THE ADVENT OF COBLENDING
HARVESTING THE ETBE ETOH SYNERGY

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BioFuels: 3 Key Entities

- European Fuel Oxygenates Association
- Italian Chemical Industry Federation
- Italian Biofuels Technology Platform
Bio-Ether (ETBE) is for Petrol what Bio-Ester (FAME) is for Gasoil
Bio-Petrol Supply Chain: Ethers in Central Position

**Biomass**
- Feedstock Growing

**Primary BioComponent**
- Ethanol Fermentation

**Derivative BioComponent**
- Ether Synthesis

**Fuel**
- Petrol Formulation

**Vehicle**
- Engine Powering

“UP-STREAM”

“DOWN-STREAM”
## Addressing RED & FQD EU Directives Challenge

| What                  | 10% Bio-energy in Fuels (RED)  
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<th>6% CO₂ Saving (FQD)</th>
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[*] Blend-stock Before Ethanol Blending
Two “Interactive” EU Directives

**FUEL QUALITY**
Directive 2009/30/EC

GHG Emissions Reduction
6% (+2% +2%)

**RENEWABLE ENERGY**
Directive 2009/28/EC

Renewable Energy Transport
10%

Sustainability Threshold
-35% (2010)
-50% (2017)
-60% (2018)
Bio-component to Address Broader Sustainability

**ECONOMIC**
- Capital Efficiency
- Growth Enhancement
- Innovation
- Margin Improvement
- Risk Management
- Shareholders Return

**ENVIRONMENTAL**
- Clean Air, Water & Land
- Emissions Reductions
- No Waste, Releases & Spills
- Biodiversity
- Access to Potable Water
- Crisis Management
- Environmental Justice
- Environmental Regulations
- Global Climate Change
- Safety & Health
- Life-Cycle Management
- Product Stewardship
- Products to Services
- Resource Efficiency

**SOCIAL**
- Community Outreach
- Diversity
- Human Rights
- Indigenous Communities
- Labour Relations
- Business Ethics
- Job Creation
- Local Economic Impacts
- Security
- Skills Enhancement
- Social Investments
- Access to Potable Water
- Crisis Management
- Environmental Justice
- Environmental Regulations
- Global Climate Change
- Safety & Health

**Sustainable**
-熊able
- Viable
- Equitable

- Capital Efficiency
- Growth Enhancement
- Innovation
- Margin Improvement
- Risk Management
- Shareholders Return
- Environmental
- Clean Air, Water & Land
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- Global Climate Change
- Safety & Health
FQD & Refiners big Challenge: Full Obligation vs. Partial "Control"

- 4% Crude Production
- 10% Fuel Refining
- 1% Distribution Retail
- 85% Engine Combustion

15% Oil Ind.

- 6% of total,
- 40% of O.I. bit,
- 60% of Refining one!

Operations
Energy
Efficiency

Bio-Fuels
Blending

Carbon
Capturing
& Storage
Petrol/Gasoil - Supply/Demand Unbalance: Petrol & Gasoil Domestic Demand Italy

Source: Elaboration from UP (Italian Oil Industry Association)
Petrol/Gasoil - Supply/Demand Unbalance: EU Gasoil/Petrol Ratio Growing

Balkanization of National Bio-Blending Obligations

**IRELAND**
- 4.0% (v/v)

**UNITED KINGDOM**
- 3.5% (v/v)

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

**SPAIN**
- 3.9% (e/e) Ind.
- 5.83% (e/e) Cum.

**PORTUGAL**
- Gasoil 7.0% (v/v)

**NETHERLANDS**
- 4.0% (e/e)
- Parallel Targets Pertrol & Gasoil

**GERMANY**
- Gasoil 4.4% (e/e)
- Pertrol 2.8% (e/e)

**ITALY**
- 4.0% (e/e)
- Obiettivo cumulativo Pertrol + Gasoil

**AUSTRIA**
- Gasoil 6.3% (e/e)
- Pertrol 3.4% (e/e)

**FINLANDI**
- 4.0 (e/e)

**POLAND**
- 5.75% (e/e) Indicative

**CZECH REPUBLIC**
- Gasoil 4.5% (v/v)
- Pertrol 3.5% (v/v)

**SWEDEN**
- 5.75% (e/e) Indicative

**POLAND**
- 5.75% (e/e) Indicative

**SLOVAKIA**
- 5.75% (e/e) Indicative
Consumers Resistance to “High-Bio” Grades (E10)
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
ETBE: A Multifaceted Benefits Carrier

- Vehicular Efficiency
- Economic Flexibility
- Environmental Impact
- Water Tolerance
- Driveability
- Hydroscopy
- Commodity Water
- CO₂
- Azeotrope
- Permeation
- H/C Ratio
- Logistics
- Bioenergy
- Volatility
- VOCs
- Carbon Dioxide

Benefits Carrier: ETBE
..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 “Dual BBEB”[^] for E5/E10

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

[^] Blend-stock Before Ethanol Blending
Exploiting Bio-related Petrol Specifications Limits (E5)

- Oxygen: 2.7% m/m
- ETBE: 15.0% v/v
- Ethanol: 5.0% v/v
53% more bio-energy into E5 via “Co-blending”

<table>
<thead>
<tr>
<th></th>
<th>“Alcohol-only” Ethanol</th>
<th>“Ether-only” ETBE</th>
<th>“co-blending” ETBE+ETOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limiting Petrol Spec.</td>
<td>5% v/v ETOH</td>
<td>15% v/v ETBE</td>
<td>2.7% m/m O₂</td>
</tr>
<tr>
<td>Bio-energy Content</td>
<td>3.3%</td>
<td>4.6%</td>
<td>5.1%</td>
</tr>
<tr>
<td>ETBE Content</td>
<td>0%</td>
<td>15%</td>
<td>5.55%</td>
</tr>
<tr>
<td>Oxygen Content</td>
<td>1.8%</td>
<td>2.3%</td>
<td>2.7%</td>
</tr>
<tr>
<td>O₂ Limit Exploitation</td>
<td>68.2%</td>
<td>86.3%</td>
<td>100%</td>
</tr>
</tbody>
</table>
German Example (1):
Bio-energy Targets and E5 Blend “Options”

- E5 Petrol
- Gasoil

- Fuel-type-specific target
- Maximum bio-energy contribution above minimum target
- Excess from B7 available for petrol (excluding B100 contribution)
- Residual Gap to cumulative target (excluding B100 and E85 contribution)
German Example (2):
53% more bio-energy into E5 via “Co-blending”

- Residual contribution from biodiesel exceeding bio-energy cumulative target in gasoil (B7)
- Maximum bio-energy contribution
- Residual Gap to cumulative target (excluding B100 and E85 contribution)
German Example (3):
E5: “Co-blending” Enables Significant Non-compliance Penalty Saving

“Alcohol-only” Ethanol

“co-blending” ETBE+ETOH

Bio-energy Content → %e/e

3.3

0

5.1

0

Additional [1] Penalty Avoidance Value

€/T_{PET}

Mill-€/Y [2]

0

14.0

0

21.0

[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
**“Dual” BOBs for E5 and E10**

**BOBcb** = ETBE-containing E5/E10-dual-BBEB that, when blended with 5%v/v ETOH, yields E5 @ 2.7%m/m O$_2$

**BOBdb** = Oxy-free E5/E10-dual-BOB, yielding E5 with 5%v/v ETOH, and E10 with 10%v/v ETOH

**E5cb** = E5 petrol (protection grade) “co-blend” ETBE/ETOH – 2.7%m/m O$_2$

**E10cb** = E10 petrol “co-blend” ETBE/ETOH – 3.7%m/m O$_2$

**E5db** = E5 petrol containing only ETOH @ 5%v/v

**E10bd** = E10 petrol containing only ETOH @ 10%v/v
Co-blending: HC Blend-stock RVP & MON Savings

**BOBcb** = ETBE-containing E5/E10-dual-BBEB that, when blended with 5%v/v ETOH, yields E5 @ 2.7%v/vO2

**BOBdb** = Oxy-free E5/E10-dual-BOB, yielding E5 with 5%v/v ETOH, and E10 with 10%v/v ETOH

Conservatively neglecting positive non-linear “co-solvency” effects of ETBE
Co-blending avoids RVP “give-away” on E5

In order to be used for both E5 and E10 petrol grades, and due to the non-linear blending volatility behaviour of ethanol, the oxygen-free dual-BOB has to feature lower than specification volatility, to ensure RVP specs compliance of E5. This unwanted effect doesn’t occur with ETBE-containing dual BBEB.
Co-blending Addresses ETOH E70 Boost

<table>
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<tr>
<th>Blending Type</th>
<th>Fossil HC Blendstock</th>
<th>E5 Grade</th>
<th>E10 Grade</th>
<th>E5 Grade</th>
<th>E10 Grade</th>
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<tr>
<td></td>
<td>BOB</td>
<td>E5db</td>
<td>E5cb</td>
<td>E10db</td>
<td>E10cb</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ETOH-only 5%v/v</td>
<td>Co-blend ETOH/ETBE</td>
<td>ETOH-only 10%v/v</td>
<td>Co-blend ETOH/ETBE</td>
</tr>
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</table>

- 6.4 (absolute)
- 40% (increase)
ETBE Further Reduces CO₂ Emissions

HART July 2007

“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”

CE-Delft October 2007

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

IFEU August 2008

“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 CO₂ emissions”
ETBE: Two Relevant CO₂ Saving Contributions

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

[1] Key ETBE blending properties, like vapour pressure, distillation characteristics and octane contribution, affecting fuel formulation, reduce refinery operations’ CO₂ emissions, by reducing carbon and aromatics content as well as the use of refinery fuel.

[2] Based on CO₂ cost at current ETS value of 20 €/T_{CO2}

65% UPSTREAM \rightarrow 0.618 \rightarrow +54% \rightarrow 35%^{[1]} \rightarrow 0.335 \rightarrow 100% FIELD-TO-TANK \rightarrow 0.953

28^{[2]} $/T_{ETBE}
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.
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.