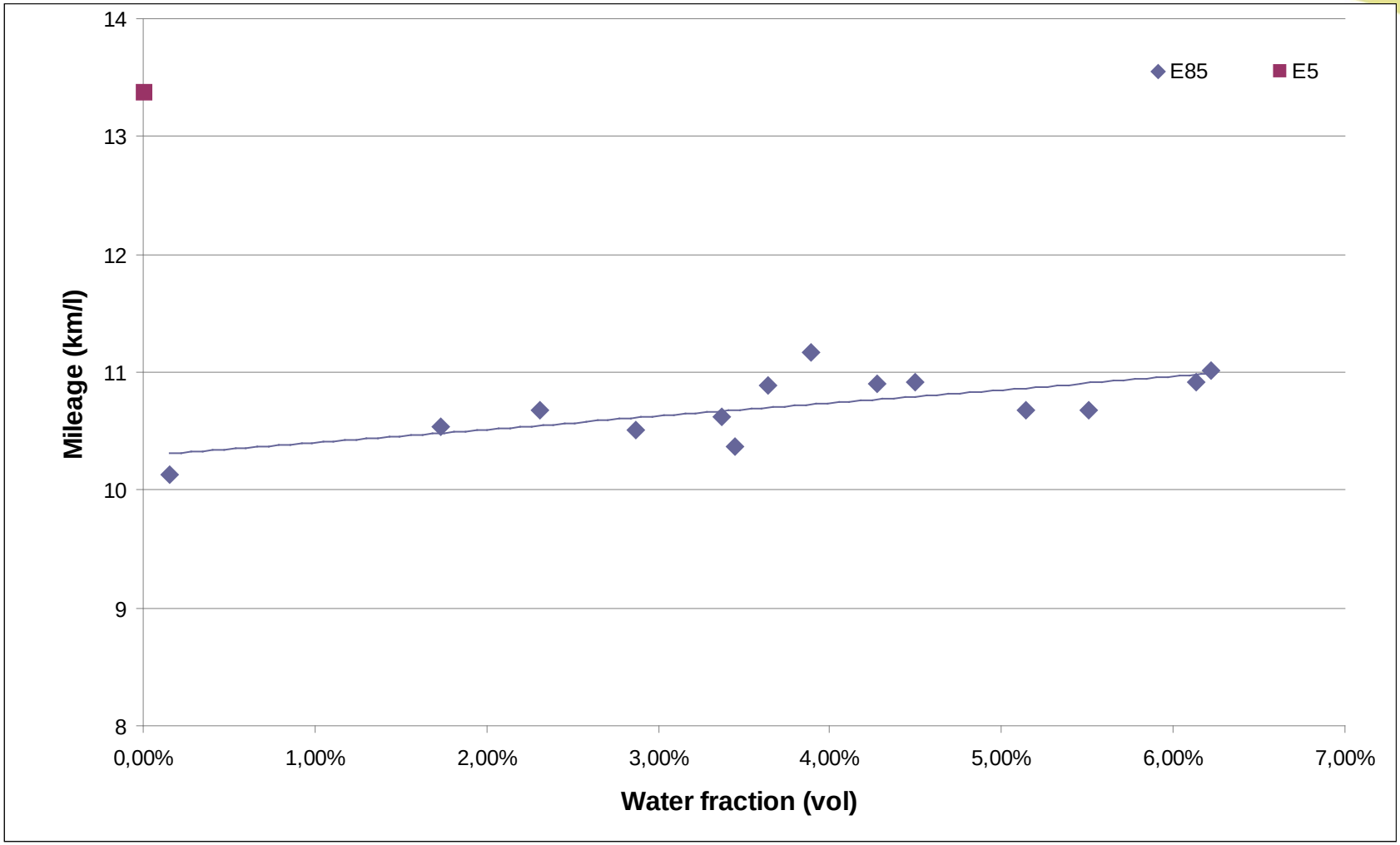
“Water injection” effect on mileage



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Hydrous E15 (hE15) sold at public pumps in the Netherlands since 2008

Revision of 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%	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

Conclusions

- E10 in the US is probably less corrosive than E10 in Europe due to a higher water content in the ASTM D 4806
- We need a minimum water content in the fuel ethanol for direct blending of E5, E10 and higher blends to avoid alcoholate (alkoxide) corrosion.
- We also need to set a maximum water content for E5, E10 and higher blending applications to ensure that we do not run into phase separation issues.
- More hydrous ethanol blends do not pick up more contaminants. They are less hygroscopic and part of the overall water tolerance is already filled up with clean distilled water.
- Water injection has a positive effect on the Well to Wheel energy efficiency and reduces overall emissions.

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