



# BIO-OILS IN REFINERY OPERATIONS:

## Hybrid fuel production in FCC unit

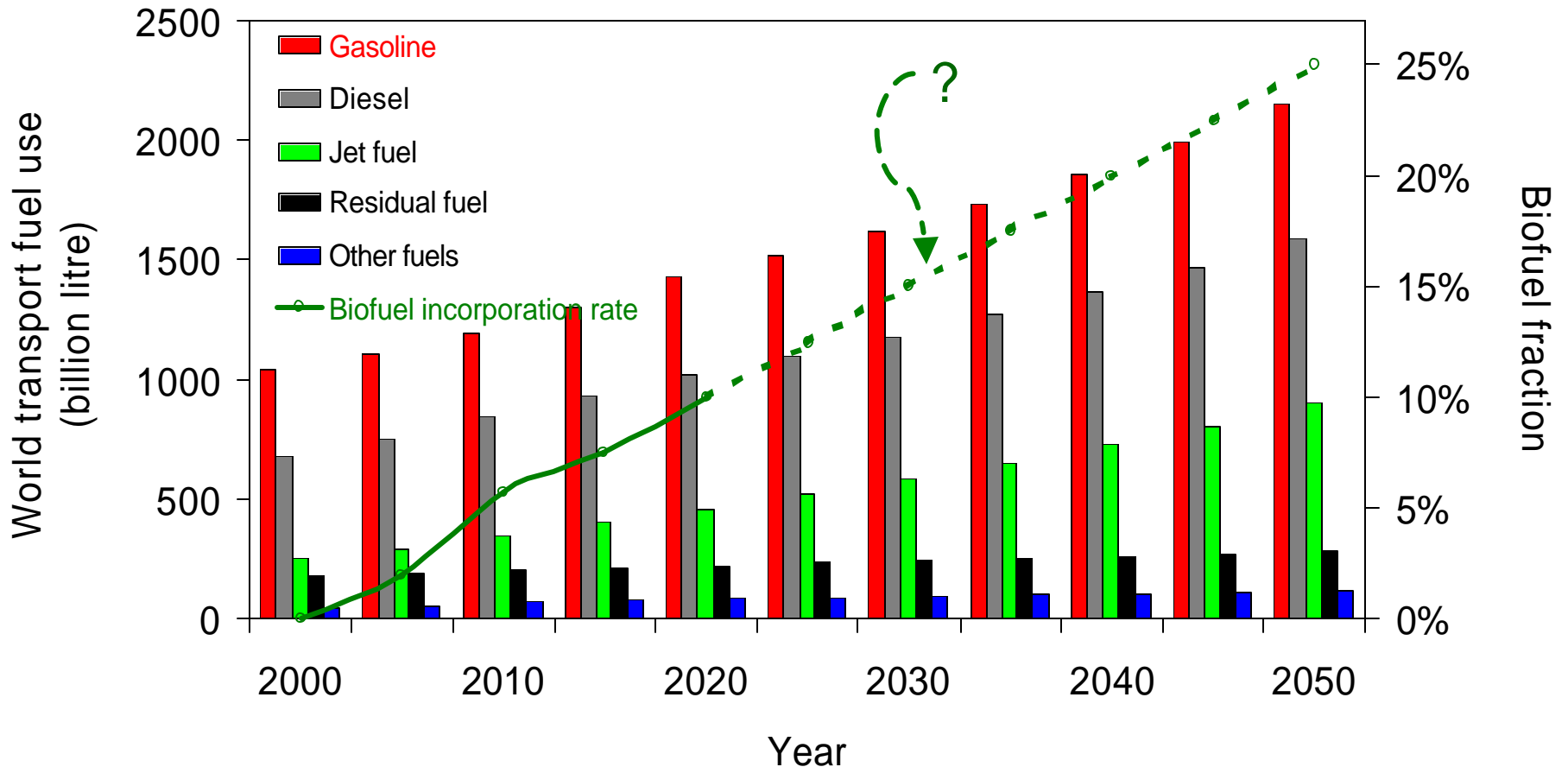
Gabriella Fogassy, Yves Schuurman, Claude Mirodatos

NWBC – 2009, September 3, 2009, Helsinki

# Bio-fuel directives: increasing % of renewable products

## Which strategy: blending or co-processing?

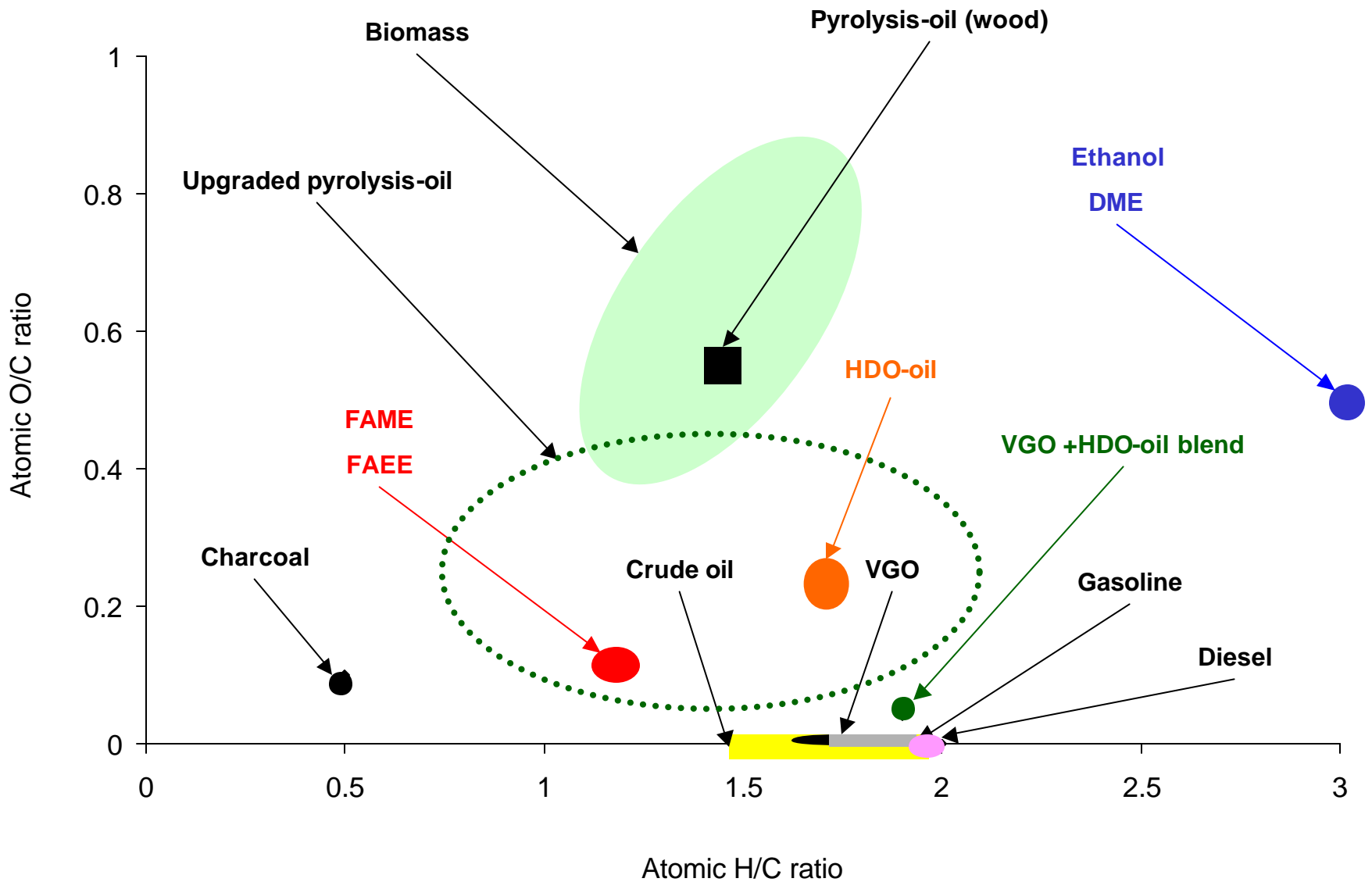
### Which fuel is concerned?



Source: IEA/SMP Spreadsheet model calculations

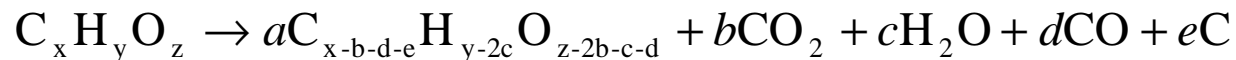


# Van Krevelen diagram for fuels



# Challenge : maintain gasoline quality after adding 20 wt.% pyrolysis-oil to the VGO cracking

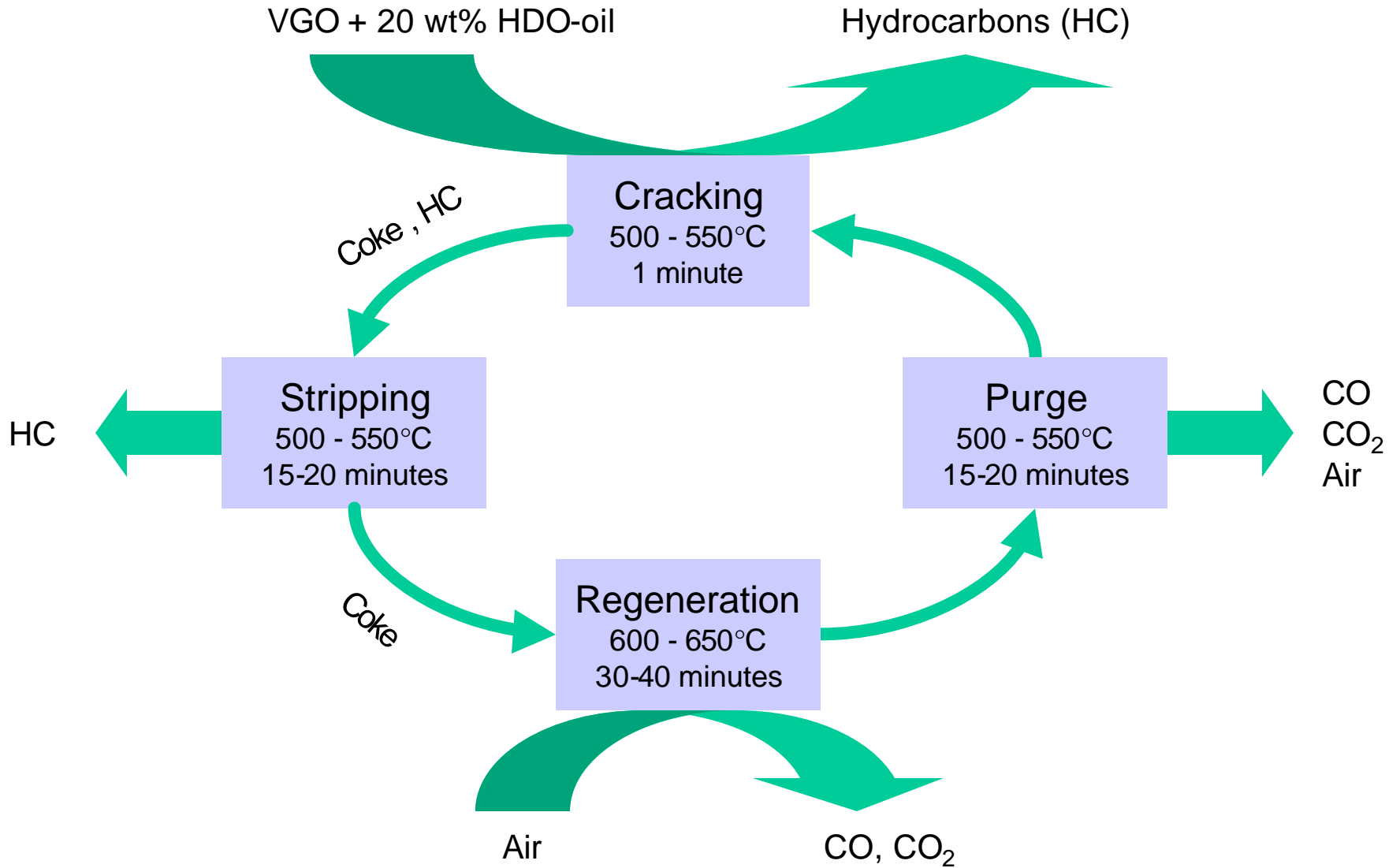
- Raw pyrolysis oil: > 300 oxygenated hydrocarbons<sup>1</sup> : acids, aldehydes, ketones, alcohols, glycols, esters, ethers, phenols and phenol derivatives, carbohydrates and derivatives, and lignin-derived oligomers
- Oxygen rich composition  $\implies$  lower heating value, immiscibility with hydrocarbon fuels, chemical instability, high viscosity, corrosiveness
- Conversion of biomass-derived molecules over FCC catalyst requires large amount of hydrogen:



- Which impact on VGO cracking?

<sup>1</sup> J.H. Marsman, J. Wildschut, F. Mahfud, H.J. Heeres, Journal of Chromatography, 1150 (2006) 21-27.

# Catalytic cracking cycle



# Product classification

Coke

Slurry oil (SO):  $425^{\circ}\text{C} <$

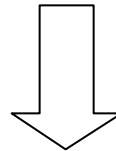
Heavy cycle oil (HCO):  $370\text{-}425^{\circ}\text{C}$

Light cycle oil (LCO):  $221\text{-}370^{\circ}\text{C}$

Gasoline:  $\text{C}_5 - 221^{\circ}\text{C}$

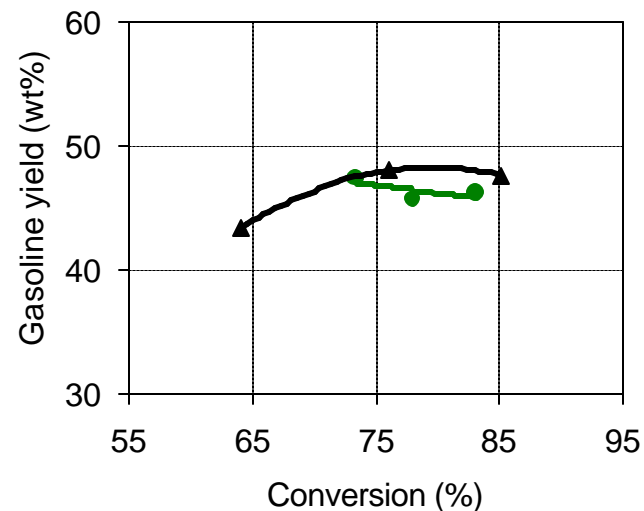
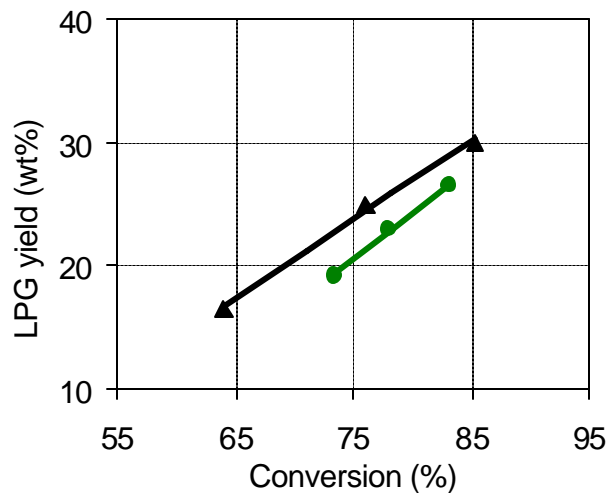
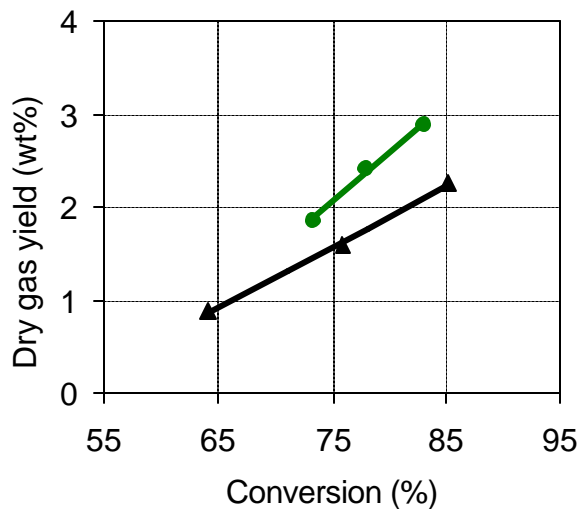
Liquefied petroleum gas (LPG):  $\text{C}_3\text{'s} + \text{C}_4\text{'s}$

Dry gas:  $\text{H}_2 + \text{CH}_4 + \text{CO}_2 + \text{C}_2\text{'s} + \text{H}_2\text{S}$



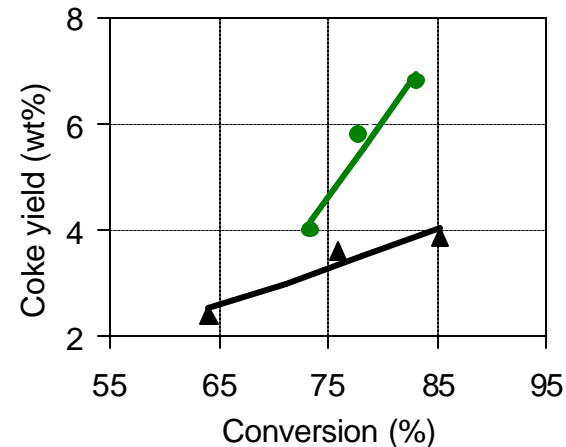
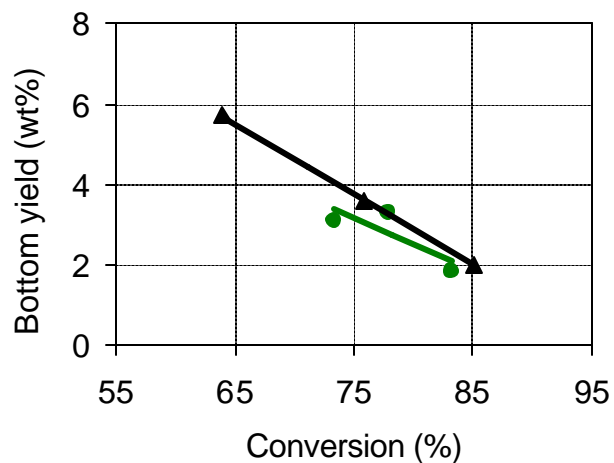
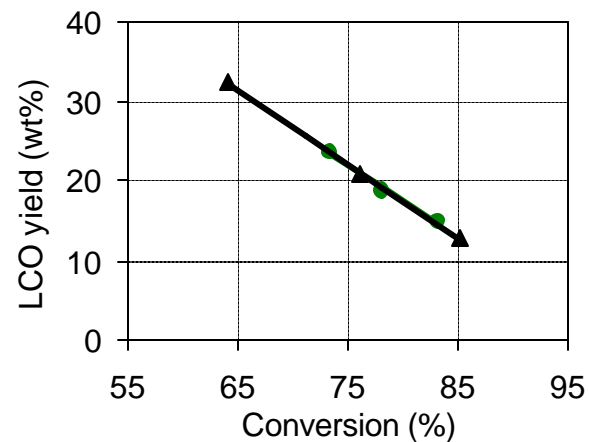
**Conversion**

# Product distribution: gas, liquid fractions and coke

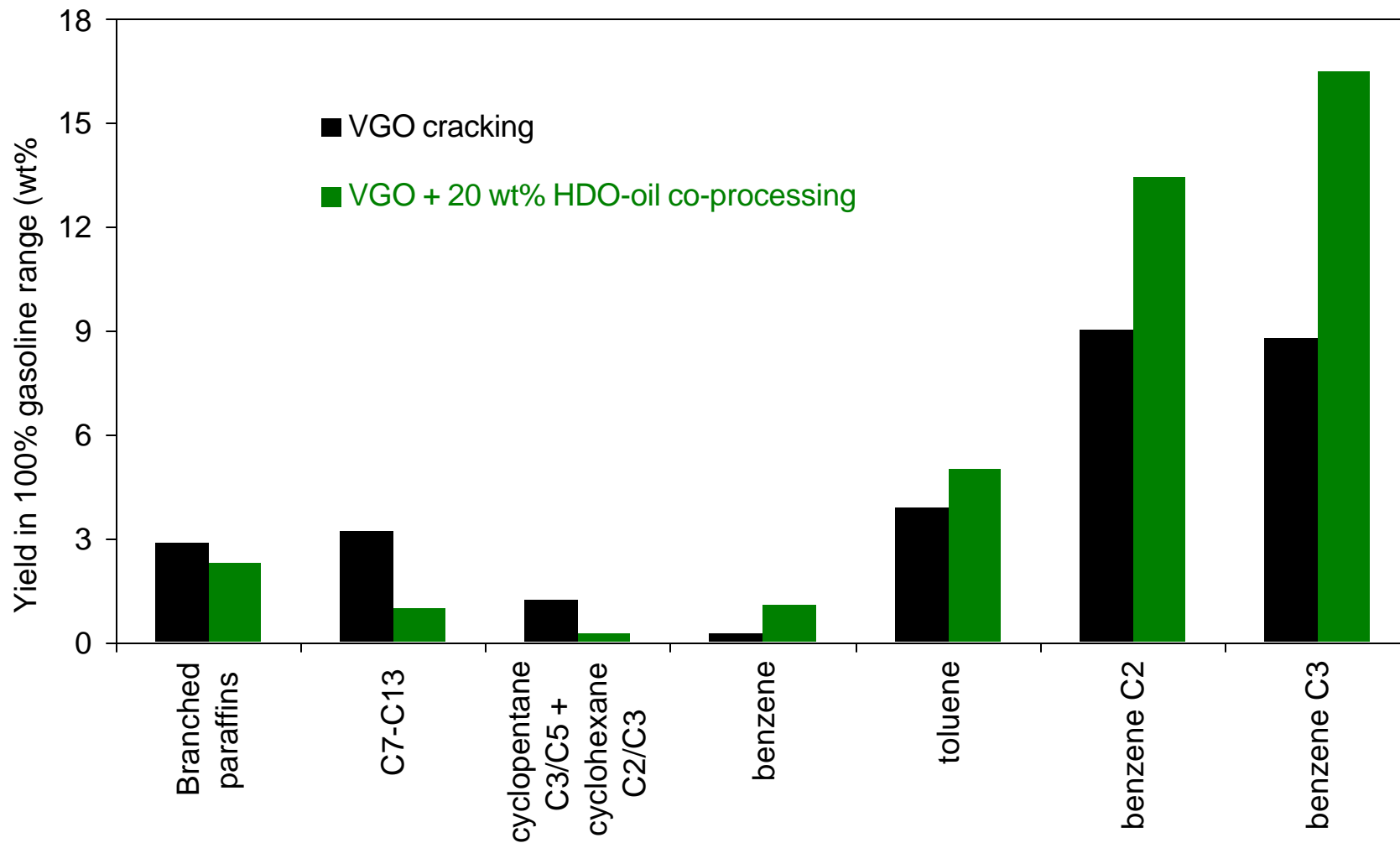


? VGO cracking

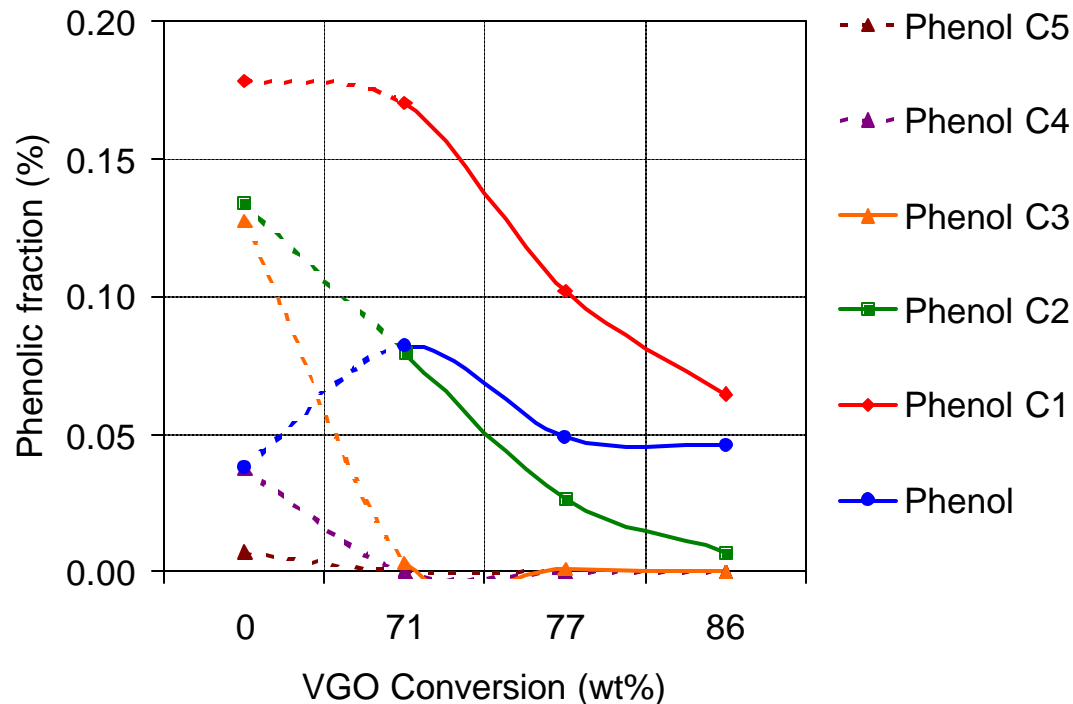
● VGO/HDO-oil co-processing



# Gasoline range composition

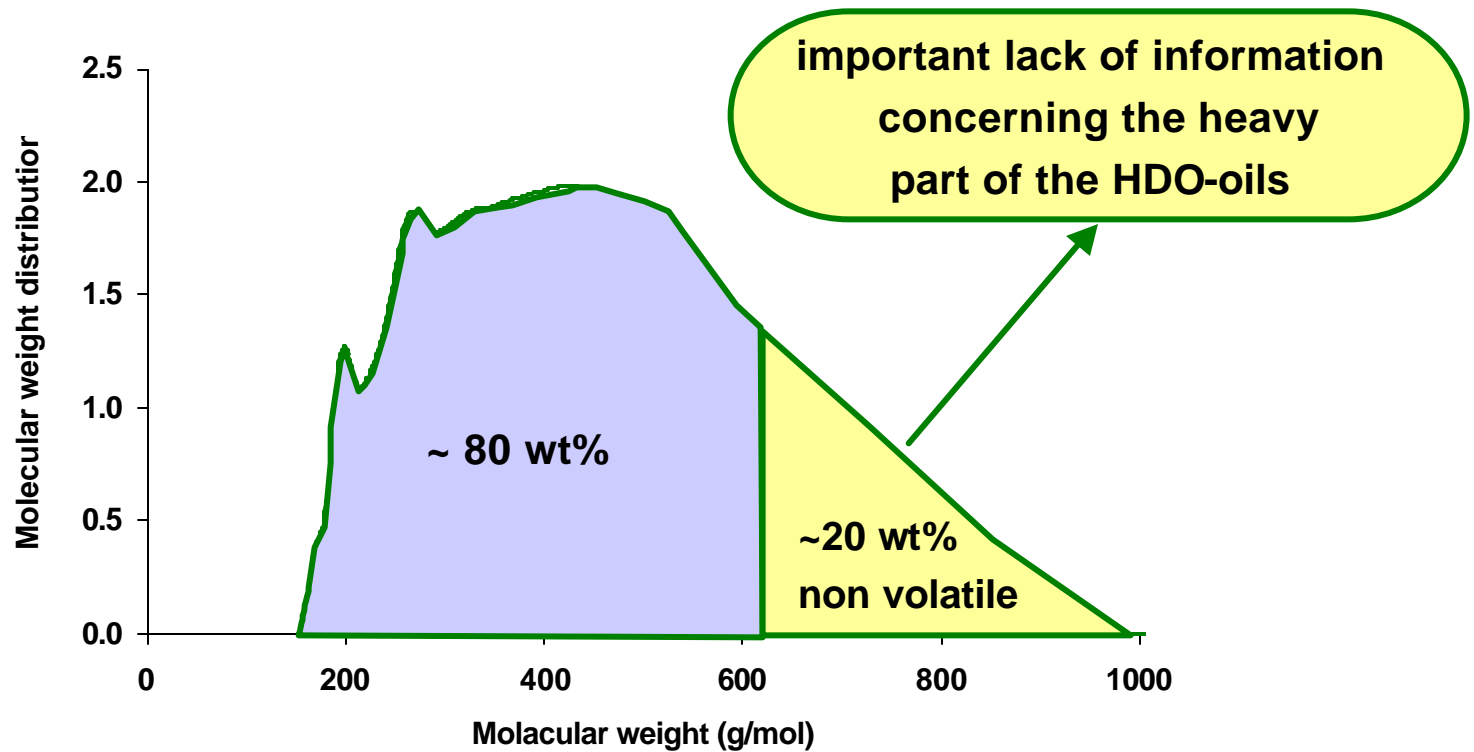


# In depth analysis of co-processing impact: e.g. degradation of alkylphenols



- Full conversion of oxygenates remains challenging
- The residual concentration must fulfill environmental requirements
- Similar approach for aldehydes and other major oxygenates from bio-oils

# Gel permeation chromatography



# CONCLUSIONS

Co-processing requires adapted analytic tools:

- 2D GC efficient technique to determine product quality with complex composition
- GPC information about heavier non-volatile fractions

Co-processing of VGO + 20 wt% HDO-oil compared to pure VGO cracking:

- similar gasoline yields but different compositions
- higher coke yield
- traces of oxygenated compounds among the products
  
- For in-depth understanding, investigating of model compounds co-processing