



EFFECTIVENESS OF CoMo AND NiMo CATALYST ON Co-HYDROPROCESSING OF HEAVY ATMOSPHERIC GAS-OIL/WASTE COOKING OIL

S. Bezergianni
A. Dimitriadis



Laboratory of Environmental Fuels & Hydrocarbons
Chemical Processes & Energy Resources Institute
Centre for Research & Technology Hellas

S.J. Kiartzis
M.C. Magiliotou
A.N. Skandilas
V.S. Dimitropoulos



Hellenic Petroleum S.A.
Thessaloniki, Greece



Bio4SuD

Thessaloniki Greece
www.bio4sud.gr
19-20 November, 2012

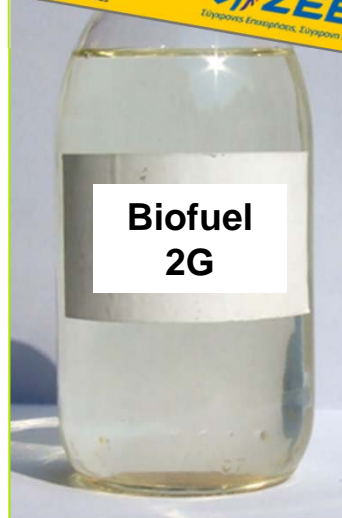


CERTH

Waste Cooking Oil → Diesel-2G



+ H₂
catalyst



- Better combustion (increased cetane)
- More economic (high HHV)
- More stable (no TAN, high IP)
- Sustainable



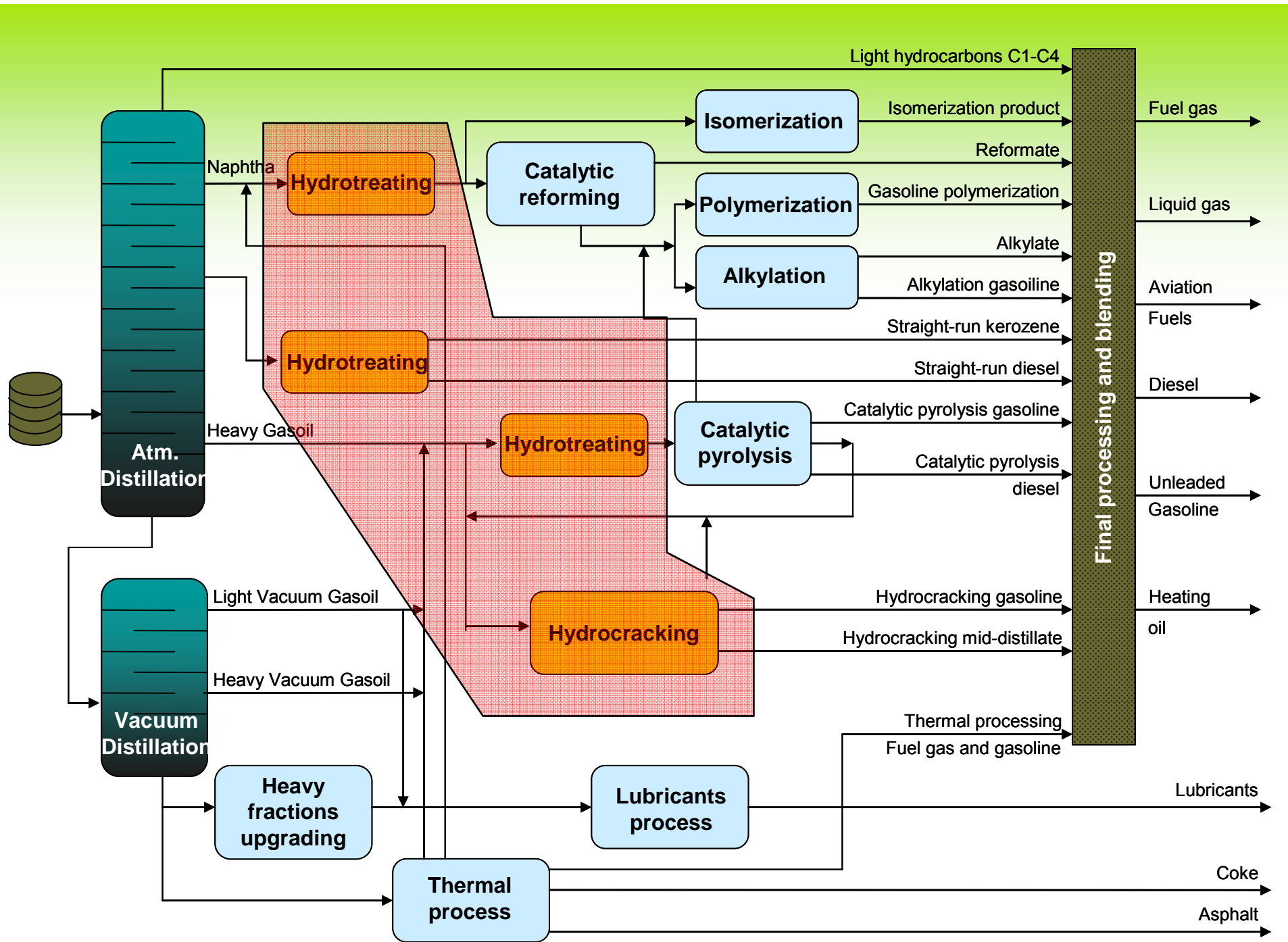
- Large-scale units require large investments

Potential to cover 9,5% of Greek diesel demand



www.biofuels2g.gr







CERTH

SustainDiesel Project

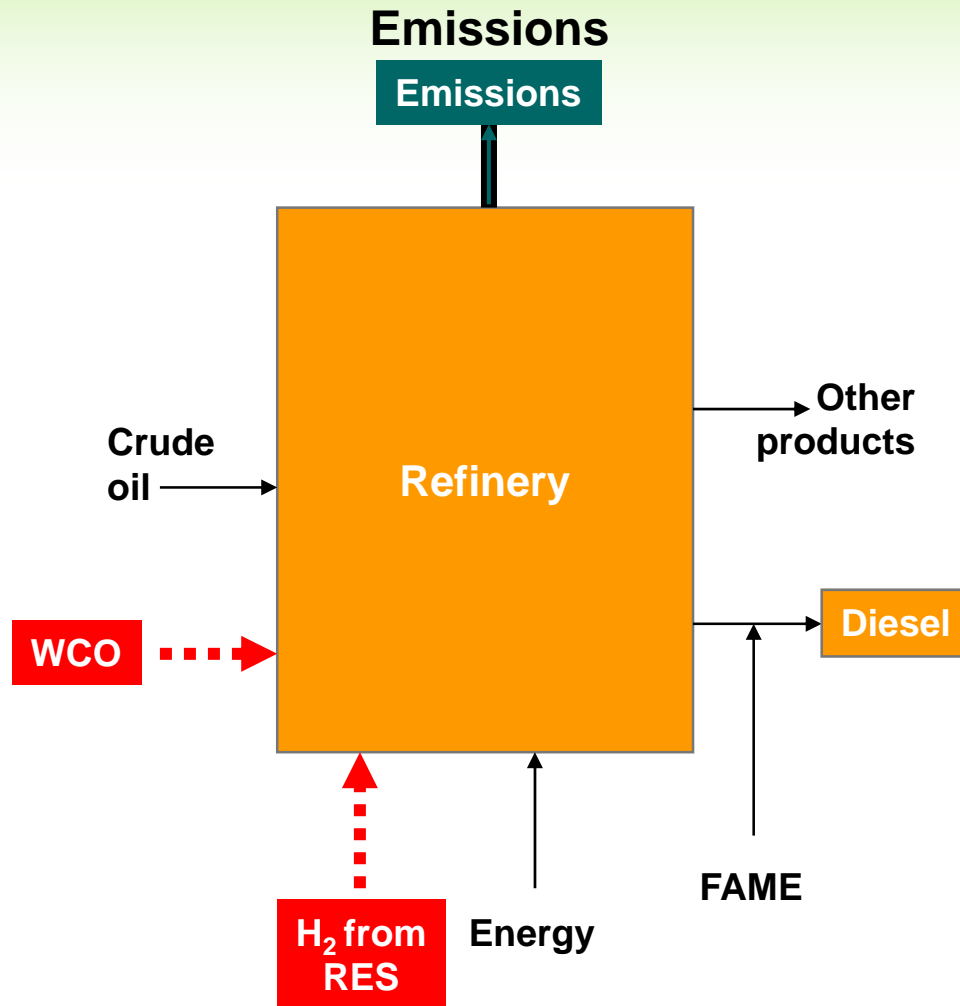
- Aim: Improvement of diesel sustainability by incorporating WCO and RES in existing refinery
- Project duration: 23.3.2011 – 22.3.2014
- Partners:
 - Coordinator: Centre for Research & Technology Hellas (CERTH)
 - Academic partners: Aristotle University of Thessaloniki & National Technical University of Athens
 - Industrial partners: Hellenic Petroleum & Sunlight S.A.
- Financing: Program Competitiveness (ESPA) with funds from EU and Greek Government





CERTH

SustainDiesel Technology Overview



- A. Evaluate technical feasibility of incorporating WCO as alternative feedstock for diesel production
 - Same infrastructure & operation
- B. Assess carbon footprint and GHG emissions improvement versus current market diesel

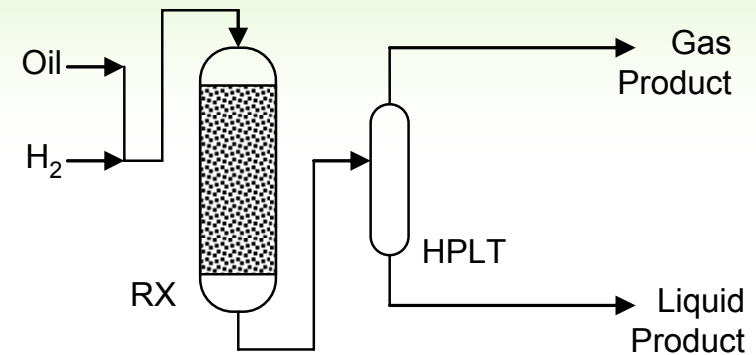




CERTH

Technical Feasibility Study

- 1 Evaluation of hydrotreating catalyst ✓
- 2 Determine optimal operating conditions ✓
 - T, P, H₂/oil, LHSV
- 3 Determine max WCO mixing ratio
- 4 Evaluate emissions & engine performance

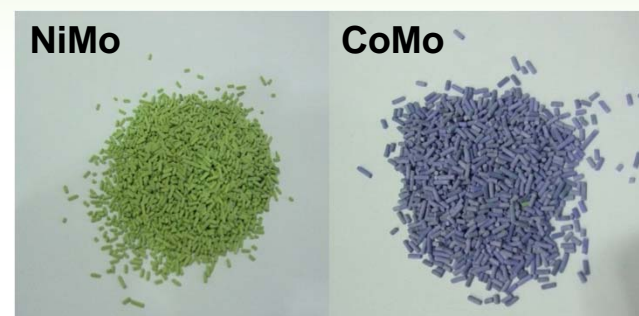




CERTH

Experimental Methodology (1/3) Overview

- Two commercial catalyst
 - Commercial NiMo
 - Commercial CoMo
- Three feedstocks
 - Heavy Atmospheric Gas Oil 100% (HAGO)
 - HAGO with 10% waste cooking oil (WCO)
 - HAGO with 30% waste cooking oil (WCO)
- Small scale hydroprocessing pilot plant
- 8 experimental runs





CERTH

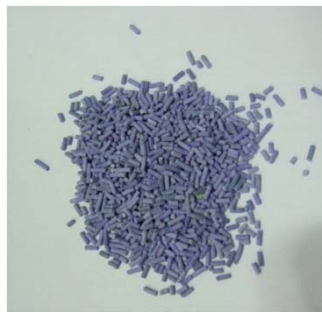
Experimental Methodology (2/3) Catalysts & Operating Parameters

NiMo Catalyst



Temperatures	330°C	350°C	370°C
Feedstock (HAGO/WCO)	100/0	100/0	100/0
	90/10	90/10	90/10
	70/30	70/30	70/30

CoMo Catalyst



Temperatures	330°C	350°C	370°C
Feedstock (HAGO/WCO)	100/0	100/0	100/0
	90/10	90/10	90/10
	70/30	70/30	70/30

Pressure (psig)	812
LHSV (hr ⁻¹)	1
H ₂ /Oil (scfb)	3000

Comparison

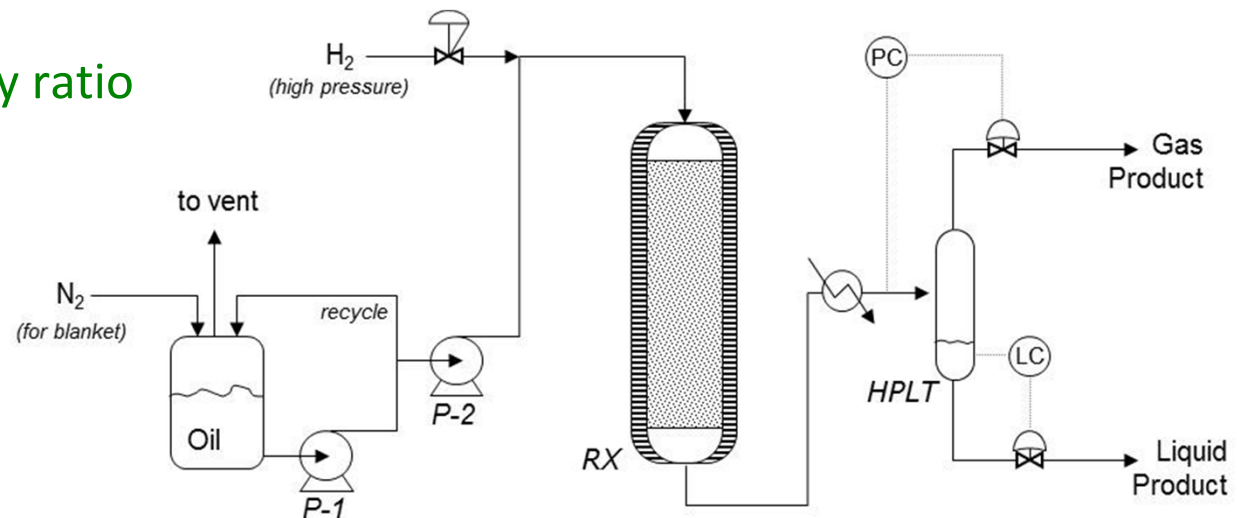




CERTH

Experimental Methodology (3/3) Infrastructure & Experiments

- Hydrotreating effectiveness parameters
 - Heteroatom removal (S, N)
 - Saturation of double bonds (Br, H/C)
 - Diesel yields (180°C - 360°C)
 - Conversion
 - Catalyst decay ratio

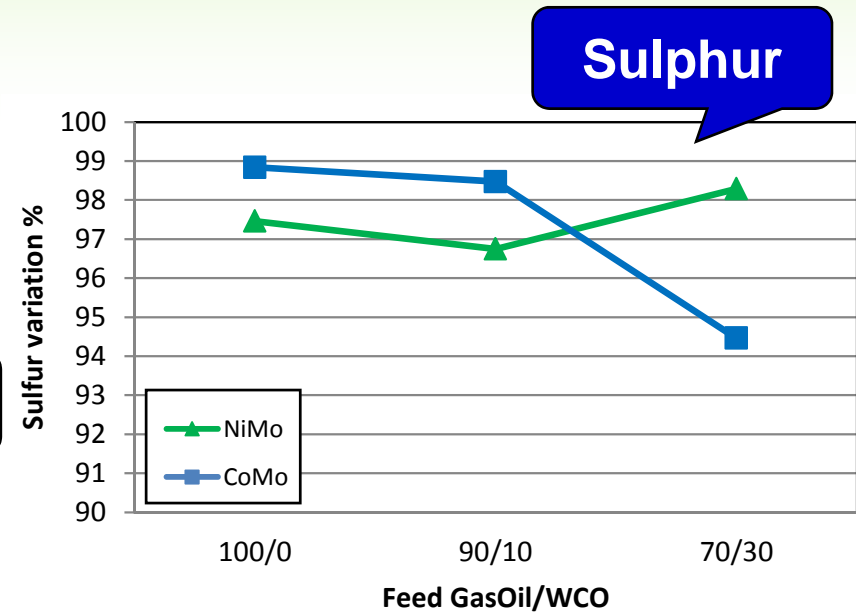
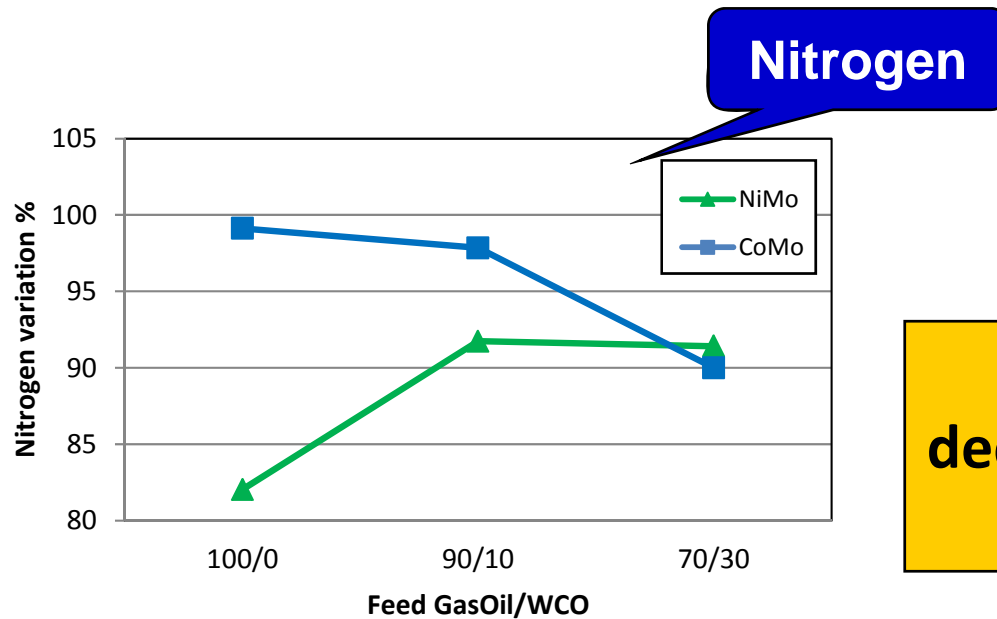




CERTH

Heteroatom removal

- **NiMo** catalyst showed a performance increase for the feedstock with the largest WCO content
- **NiMo** catalyst exhibited increased HDN performance with increasing WCO content



WCO addition does not decrease product quality when NiMo catalyst is used



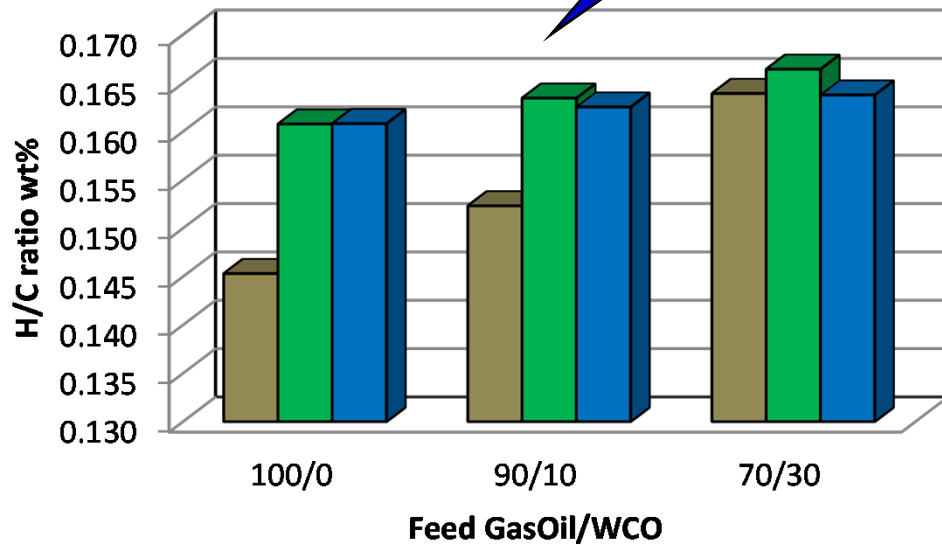


CERTH

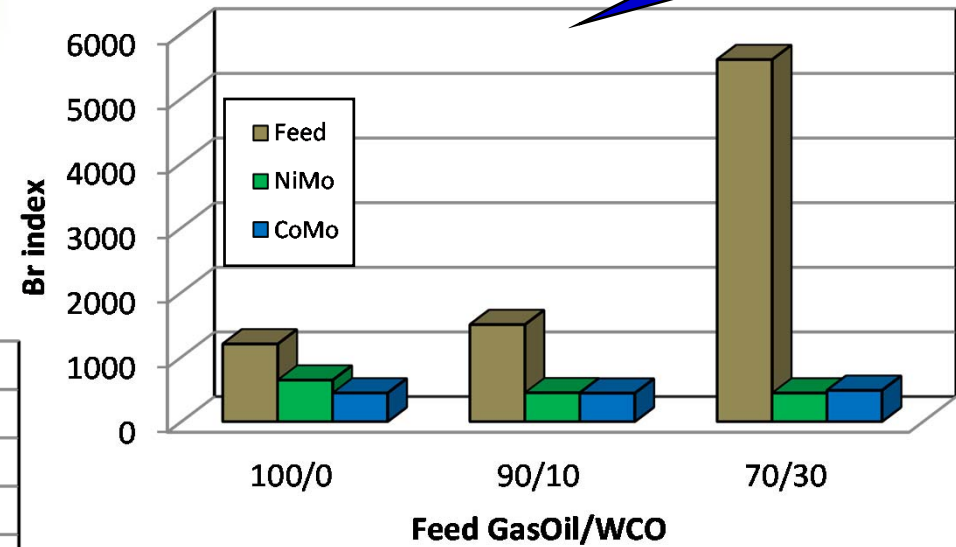
Saturation

- Both catalysts provide good saturation of double bonds for all type of feedstocks

H/C



Br.Index



WCO addition does not limit saturation

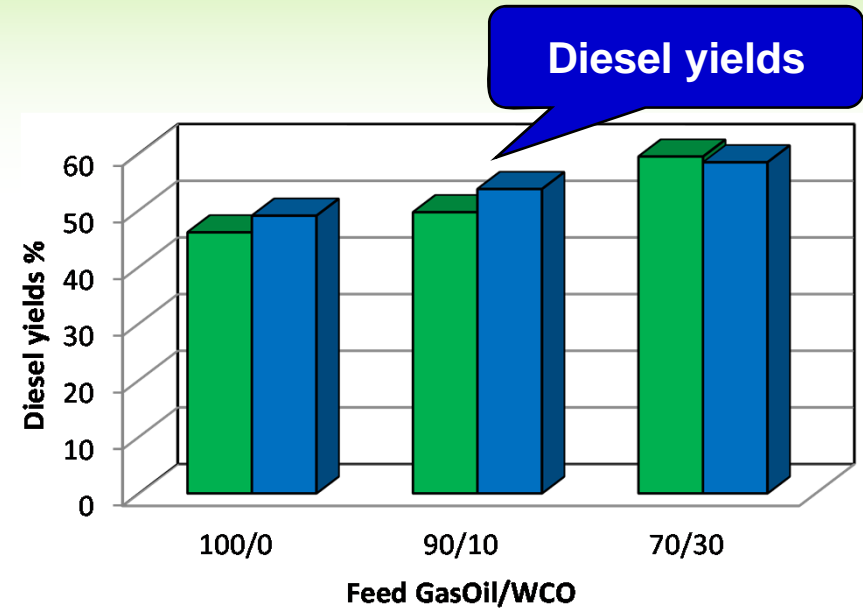
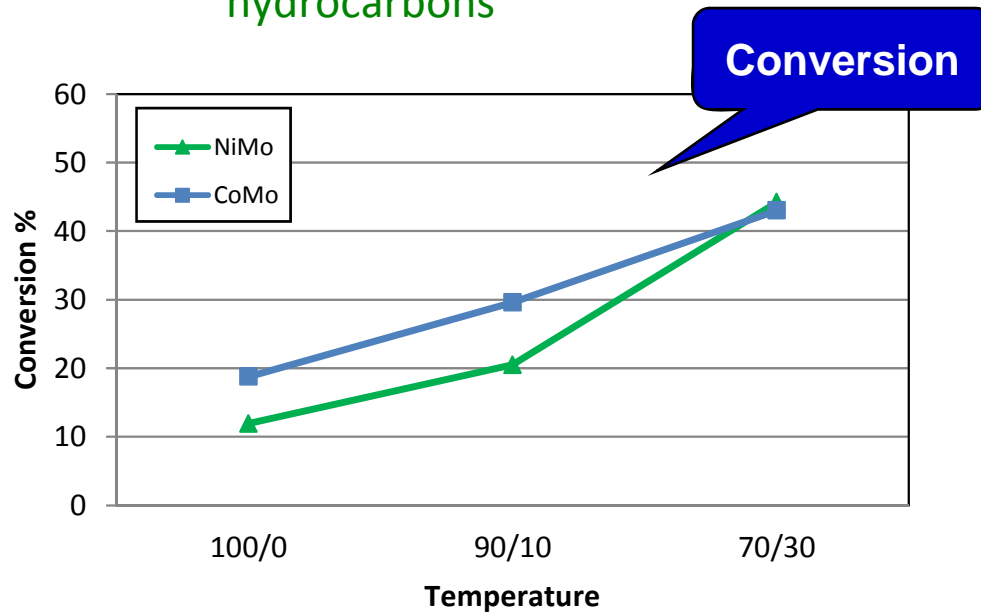




CERTH

Diesel Yields-Conversion

- **CoMo** offers higher conversion and diesel yields for pure HAGO and low WCO content
 - Triglycerides contained in WCO can be more easily converted into diesel range hydrocarbons



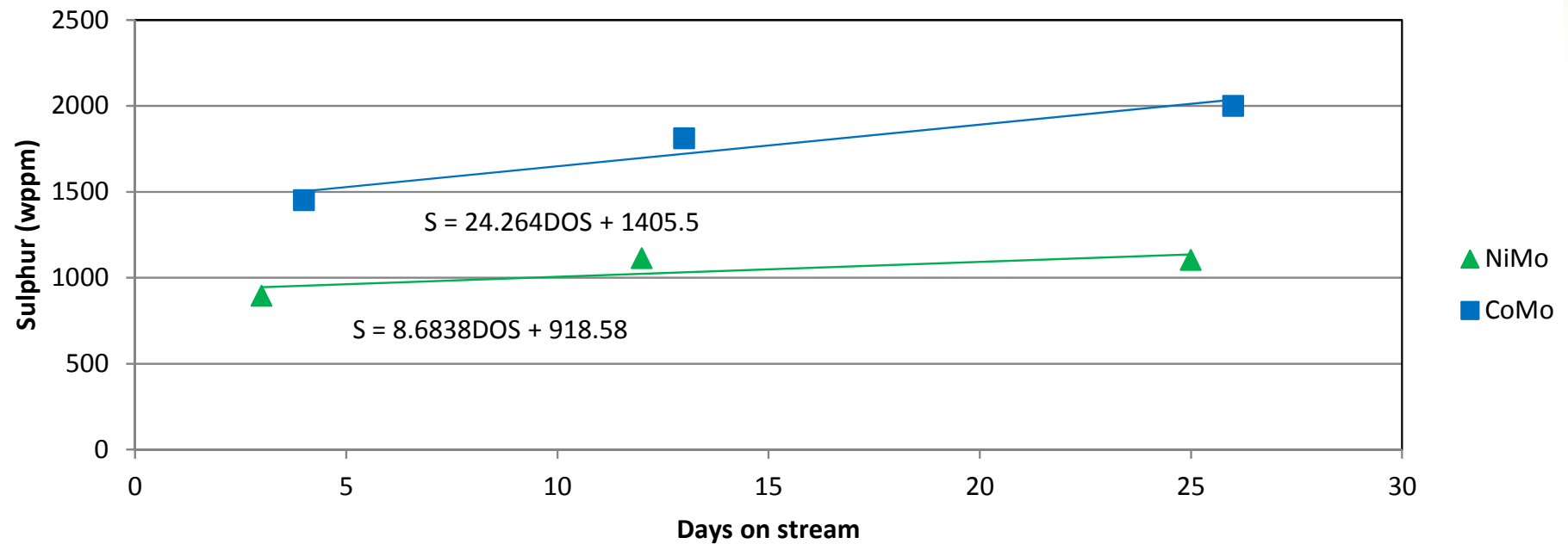
WCO addition increases conversion and improves diesel yields





CERTH

Catalyst Deactivation



NiMo deactivation rate is 3 times smaller than CoMo





CERTH

Conclusions & Future Steps

- WCO addition in HAGO hydrotreatment does not limit targeted reactions (heteroatom removal and saturation)
- WCO addition increases conversion and diesel yield
- NiMo catalyst more suitable for WCO containing feedstocks
- Future steps
 - Evaluation of maximum WCO ratio that can be incorporated in existing refinery
 - Assessment of maximum potential GHG emission benefits by incorporating WCO and H₂ from RES
 - Economic feasibility analysis





CERTH

Thank you

for your attention

