Co-processing of Upgraded Bio-Liquids in Standard Refinery Units - Fundamentals

Andrea Gutierrez HUT (Finland), Marcelo E. Domine CNRS (France)

VTT, University of Twente, Shell Global Solutions International, CNRS, ARKEMA, BTG, UHPT, Metabolic Explorer, STFI-PACKFORSK, University of Groningen, Helsinki University of Technology, Institute of Wood Chemistry, Slovenian Institute of Chemistry, Boreskov Institute of Catalysis, ALMA Consulting group, Albemarle, CHIMAR, Technical University of Eindhoven

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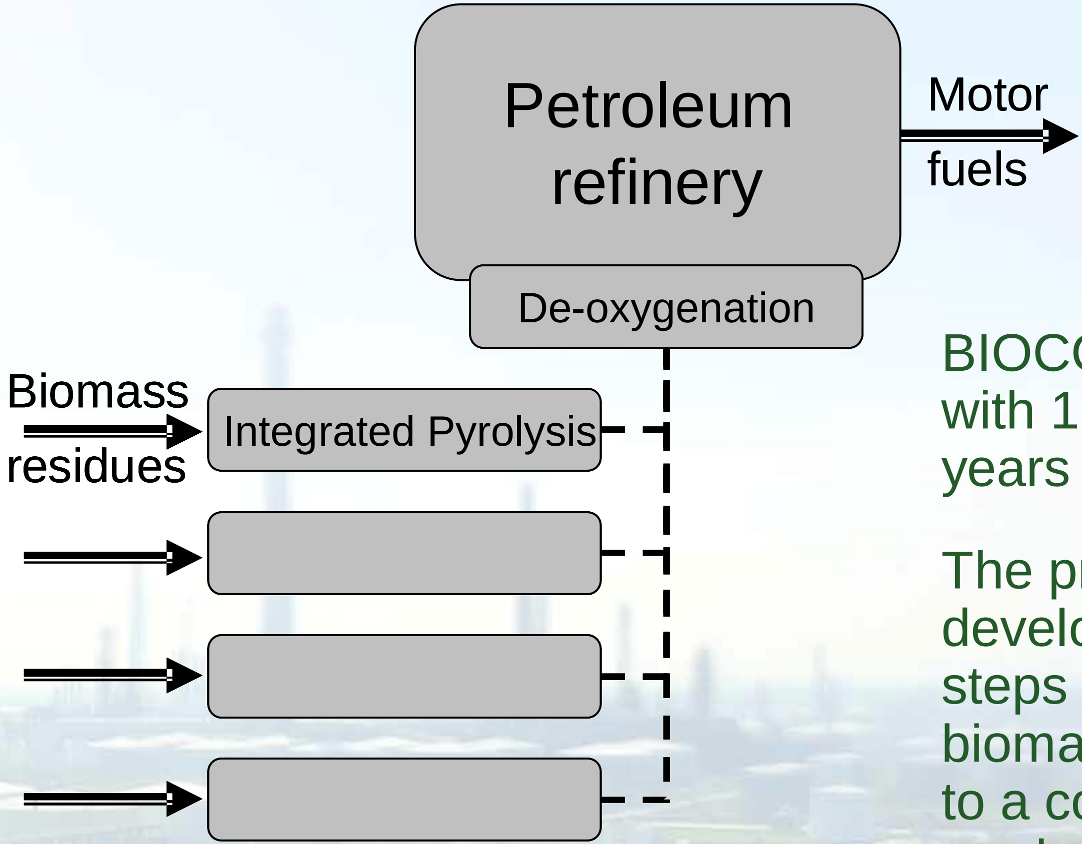
Abbreviations

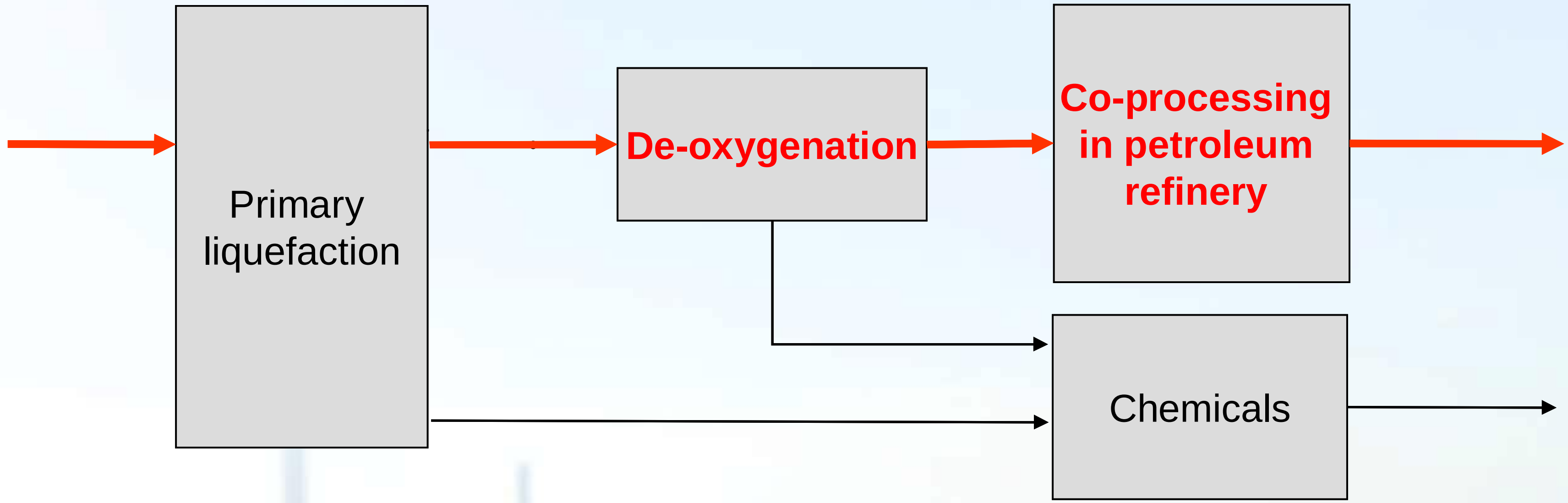
Bio-oil, bio-liquid	A generic term including all biomaterial derived liquids
Pyrolysis oil	A liquid biofuel produced by pyrolysis
Fast pyrolysis	A concept, where residence time for (biomass) solids is in the order of a few seconds
Integrated pyrolysis	A concept, where fast pyrolysis is integrated to a fluidized-bed boiler
Deoxygenation	Oxygen removal from primary bio-oil either by thermal treatment, hydro-deoxygenation (HDO), or decarboxylation (DCO)
HDS	Hydro-desulfurisation (a refinery unit operation)
FCC	Fluid-catalytic cracking (a refinery unit operation)
SRGO	Straight run gas oil



BIOCOUP started June 2006 with 17 partners, duration five years

The project is aimed at developing a chain of process steps to allow a range of biomass feedstocks to be co-fed to a conventional oil refinery to produce energy and oxygenated chemicals.

Overall Biomass Processing Chain

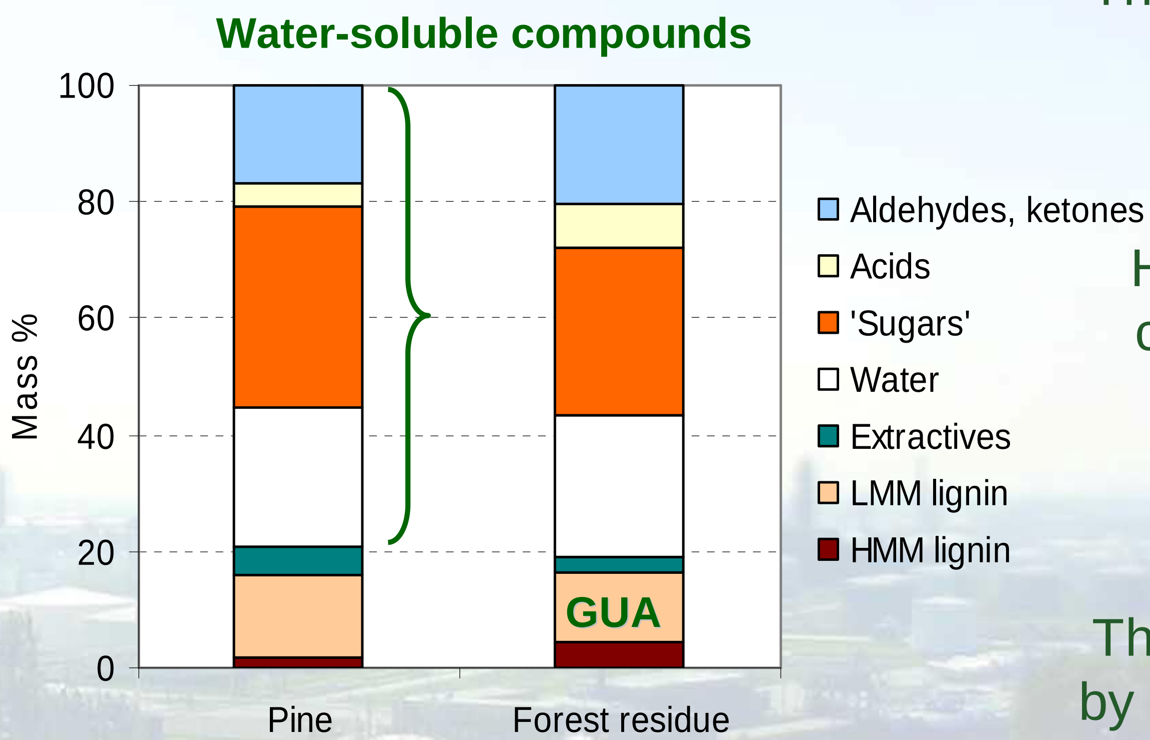


The presentation will deal with fundamentals of two process steps in the chain

- De-oxygenation of primary bio-liquids (three variants studied, hydro-deoxygenation reported today)
- Co-processing in a petroleum refinery

Properties of Wood Derived Bio-Liquids

Complex mixtures of oxygen containing compounds



Thermally unstable: **No heating**

High polarity: **Insoluble in mineral oils**

High molecular mass (HMM) compounds: **High viscosity**

The properties can be improved by partial or complete elimination of oxygenated compounds

Hydrodeoxygenation

Bio-liquids → Hydrodeoxygenation (HDO) Catalytic reaction in presence of H_2 → Hydrocarbons + H_2O

The composition of bio-liquids makes HDO challenging…

- Viscosity and solubility problems
- Large amount of reactions
- Analytical challenges

→ Behavior of real bio-liquids simulated with model compounds

HDO – Lab Scale Results

Guaiacol

- Representative of degraded lignin fraction
- Coke precursor

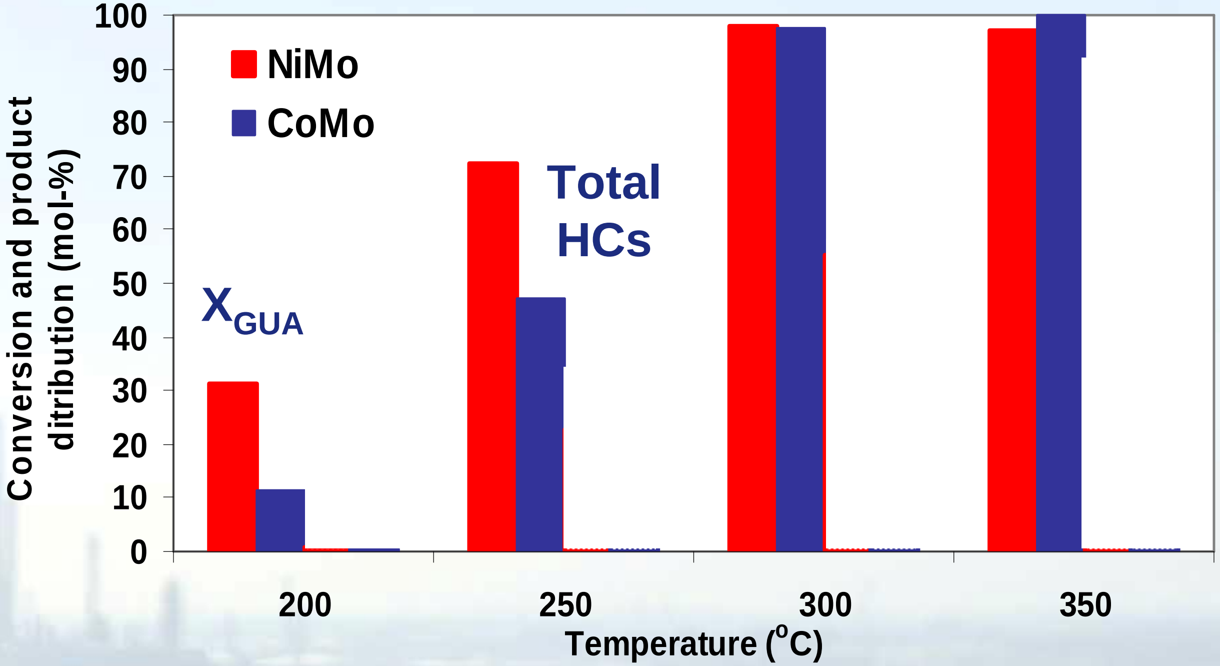
Products

- **Hydrocarbons**

benzene, cyclohexane, toluene

- **O-compounds**

phenol, cyclohexanol



Temperature affects GUA conversion and HDO products concentration

- NiMo more active at T below 300 °C
- CoMo more HDO selective at the highest T tested

What is Expected from HDO?

Based on single model compounds and mixtures

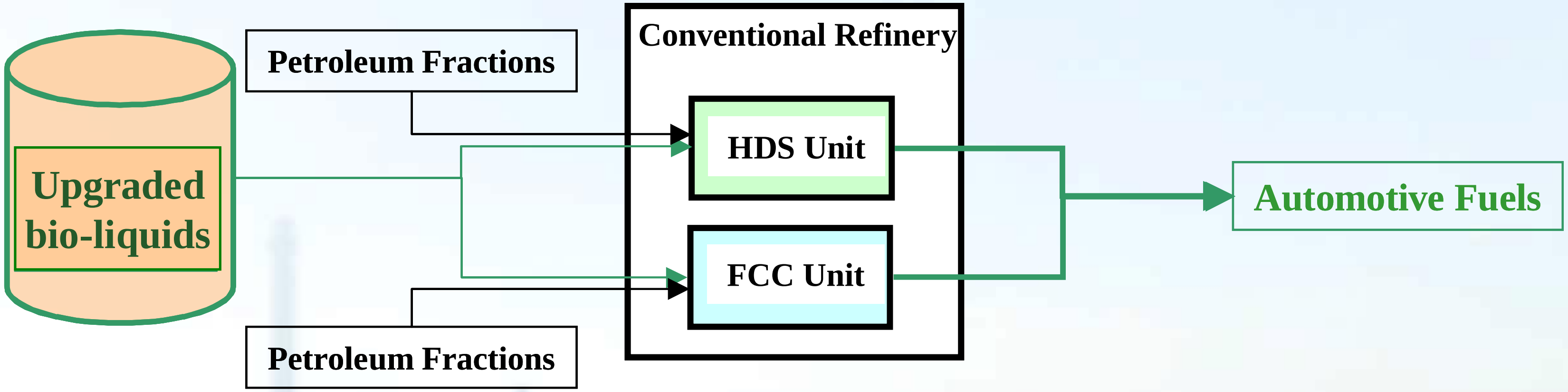
- Better understanding of HDO reactions
- Selection of catalysts

    à Testing of existing catalysts and development of new ones (active metal and support material)

- Selection of operation conditions for industrial scale HDO

Main Objectives in Co- Processing

Viability of upgraded bio-liquids co-processing in standard refinery units



- Technical feasibility of upgraded bio-liquids co-processing (2-10 wt-%) in: fluidized catalytic cracking (FCC) units, and hydrotreating (HDS) units

- Effect of bio-liquids co-processing on key refinery unit parameters and necessary bio-liquids specifications after upgrading (i.e. metals, water, oxygen and other hetero-atoms)

- Technical data on product yields to determine the contribution from the bio-component (model compounds studies)

Preliminary Result - Hydrotreating

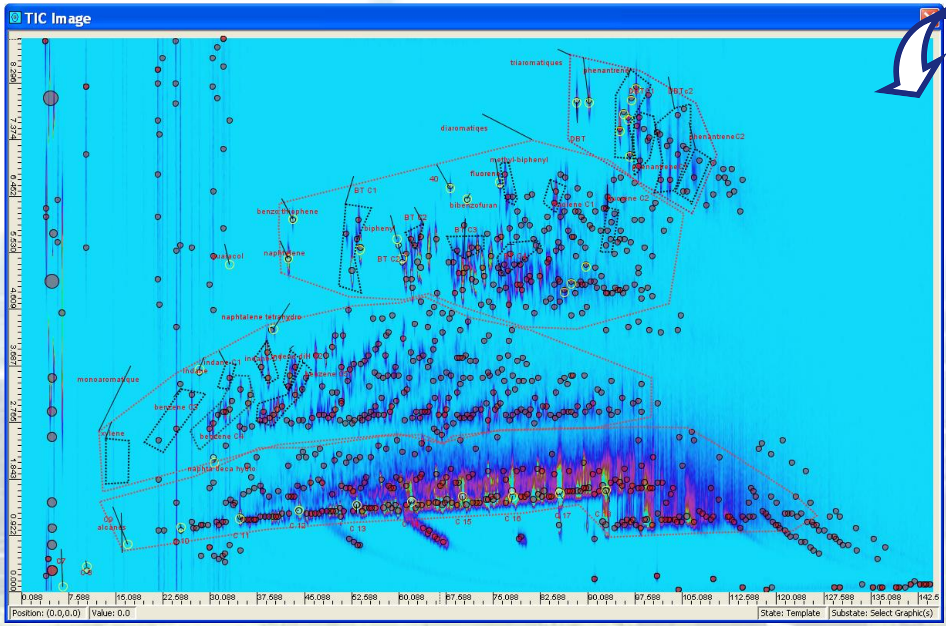
Methodology:

Investigation of the performances of CoMo and NiMo on alumina HDT catalysts in the conversion of a SRGO in a micropilot unit (40 bars, 320-370ºC)

1 stage : addition of model molecules

2 stage : addition of upgraded bio-liquids

3 stage : increasing the amount of bioliquids



Evaluation of the performances total sulfur content, density, 2D GC chromatography

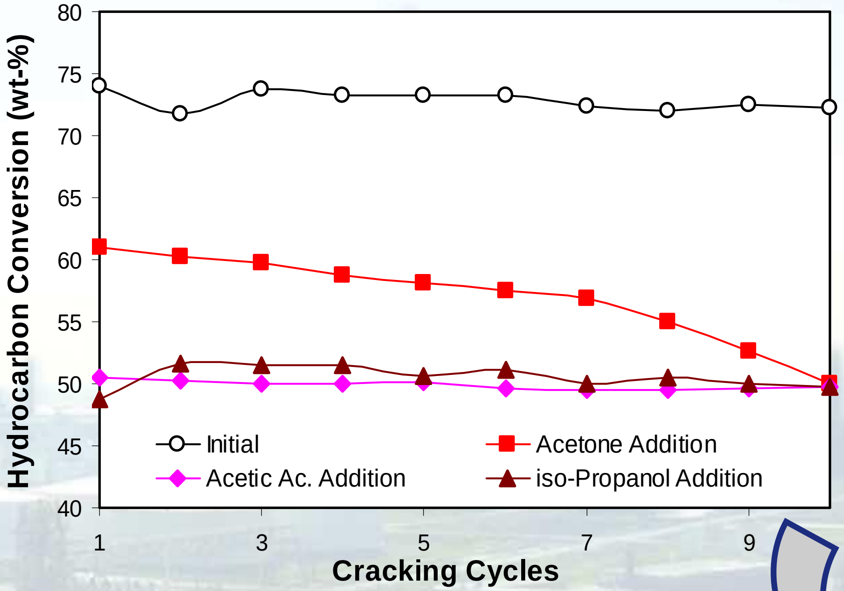
Guaiacol, napthol, benzoquinone, iso-propanol do not inhibit the conversion of the S-compounds and they are **totally converted** at 320°C

Preliminary Results – Fluid Catalytic Cracking (FCC)

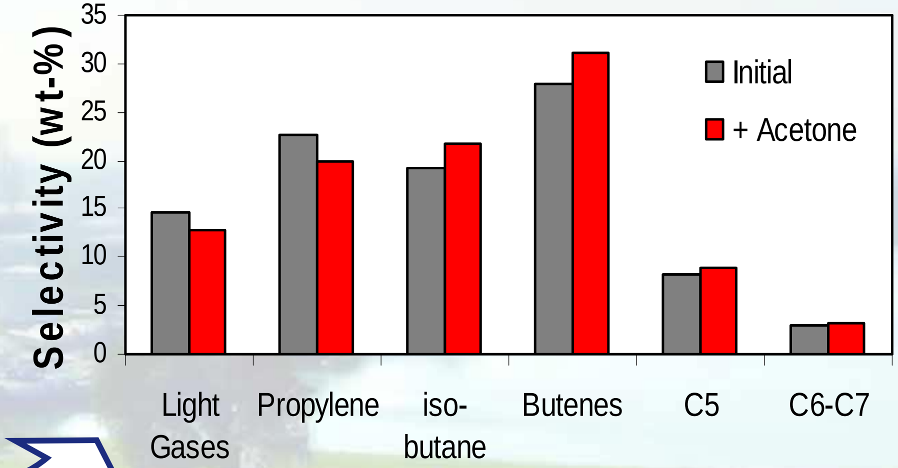
Methodology:
Simulating FCC lab-scale reactor at 530 ºC

Feed: Hydrocarbon (C_8) + 2 wt-% oxygenates
Catalyst: FCC eq. sample (1 g) - Cat/Oil = 15
Cycles of cracking/stripping/regeneration/purge

Effect of oxygenated compounds addition on the hydrocarbon (C_8) catalytic cracking



Comparison of product distribution at iso-conversion



With 2 wt-% of Oxygenates:

Conversion **Coke**

What is Expected from Co-processing?

- Feed delivery systems for co-processing
- Co-processing in HDS units: catalyst stability (with steam), product quality, process conditions
- Co-processing in FCC units: i) product distribution and quality (low coke, high selectivity to diesel, gasoline or light olefins, high quality of liquids products, good control gaseous emission, etc); ii) catalyst lifetime, hydrothermal stability, and possibility of regeneration.
- Bio-liquids specifications and special requirements for their adequate co-processing in refinery units

Hydrodeoxygenation - Directions

- BIOCOUP will develop methods to, at least partially, de-oxygenate the bio-liquids before the final upgrading. This should improve the competitiveness of bio-liquids upgrading; e.g. by reducing hydrogen consumption.
- New catalyst will be developed for bio-liquids HDO
- Generate data need for scale up of the HDO unit (mixture of model compounds and real bio-liquids)

Co-Processing - Directions

- Evaluation of the viability of upgraded bio-liquids co-processing in refinery units (HDS, FCC, and others)
- Basic knowledge of the co-processing effect on key refinery units parameters
- Bio-liquids specifications for the adequate feeding and co-processing in refinery units (Study with real upgraded bio-liquids)
- Developing better, more robust catalysts by increased understanding of the reaction kinetics and the relationship with the catalyst structure.

Acknowledgements