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RESEARCH & TECHNOLOGY
HELLAS

DECARBONIZATION OF TRANSPORTATION FUELS VIA CO-HYDROPROCESSING BIO-BASED FEEDSTOCKS WITH PETROLEUM FRACTIONS

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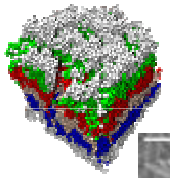
2nd World Congress on Petrochemistry and Chemical Engineering
October 27-29, 2014 Las Vegas, USA

CPERI
Chemical Process and Energy Resources Institute

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CERTH Introduction

- Largest researcher center in Northern Greece
- Mission
  - High quality scientific research / Emphasis on R&D&I
  - Cooperation with Universities & Research Institutes
  - Strong collaboration with industry
- CPERI R&D activities
  - Fuels, biofuels production processes
  - Materials (filter, membranes, ceramics, catalysts, etc)
  - Renewable energy systems
  - Modeling & optimization





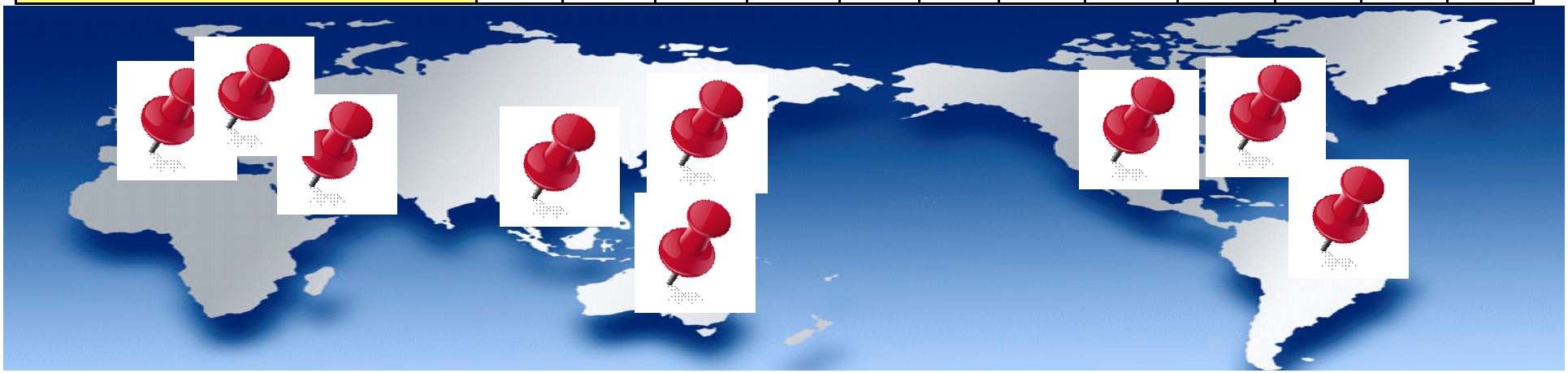

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CERTH in figures

CERTH	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011
Personnel	206	231	305	342	384	389	471	486	513	466	472	472
Direct public funding in M€	1.58	2.43	1.96	1.69	2.34	2.06	3.20	2.80	2.74	2.29	2.36	1.68
EU & GSRT R&D funding in M€	7.26	4.73	7.33	9.48	12.44	11.11	19.32	14.05	15.49	12.12	11.27	18.65
Industrial/service contracts in M€	1.17	2.21	1.91	2.39	3.02	3.49	3.13	3.16	3.98	3.98	3.60	3.68
Other sources of income in M€	0.25	0.20	0.63	1.00	0.51	1.27	1.13	2.21	1.48	0.90	0.39	0.59
Total annual funds in M€	10.27	9.57	11.84	14.56	18.31	17.94	26.79	22.23	23.70	19.30	17.88	24.6
Active projects per year	113	159	213	232	237	270	294	275	271	236	229	229
Publications in conference proceedings	162	248	220	188	253	295	257	268	249	179	223	210
Journal publications	71	64	80	91	114	111	123	134	134	146	162	190
Citations	387	406	582	766	869	2,612	2,681	2,969	3,189	3,662	4,100	5,500
Patents	-	-	1	-	2	2	2	-	-	-	-	5



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Infrastructure

General Infrastructure



Analytical Equipment



Pilot Plant units





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Biomass Conversion to Biofuels

- ✓ Renewable



- ? Low H/C ratio
- ? Contains water
  - — Corrosion problems
- ? High oxygen content (aldehydes, acids, cetones)
  - — Reduced heating value
  - — Reduced oxidation stability
  - — Increased acidity

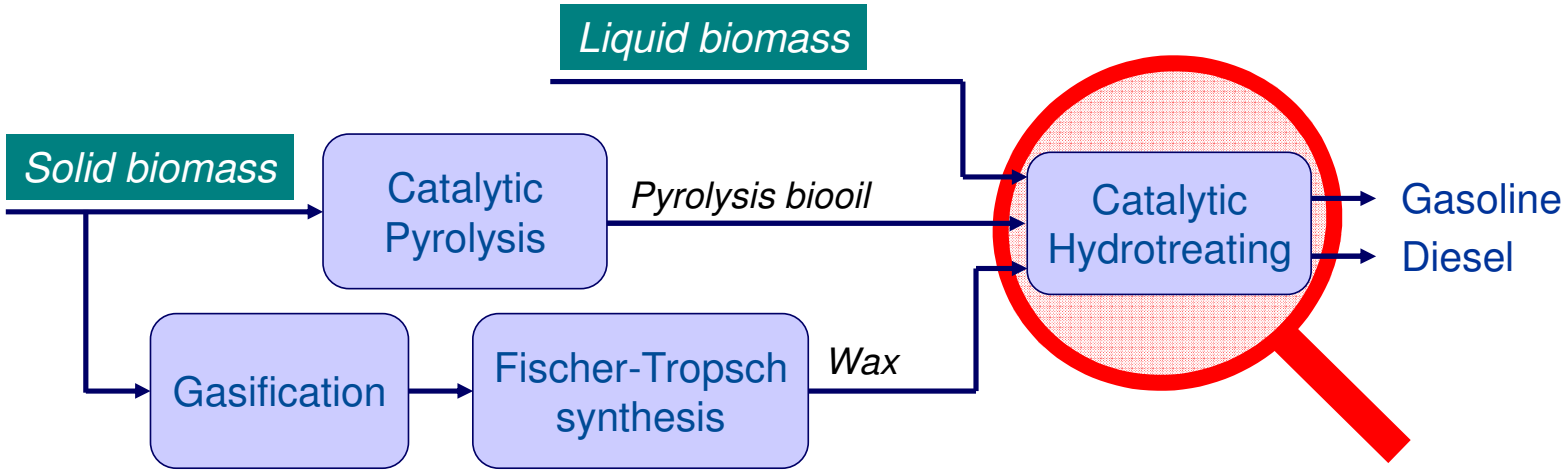
Engine performance problems



Biomass requires H/C increase, oxygen and H_2O removal

Hydrotreating & Biomass Upgrading

- Common refining conversion technology
  - H/C ratio increase
  - Heteroatom (S, N, O) and metals removal
  - High conversion
  - Feedstock variability
  - No by-products
- Most effective technology for biomass upgrading



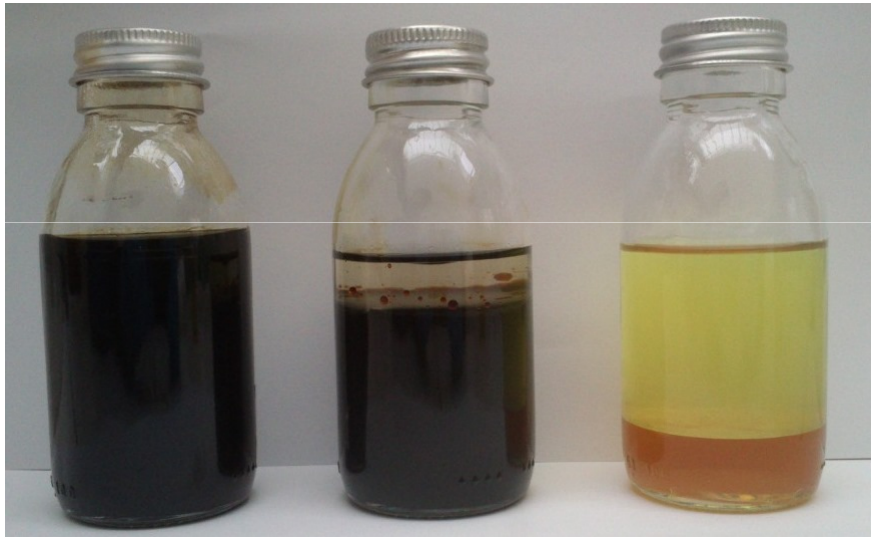
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Bio-oil Upgrading

- Development of reactor loading procedure
  - Catalytic system (catalyst, reactor filling material) & reactor zones
- Exploration of temperature profile effect on upgraded product quality
- Significant improvement of fuel quality

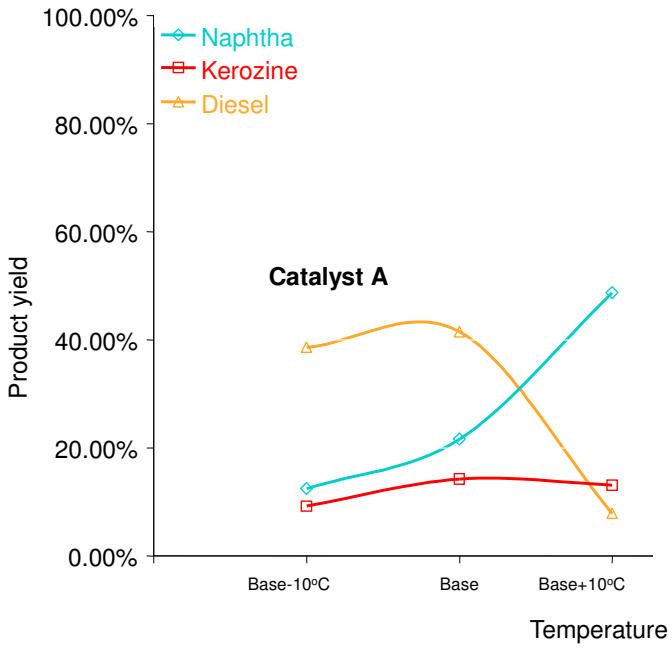
	Improvement* (%)
Density	25
H/C	30
O content	96
H_2O content	99
TAN	>99

** Improvement of 2nd stage product*



Fischer-Tropsch Wax Upgrading

- Development of operating protocol for wax hydrocracking
- Catalyst & T affect products yields & selectivities





Biomass **FT-wax** **FT-diesel**

Source: *Renew EU project (http://www.renew-fuel.com)*
Laboratory of Environmental Fuels and Hydrocarbons
Centre for Research and Technology Hellas (CERTH)

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Waste Lipids Upgrading

www.biofuels2g.gr



+ H_2

catalyst



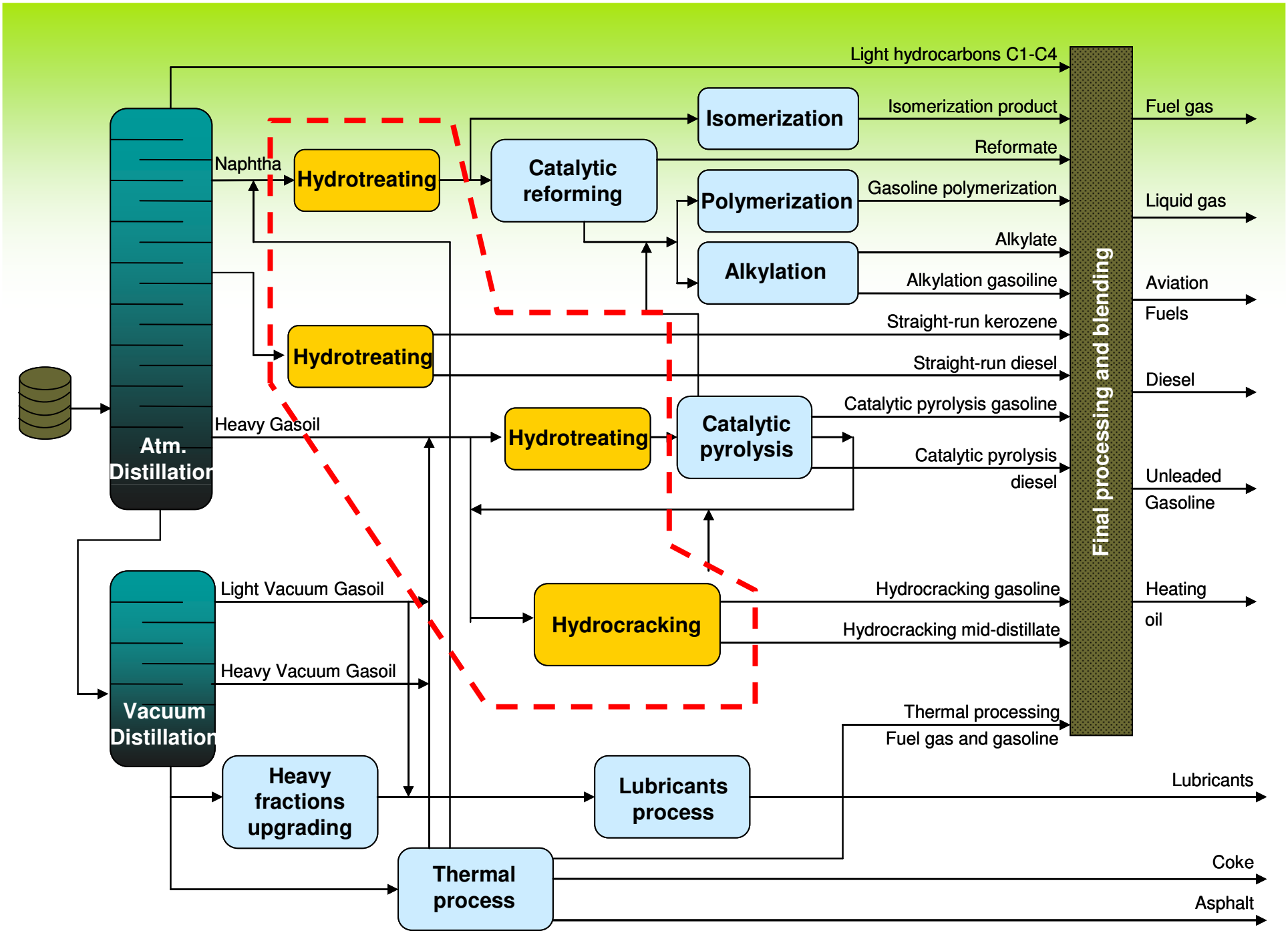
Potential to cover 9,5% of Greek diesel demand

✓

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

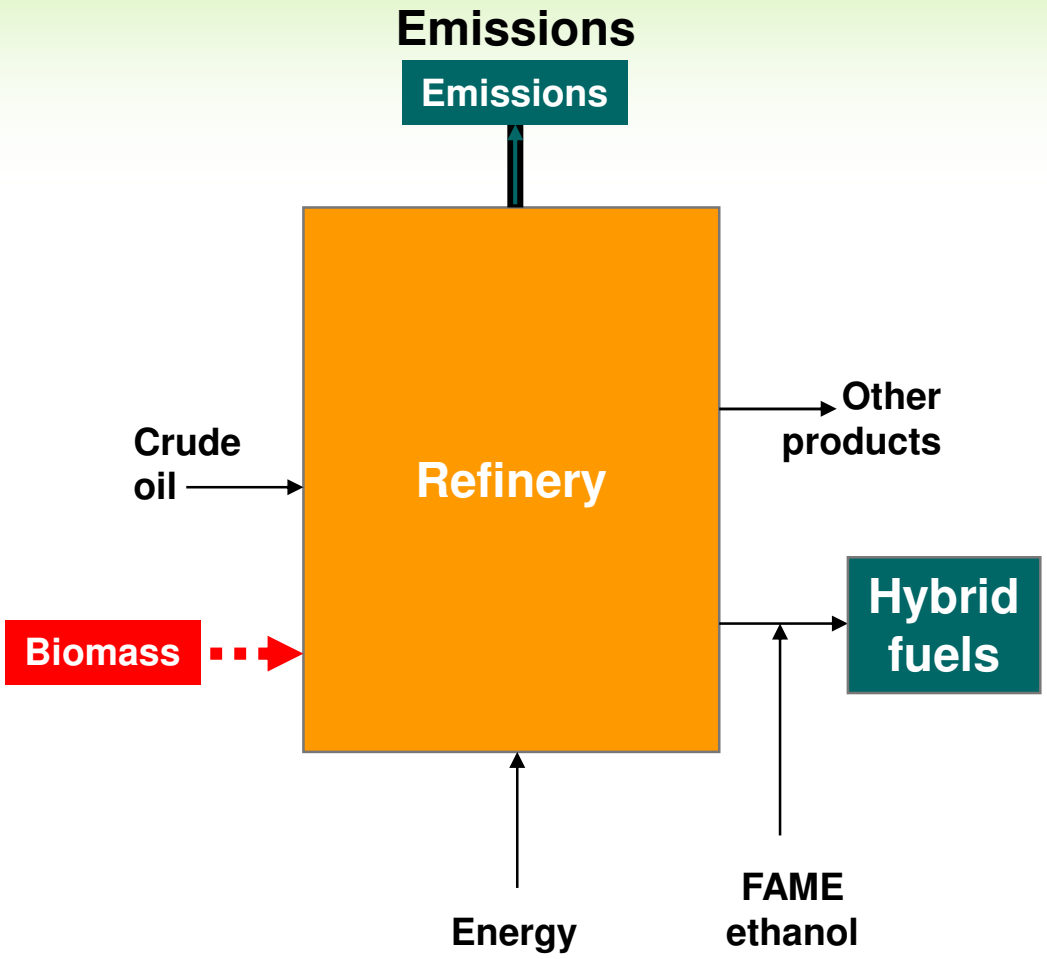
?

- Large-scale units require large investments


Light hydrocarbons C1-C4
Isomerization
Isomerization product
Fuel gas
Naphtha
Hydrotreating
Catalytic reforming
Reformate
Polymerization
Gasoline polymerization
Liquid gas
Alkylate
Alkylation
Alkylation gasoiline
Aviation Fuels
Straight-run kerozene
Hydrotreating
Straight-run diesel
Diesel
Catalytic pyrolysis gasoline
Heavy Gasoil
Hydrotreating
Catalytic pyrolysis
Catalytic pyrolysis diesel
Unleaded Gasoline
Atm. Distillation
Final processing and blending
Light Vacuum Gasoil
Hydrocracking gasoline
Heating oil
Hydrocracking
Hydrocracking mid-distillate
Heavy Vacuum Gasoil
Thermal processing Fuel gas and gasoline
Vacuum Distillation
Heavy fractions upgrading
Lubricants process
Lubricants
Thermal process
Coke
Asphalt

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Co-Processing Biomass
Technical & Environmental Targets



A. Technical feasibility
- Utilize existing infrastructure
- Maintain similar operation
- Maintain same product quality

B. Environmental performance
- Mitigate energy consumption
- Reduction of emissions (WTT)

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A Co-Processing Case Study
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

HELLENIC PETROLEUM

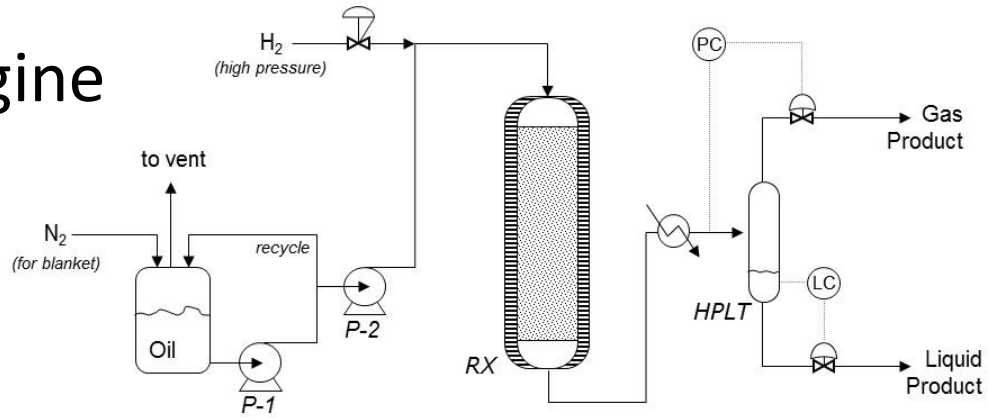
SUNLIGHT creating energy

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Technical Feasibility Assessment

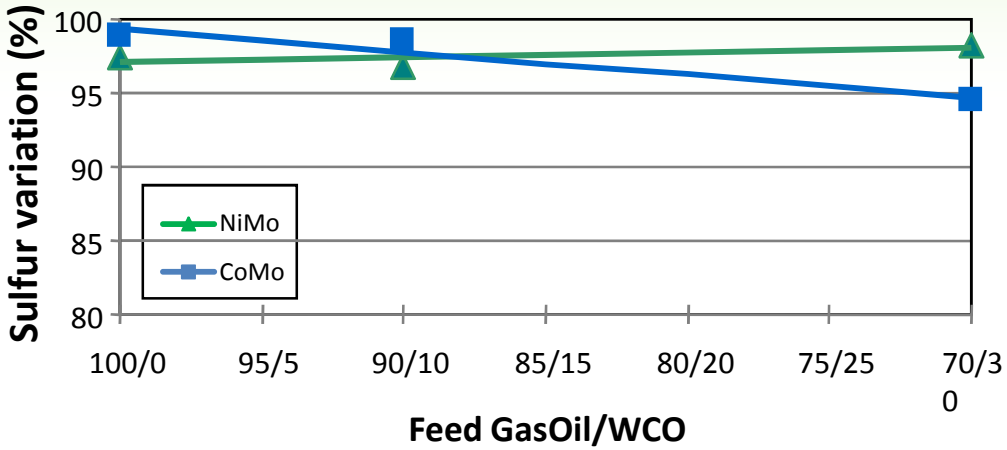
1. Evaluation of hydrotreating catalyst
2. Determine optimal operating conditions
   - T, P, H_2/oil, LHSV
3. Determine max WCO mixing ratio
4. Evaluate emissions & engine performance

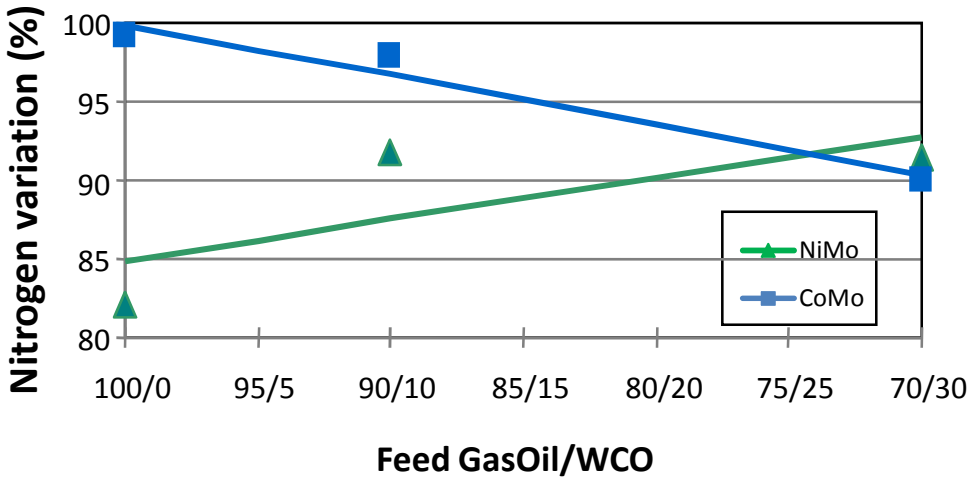




Catalyst Evaluation
Heteroatom Removal

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

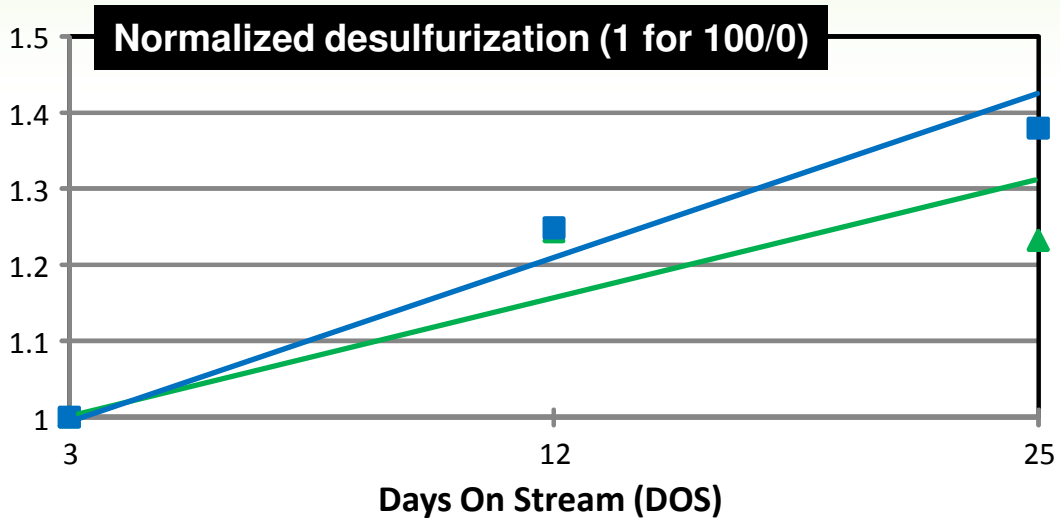




WCO addition does not decrease product quality when NiMo catalyst is used

Catalyst Evaluation
Deactivation Rate

- Catalyst deactivation rate is extremely important for catalyst selection
- Deactivation rate determined based on desulfurization efficiency at different DOS

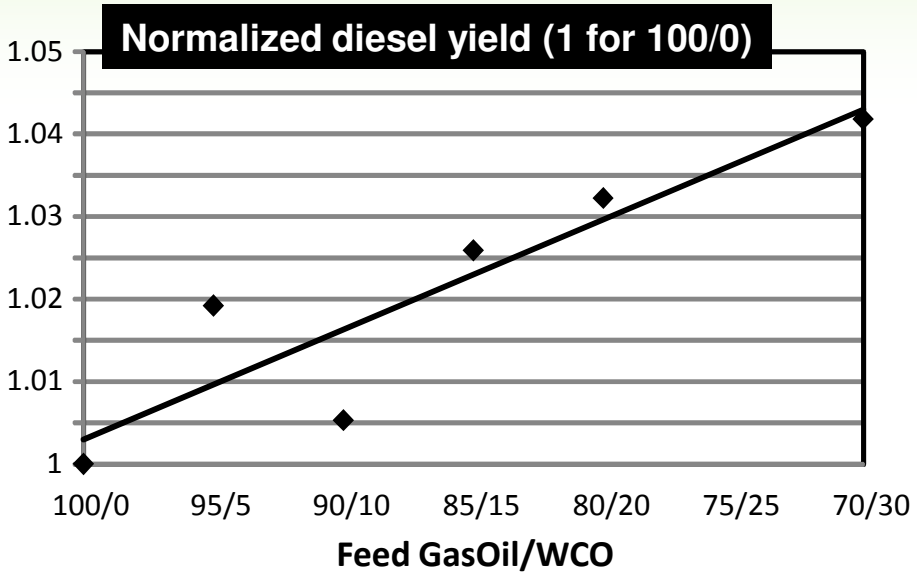


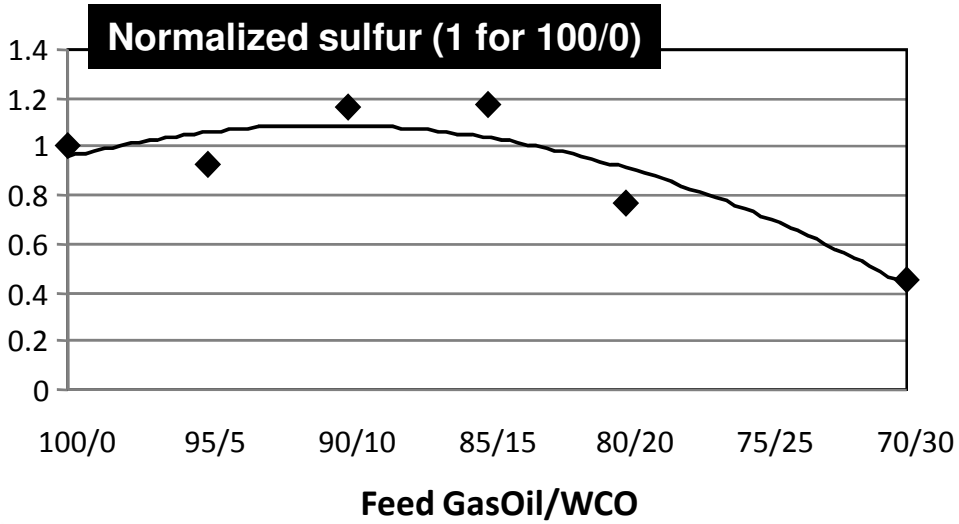
NiMo deactivation rate is 3 times smaller than CoMo

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Effect of Biomass Content Heteroatom Removal & Diesel Yields

- Diesel yield favored with increasing WCO
  - WCO contained triglycerides can be more easily converted into diesel range hydrocarbons
- Desulfurization shows an optimum rate at ~10% WCO
  - Desulfurization efficiency decreases for high WCO ratios

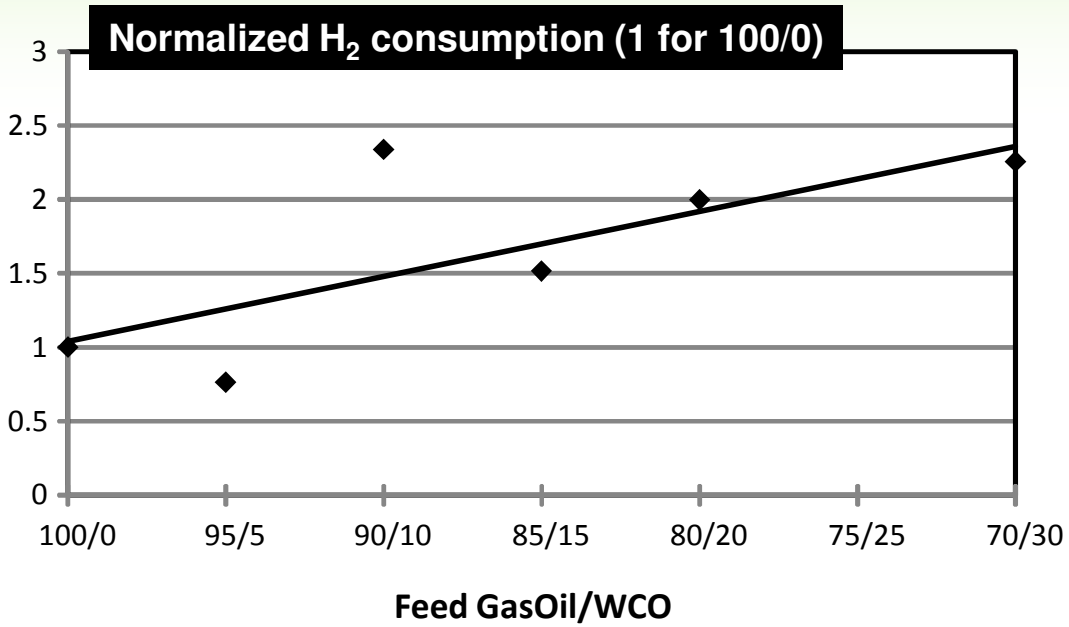




WCO favors diesel yields but at higher ratios limits HDS

Effect of Biomass Content
Hydrogen Consumption

- Hydrogen consumption affects process economics
- Hydrogen consumption increases due to underlying HDO kinetics
- Smaller WCO rates (<90%) are preferred for economic feasibility of WCO integration

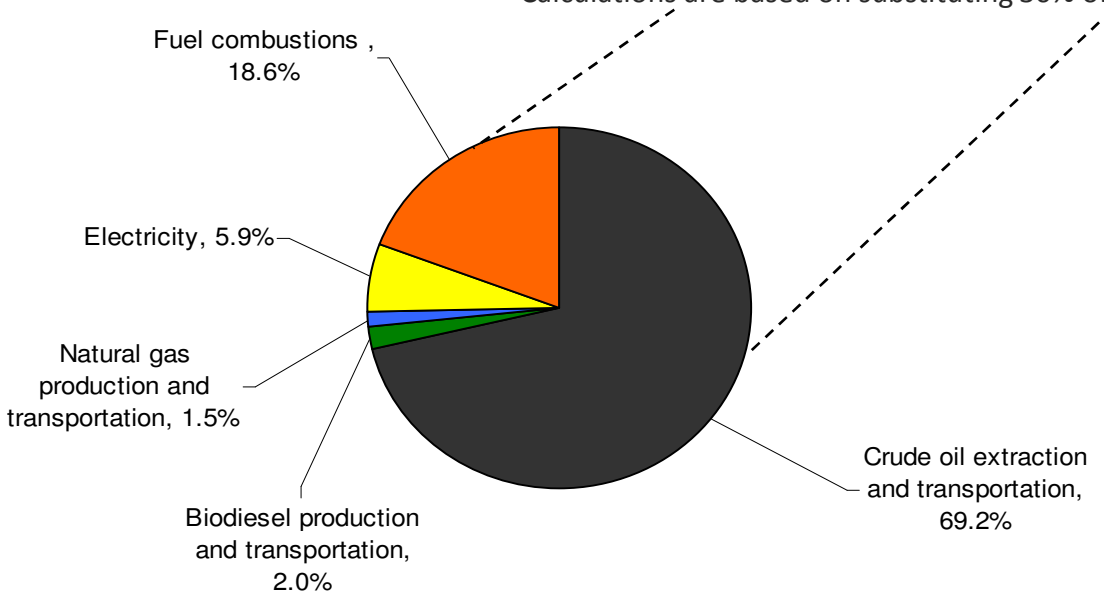


WCO increases H_2 consumption

Environmental Performance Assessment

	Current Diesel Production	Proposed WCO incorporation*
Diesel emissions	0.573 kg CO_2 eq-/kg	0.478 kg CO_2eq-/kg
Total refinery emissions	2,119 Mt CO_2eq-/yr	1,679 Mt CO_2eq-/yr

* Calculations are based on substituting 30% of fossil fraction (HAGO) with WCO



Expected reduction of GHG emissions by 20.75%

Conclusions

- Catalytic hydrotreatment is an effective process for biomass upgrading
  - Bio-based intermediates & lipids upgrading
  - Compatibility with fossil fuels, attractive properties
- Co-hydroprocessing can allow immediate and sustainable biomass integration with energy markets
  - No requirement of investments on new infrastructure
  - No significant technology limitations
  - Improvement of fuel sustainability (lower carbon foot-print)

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ΑΝΤΑΓΩΝΙΣΤΙΚΟΤΗΤΑ ΕΠΙΧΕΙΡΗΜΑΤΙΚΟΤΗΤΑ
ΕΠΙΧΕΙΡΗΣΙΑΚΟ ΠΡΟΓΡΑΜΜΑ
ΕΠΑΝ ΙΙ
ΕΣΠΑ 2007-2013
η περιφέρεια στο επίκεντρο της ανάπτυξης

ΕΣΠΑ 2007-2013
πρόγραμμα για την ανάπτυξη