THE ADVENT OF COBLENDING
HARVESTING THE ETBE ETOH SYNERGY

Dr. Walter R. Mirabella
Chairman Biofuels of European Fuel Oxygenates Association

6th Annual Global Refining Summit 2012
Barcelona– Spain 23rd May 2012
Addressing RED & FQD EU Directives

Ambitious Targets

Multiple Challenges

Limited Possibilities

Existing Solution
Challenges (examples)

- FQD: Refiners Obligations vs. Actual “Control”
- RED: Petrol/Gasoil Supply/Demand Unbalance
- Balkanization of EU MS’s Implementation Rules
- Consumers Resistance to “High-Bio” Grades
- Fuel Specifications Limits
FQD & Refiners big Challenge: Full Obligation vs. Partial "Control"

- 6% of total, - 40% of O.I. bit, - 60% of Refining one!
Petrol/Gasoil - Supply/Demand Unbalance: EU Gasoil/Petrol Ratio Growing

- Refineries not designed/structured for current fuels demand ratio
- Petrol export & gasoil import impacting economics & CO₂ emissions (transport)
- Diesel production maximization disoptimising refinery operations & increasing CO₂ emissions
- FAME content specification (7%v/v) limiting actual bio-blending in diesel

Source: Total 2012
Balkanization of National Bio-Blending Obligations

- **IRELAND**
  - 4.0% (v/v)
  - Cumulative Target
  - Petrol + Gasoil

- **NETHERLANDS**
  - 5.25% (e/e)
  - Parallel Targets
  - Petrol: 3.5% (e/e)
  - Gasoil: 3.5% (e/e)

- **NORWAY**
  - 5.0% (v/v)
  - Parallel Targets
  - Petrol: 3.5% (e/e)

- **FINLAND**
  - 6.0% (e/e)
  - Cumulative Target
  - Petrol + Gasoil

- **UNITED KINGDOM**
  - 4.5% (v/v)
  - Cumulative Target
  - Petrol + Gasoil

- **FRANCE**
  - 7.0% (e/e)
  - Parallel Targets
  - Petrol & Gasoil

- **BELGIUM**
  - 6.25% (e/e)
  - Parallel Targets
  - Petrol: 3.5% (e/e)
  - Gasoil: 4.4% (e/e)

- **GERMANY**
  - 6.25% (e/e)
  - Gasoil: 4.4% (e/e)
  - Petrol: 2.8% (e/e)

- **BELGIUM**
  - 4.0% (e/e)
  - Parallel Targets
  - Petrol & Gasoil

- **GERMANY**
  - 5.0% (v/v)
  - Cumulative Target
  - Petrol + Gasoil

- **AUSTRIA**
  - 4.5% (e/e)
  - Cumulative Target
  - Gasoil: 5.2% (v/v)
  - Petrol: 3.1% (v/v)

- **CZECH REPUBLIC**
  - 6.0% (v/v)
  - Gasoil: 6.0% (v/v)
  - Petrol: 4.1% (v/v)

- **POLAND**
  - 6.2% (e/e)
  - Cumulative Target
  - Petrol + Gasoil

- **SLOVAKIA**
  - 5.75% (v/v)
  - Gasoil: 5.2% (v/v)
  - Petrol: 3.1% (v/v)

- **HUNGARY**
  - 4.0% (v/v)
  - Parallel Targets
  - Petrol & Gasoil

- **PORTUGAL**
  - 5.0% (e/e)
  - Gasoil: 6.75% (e/e)
  - Petrol: 2.5% (e/e)

- **ITALY**
  - 4.5% (e/e)
  - Cumulative Target
  - Gasoil: 4.0% (v/v)
  - Petrol: 2.0% (v/v)

- **BULGARIA**
  - 5.0% (v/v)
  - Gasoil: 5.0% (v/v)
  - Petrol: 4.0% (v/v)

- **LATVIA**
  - 5.0% (e/e)
  - Parallel Targets
  - Petrol & Gasoil

- **FINLAND**
  - 6.0% (e/e)
  - Cumulative Target
  - Petrol + Gasoil
Bio-blending Obligations in Largest EU Fuel Markets
Consumers Psychological Resistance to E10

“My car is on the E10 not-suitable list by OEM”

“It might damage my car”

“It will compromise my vehicle warranty”

“It will worsen car performances”

“It would provoke engine efficiency loss”

“I buy litres, but I need energy (oxygen doesn’t burn)”

“If «they» discount it, there must be something dirty”

“High bio compete with food and feed”

“This thing is too new: let others be the guinea pigs”
Vehicle/Engines Compatibility/Operability

Fuel filter blockage

Galvanic corrosion

Enleanment

Drivability

Deposit formation

Material compatibility
Only Few Possibilities

**CO₂ Reduction Effectiveness of Bio-components**

**High Bio-components Blending Percentage**

**Exploitation of «best seller» Petrol Grade (E5)**
Existing Solution

- Adopting Immediately Available Consolidated Options
- Maximizing Actual Bio-energy Blending within E5
- Optimizing Logistics & Operations
- Capturing Bio-components WTW CO₂ Saving Potential
- Harvesting Synergetic «Non-linear» Effects
Fuel-Ethers % Content % in UE27 Petrol

Fuel-Ethers Consumption EU 2010 ~5 million Tons

- ETBE (55%)
- TAME (5%)
- MTBE (40%)

Source: Fuel Ether Reach Consortium, EFOA
ETBE: A Multifaceted Benefits Carrier

- Environment
- VECHEL
- Economic

- VOCs
- CO₂
- Azeotrope
- Permeation
- H/C Ratio
- Logistics
- Bio-energy
- Volatility

- Driving
- Distillation
- Water Toler.
- Mechanical Comp.
- Hygroscopy

- CO₂
- Hydrogen
- Carbon

- 95 E5

- Fuel uptake
- Octane Barr.
- Blendstock
- Ref. Flexibility
- Savings
COBLENDING ETBE AND ETHANOL
..and “Co-blending” further offers Additional Specific Benefits!

Blending more Bio-energy within Petrol Specs Limits

Capturing Bio-components' Well-to-Wheels CO₂ Saving Potential

Minimizing Quality “Give-away” and fossil base-stock cost, via ETBE-containing “DBEB”[*] for E5/E10

Harvesting Synergetic "Non-linear" Effects of Bio-components

[*] Dual Blend-stock for Ethanol Blending
53% more bio-energy into E5 via “Co-blending”

“Alcohol-only”
Ethanol

Limiting Petrol Spec. → 5%v/v ETOH

Bio-energy Content → 3.3%

ETBE Content → 0%

Oxygen Content → 1.8%

O₂ Limit Exploitation → 68.2%

“co-blending”
ETBE+ETOH

2.7%m/m O₂

5.1%

5.55%

2.7%

100%
E5: “Co-blending” Enables Significant Non-compliance Penalty Saving
(German Example)

“Alcohol-only” Ethanol

“co-blending” ETBE+E Alonso

Bio-energy Content

% e/e

Δ% [1]

Additional Penalty Avoidance Value

€/TPET

Mill-€/Y [2]

[1] On top of what achievable with 5%v/v ETOH directly blended into E5 “Protection Grade”

[2] Example based on an average refinery petrol production of 1.5 million tons per year
Co-blending vs. Ethanol only: 1) The Flow

**Co-Blending**

- HCBS$_1$ (94.15%v/v, 5.85%v/v)
- ETBE

**Ethanol-Only**

- DBEB
- ETOH (95%v/v, 5%v/v, 5%v/v, 95%v/v)
- E5 (92.21%v/v, 7.79%v/v)
- E10 (10%v/v)
- HCBS$_2$ (90%v/v)

HCBS = HydroCarbon Blend-Stock
DBEB = Dual Blendstock for Ethanol Blending
Co-blending vs. Ethanol only: 2) E5 Bio-energy

Co-Blending

HCBS$_1$ 94.15%v/v 5.85%v/v ETBE

DBEB

E5

Bio-energy Content

5.1%e/e

Ethanol-Only

ETOH 95%v/v 5%v/v 5%v/v 95%v/v

HCBS$_2$

ETOH

HCBS = HydroCarbon Blend-Stock

DBEB = Dual Blendstock for Ethanol Blending
Co-blending vs. Ethanol only: 3) Dual-BOB quality

Co-Blending

HCBS₁

Motor Octane Contribution Saving\(^{(a, b)}\)

1.8 \text{MON} 0.6

Vapour Pressure Compensation Need\(^{(a, c)}\)

6.3 \text{kPa} 7.8

E5 RVP «Give-Away»\(^{(a, c)}\)

0 \text{kPa} 1.84

0 \% 3.06

Ethanol-Only

HCBS₂

(a) vs. Finished Petrol Specs
(b) The Higher the Better
(c) The Lower the Better

HCBS = HydroCarbon Blend-Stock
“The use of bio-ETBE reduces refining crude-oil need and processing intensity, requires less fuel and, implying relevant petrol composition changes, allows the reduction of carbon factor and lesser CO$_2$ emissions”

“This study indicated that, when bio-ETBE is used, the resulting modification of refinery operations determine a significant reduction of greenhouse gases emissions”

“Best results by far are obtained when ethanol is converted to bio-ETBE. The use of ETBE can allow the saving of 4 times the primary energy required to produce its fossil alternative. IFEU recommends to exploit the whole potential of bio-ETBE”
ETBE: Two Relevant CO$_2$ Saving Contributions

\[ \frac{T_{CO2}}{T_{ETBE}} = 0.953 \]

Key ETBE blending properties, like vapour pressure, distillation characteristics and octane contribution, affecting fuel formulation, reduce refinery operations’ CO$_2$ emissions, by reducing carbon and aromatics content as well as the use of refinery fuel.

[1]
The whole is more than the sum of its parts.

Aristotle, *Metaphysica*
Harvesting Synergetic "Non-linear" Effects of Bio-components

- Increasingly stringent technical and environmental petrol specifications, makes it relevant and urgent to try and fully exploit all the positive characteristics of various blend-stocks used by refiners for formulating finished fuels;

- Several studies have already demonstrated that co-mixing different blend-stocks can yield a better-than-linear blending performance;

- A specially interesting and relevant case is the co-blending of ethanol and ethers (ETBE), considering the key role that these two bio-components play in recent bio-fuels policies;

- Some of the chemical-physical reasons for the distinct synergetic blending effect of those oxygenated molecules comes from their polar nature, as well as from the hydrogen-bonding effects;

- New ad hoc studies are currently under going to better quantify and qualify those effects;

- Petrol specifications that benefit from the «co-blending effect» include volatility (BRVP), distillation curve (E70), octane performance (MON & RON) and water tolerance.
Several studies confirmed synergy

- “Synergies Between Ethanol and TAME as Gasoline Oxygenates”. Sasol. 2002


- “Addition of an azeotropic ETBE/ethanol mixture in eurosuper-type gasolines”. Federal University of Rio Grande do Sul. 2006


- “Volatility and phase stability of petrol blends with ethanol”. Institute of Chemical Technology of Czech Republic. 2009
Conclusion

Harvesting the synergy of co-blending bio-ETBE and bio-Ethanol, represents an effective, immediate and practical avenue to address both EU and MSs ambitious bio-fuel targets. It actually enables significantly higher bio-energy content, while both enhancing environmental benefits and improving operators flexibility.