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CPERI
Chemical Process and Energy Resources Institute

SUSTAINABLE HEFAs FOR AVIATION

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HyPro

2nd ECATS Conference: Making aviation environmentally sustainable
7-9 November 2016, Athens, Greece

ECATS International Association

Biomass Conversion to Biofuels

✓ Renewable

? Low H/C ratio

? Contains water

– Corrosion problems

? High oxygen content (aldehydes, acids, cetones)

– Reduced heating value

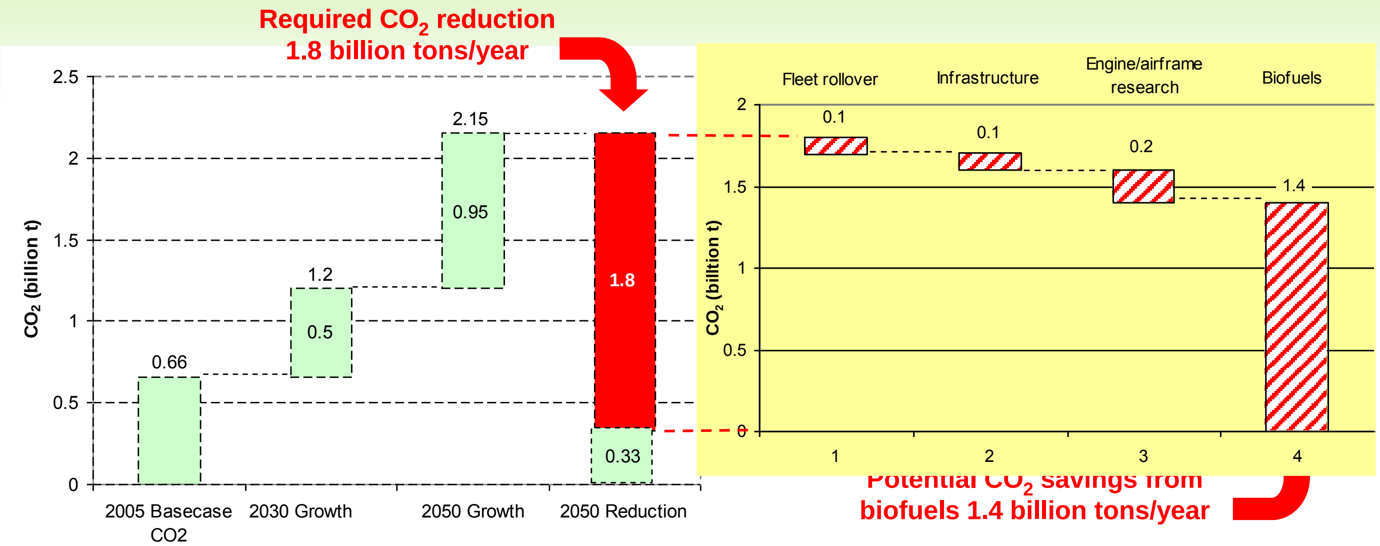
– Reduced oxidation stability

– Increased acidity

} **Engine performance problems**

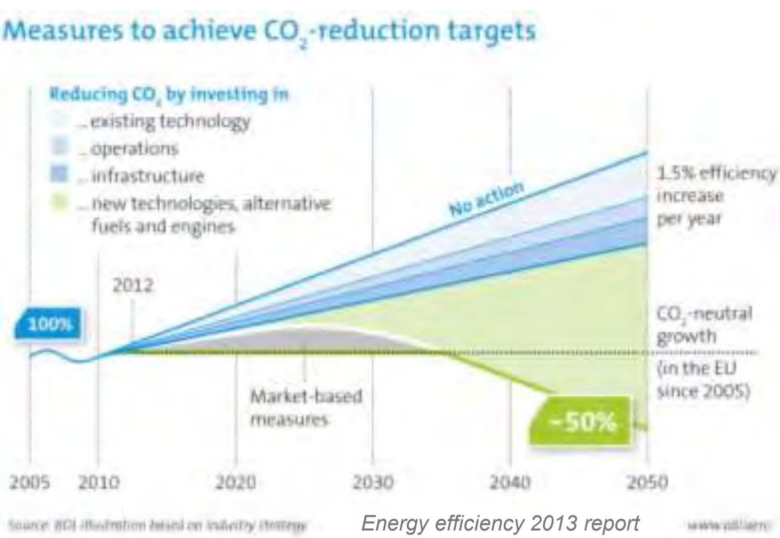
Biomass requires H/C increase, oxygen and H_2O removal

Aviation Biofuels & CO_2 Reduction Potential

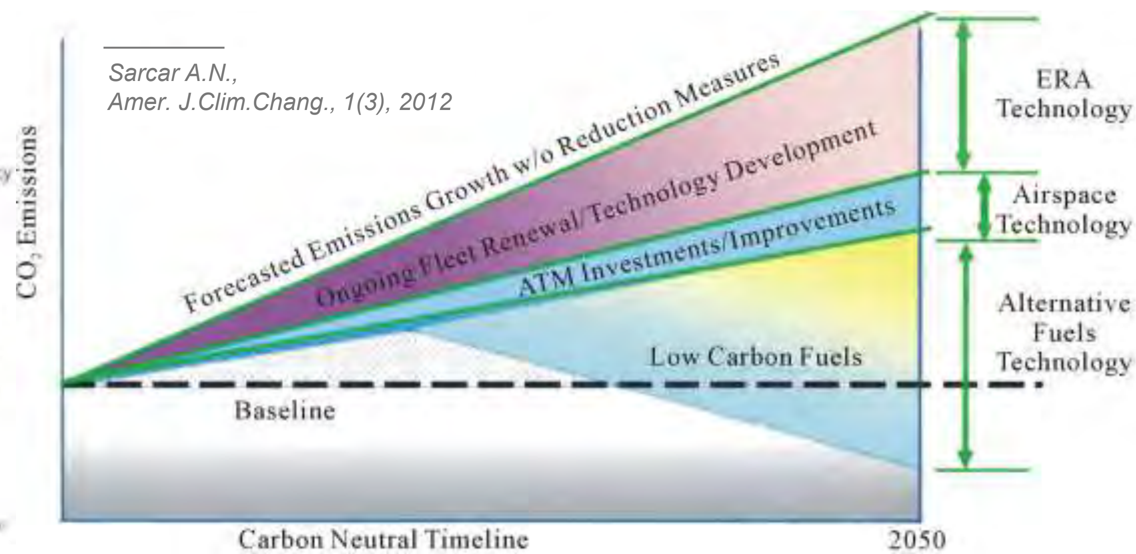


Adapted by Booz & Company, WEF, Davos 2011

Biofuels are the only way to meet the 2050 CO_2 emission targets

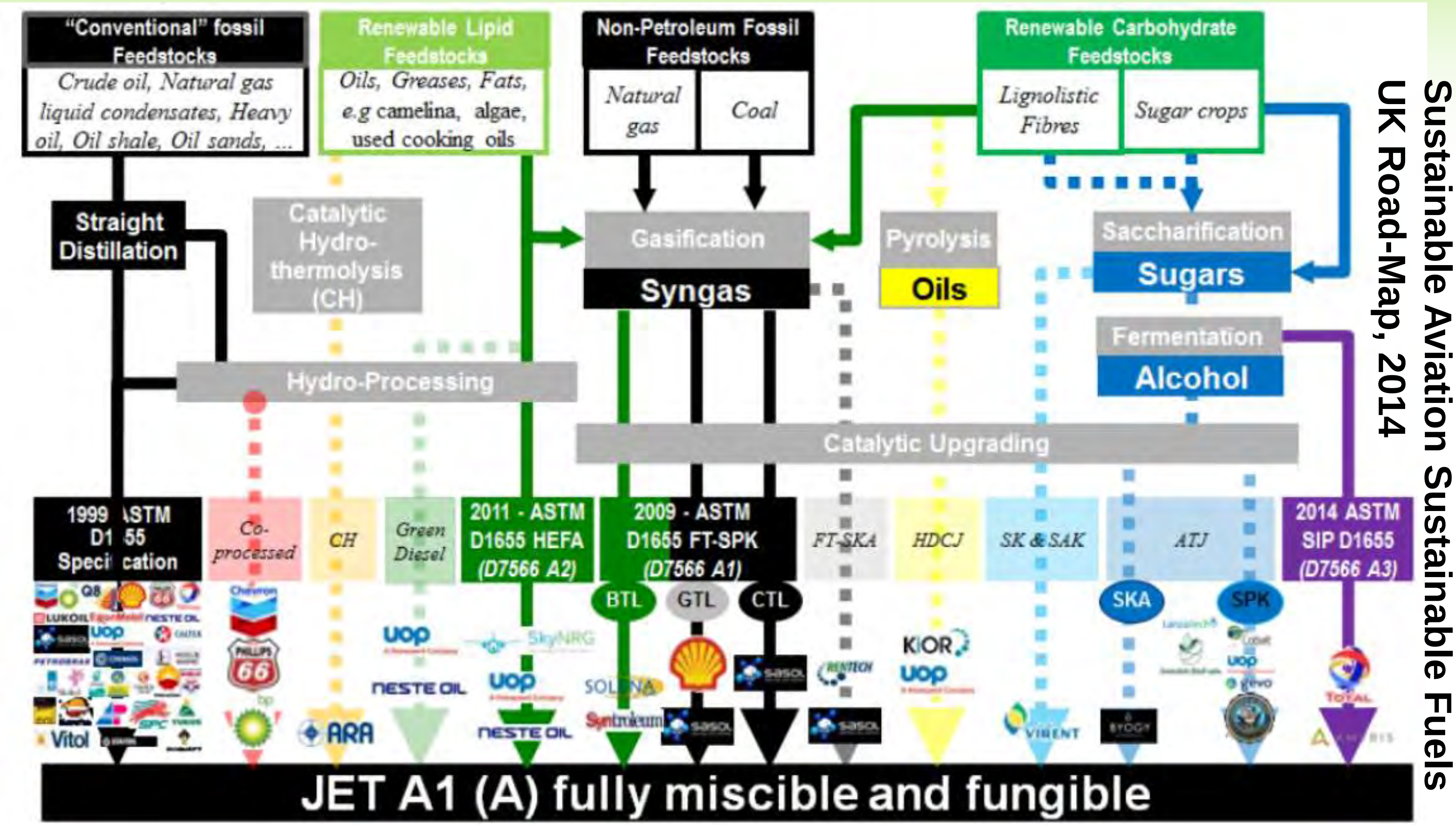


Energy efficiency 2013 report
Adopted by IATA



Sarcar A.N.,
Amer. J.Clim.Chang., 1(3), 2012

Which Biofuels Technology?



Presentation of Lucy Nattrass in Flightpath 2020 Workshop, Brussels, February 12, 2015

Environmental Criteria

- Limit aviation GHG emissions' impact on global climate
  - Target: 60% GHG emissions reduction over fossil fuels
- Limit aviation emissions' impact on local air quality
- Meet stringent sustainability standards with respect to land, water and energy use
  - Avoid direct and indirect land use change impacts
  - Not displace or compete with food/feed crops
- Provide a positive socio-economic impact
- Exhibit minimal impact on biodiversity
- Reduce the number of people affected by significant aircraft noise
- Enable harmonisation of sustainability standards in all countries

Quality Criteria

- Bio kerosene specifications relevant for Europe
  - ASTM D1655 and D7566 (US specifications)
    - ASTM D1655: Standard specification for Jet A-1 kerosene for civil aviation use
    - ASTM D7566: Specification for Synthetic kerosene & blends of synthetic (max 50%) and conventional kerosene (Blends meeting ASTM D7566 are by definition ASTM D1655 kerosene and can be used like conventional kerosene)
  - DefStan 91-91 (European specification)

Aviation Biofuels' Quality Challenge

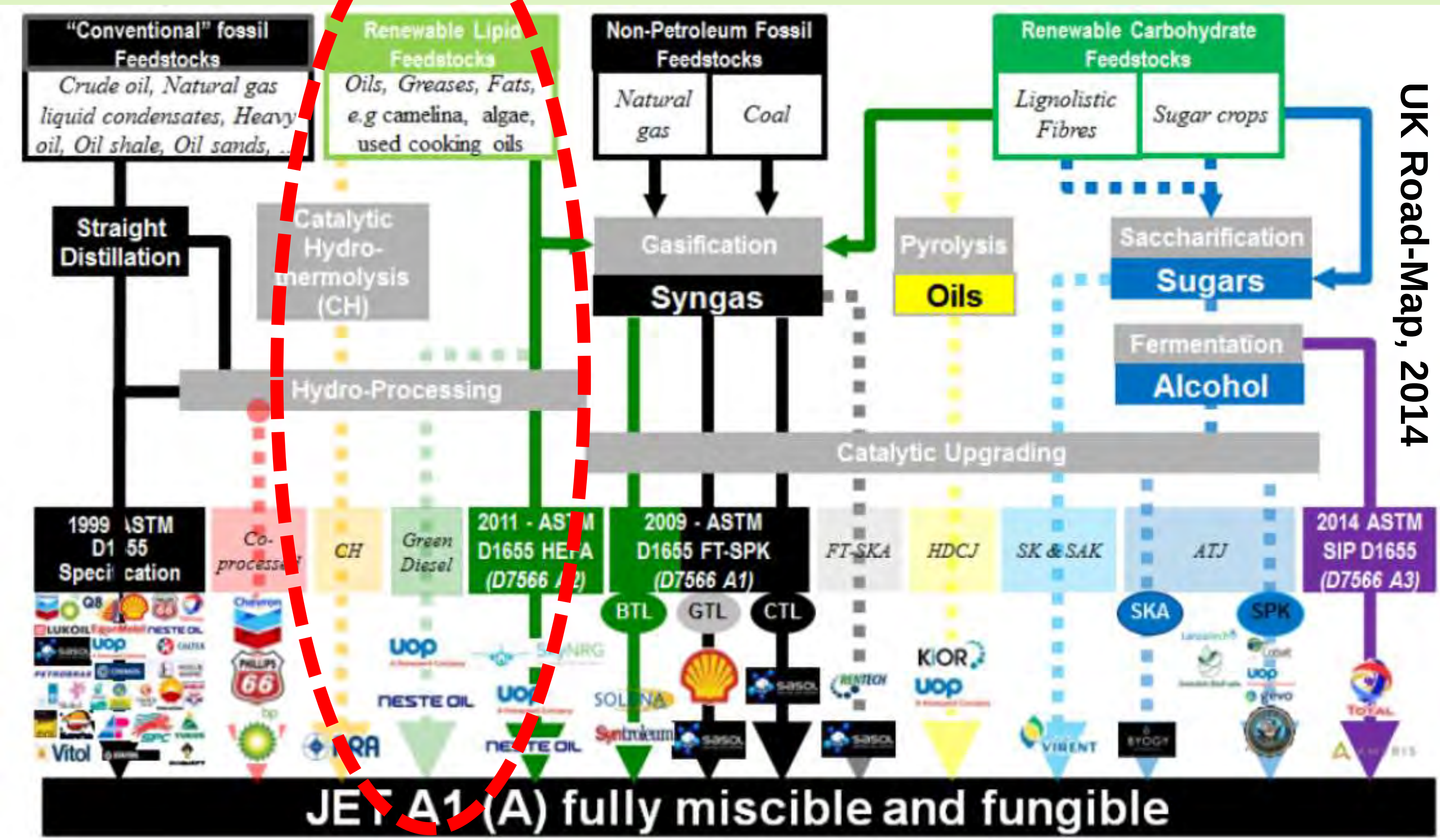
	ASTM D1655	ASTM D7566	Reason of expanded quality requirements of aviation biofuels
Aromatics (% v)	25 (max)	**8**-25	Minimum enforced to maintain engine components (ex. seals), as some biofuels do not have aromatics
Distillation T50-T10 (°C)	NA	**15 (min)**	Ensure proper and smooth range boing range distribution
Distillation T90-T10 (°C)	NA	**40 (min)**	Ensure proper and smooth range boing range distribution
Lubricity (mm)	NA	**0.85**	Specified to ensure smooth operation of moving engine parts, as biofuels are pure HC w/o polar acids

All other quality specs are identical (acidity, sulfur, mercaptans, density, flash point, viscosity, energy density, smoke point, distillation residue, corrosion, thermal stability, electrical conductivity, contaminants)

Aviation Biofuels Types

	Pros	Cons	Applications
FTs	• Lignocellulosic feedstock (agro/forest residues) • High sustainability	• High capital costs • Questionable economics • Low aromatics	• No commercial production • BioTfuel project pilot (2016 ?)
HEFAs	• Technology available	• High production costs (1700-2400$/t) • Low aromatics	• Plants in operation • Fuel tested in flights
ATJs	• Under development	• Low aromatics (need additives)	• Demo plant in operation • Fuel tested in flights
CH	• High aromatics	• Low aromatics	• Demo plant in operation

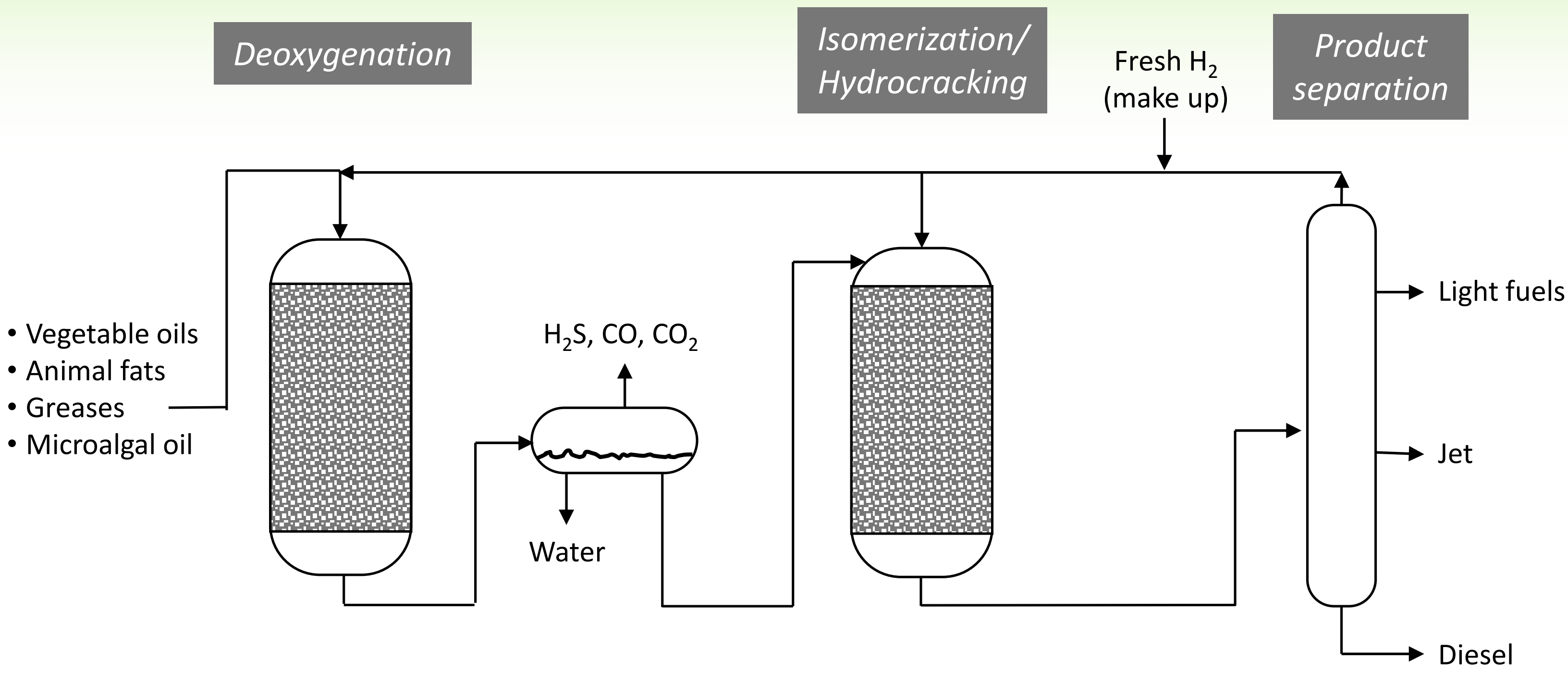
Which Biofuels Technology?



Sustainable Aviation Sustainable Fuels UK Road-Map, 2014

Presentation of Lucy Nattrass in Flightpath 2020 Workshop, Brussels, February 12, 2015

HEFAs Production Technology



- ✚ Flexibility of feedstock types
- ✚ High selectivity on biojet fuel
- ✚ Well established technology used in refining industry

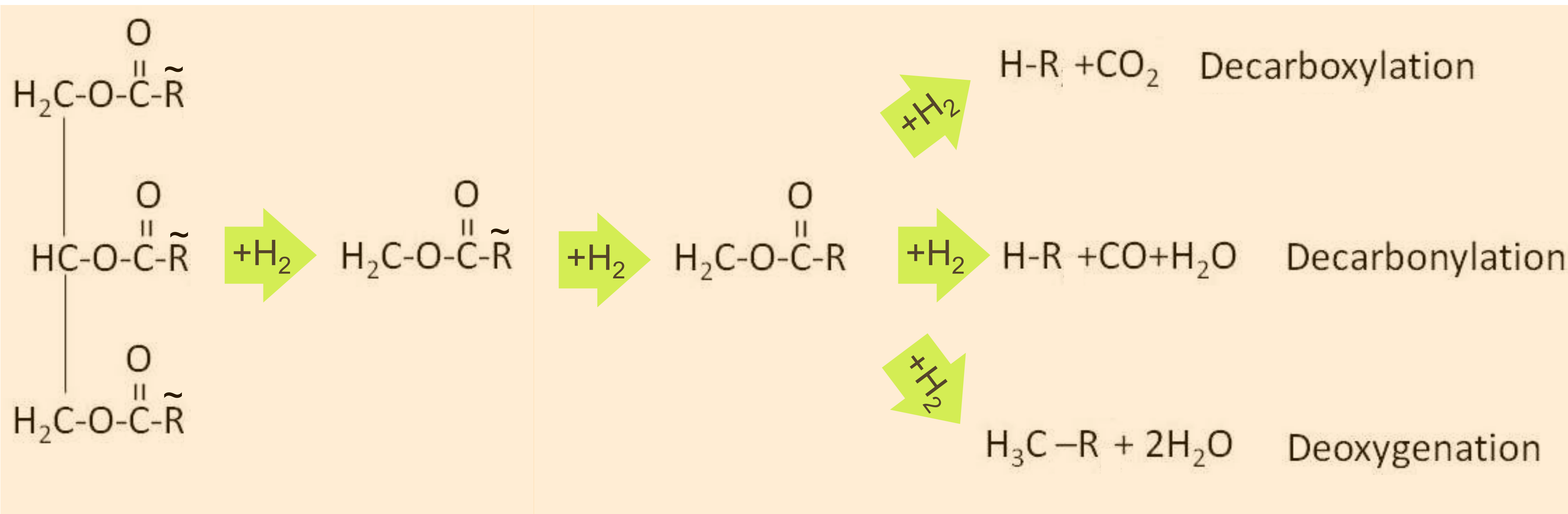
- – In-line separation of water and acid gases
- – Relatively high production cost
  - Mostly attributed to H_2 consumption

Hydrotreating Reactions (1/2)

- ρ reduction
- Diesel yield increase

- H/C increase
- Br# decrease

- TAN decrease
- Induction time increase

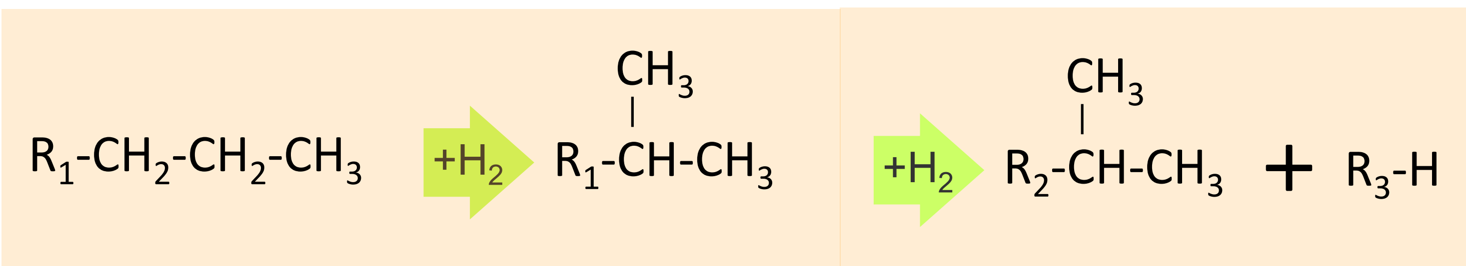


R̃ : unsaturated aliphatic chain

R : saturated aliphatic chain

Hydrotreating Reactions (2/2)

- Cold flow properties improvement
- Tailoring jet fuel molecules



$R_1=R_2+R_3$

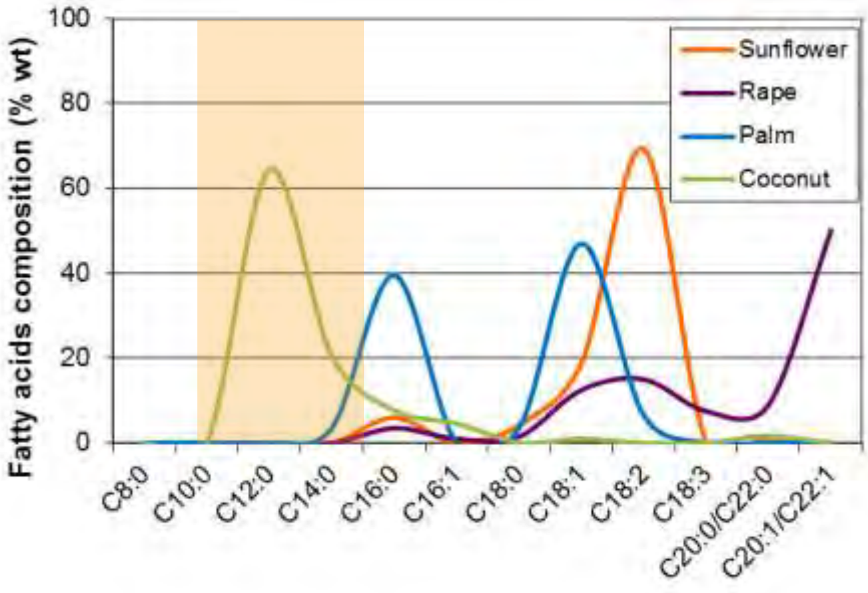
HEFA Production RXs Network

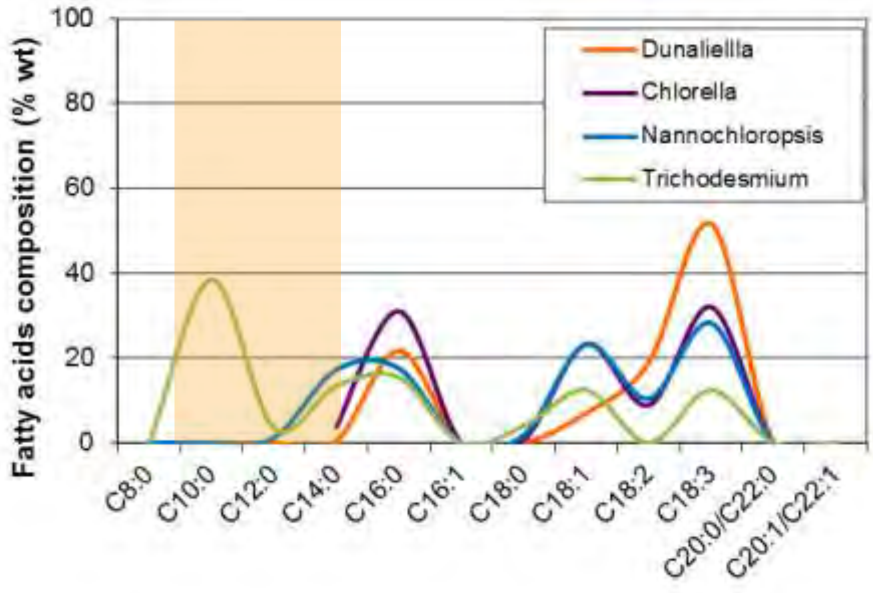
- Reactions associated with HEFA production based on a range of large and unsaturated fatty acids content of lipid feedstocks

	Reaction type	Reaction	H_2/oil (mol/100mol)
1	Triglyceride hydrogenolysis*	$CH_2\text{-}O\text{-}C(=O)\text{-}R$ / $CH\text{-}O\text{-}CO\text{-}R$ / $CH_2\text{-}O\text{-}C(=O)\text{-}R$ $+ 2 \cdot H_2 \longrightarrow 3 \cdot R\text{-}CH_2COOH + CH_3\text{-}CH_2\text{-}CH_3$	2·100
2	Saturation	$R\text{-}(CH{=}CH)_n\text{-}CH_3 + n \cdot H_2 \longrightarrow R\text{-}CH_2\text{-}CH_2\text{-}CH_3$	3·n·(50-225)***
3	Deoxygenation**	$R\text{-}CH_2COOH + 3 \cdot H_2 \longrightarrow R\text{-}CH_2CH_3 + 2 \cdot H_2O$ $R\text{-}CH_2COOH + H_2 \longrightarrow R\text{-}CH_3 + CO + H_2O$ $R\text{-}CH_2COOH + H_2 \longrightarrow R\text{-}CH_3 + CO_2$	3·100·(1-3)
4	Isomerization	$R\text{-}CH_2\text{-}CH_2\text{-}CH_3 \longrightarrow R\text{-}CH(CH_3)\text{-}CH_3$	0
5	Hydrocracking	$R\text{-}CH_2\text{-}CH_2\text{-}CH_3 + H_2 \longrightarrow R\text{-}H + CH_3\text{-}CH_2\text{-}CH_3$	3·(78-95)***

Lipid Sources

- Plant oils
  - Triglycerides
  - Coconut oil renders 85% jet range (C10-C14) molecules
- Microalgae oils
  - Mostly FFAs
  - *Trichodesmium erythraeum* renders 55% of jet molecules





Lipid Source Type vs. H_2 Consumption

Reaction type	Plant oils				Microalgae oils				Comments
	Sunflower	Rape	Palm	Coconut	Dunaliella sp.	Chlorella sp.	Nannochloropsis Oceanica	Trichodesmium erythraeum sp.	
1. Hydrogenolysis	**2.0**	**2.0**	**2.0**	**2.0**	**0.0**	**0.0**	**0.0**	**0.0**	• No H_2 consumption during hydrogenolysis of microalgal lipids
2. Saturation	**6.3**	**1.4**	**0.6**	**0.1**	**0.0**	**0.0**	**0.0**	**0.5**	• Significant H_2 consumption during this step • Need for saturated lipids feedstocks (some plant oils) • Can be improved for microalgae-based species by improving cultivation strategy & genetic modification of algae strain
3. Deoxygenation	**6.0**	**6.0**	**6.0**	**6.0**	**2.0**	**2.0**	**2.0**	**2.0**	• Highest H_2 consumption • Can be improved by catalyst design optimization
4. Isomerization	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	• Comparable consumption (negligible)
5. Hydrocracking	**2.6**	**2.6**	**2.5**	**0.5**	**0.9**	**0.8**	**0.7**	**0.4**	• Comparable H_2 consumption for all species • Can be improved for microalgae-based species only by improving cultivation strategy & genetic modification of algae strain
Total (mol H_2/mol oil)	**16.9**	**12.0**	**11.1**	**8.5**	**2.9**	**2.8**	**2.7**	**2.4**	
Total (mol H_2/mol jet)	**5.6**	**4.0**	**3.7**	**2.8**	**2.9**	**2.8**	**2.7**	**2.4**	

Microalgal Oil Experimental Tests

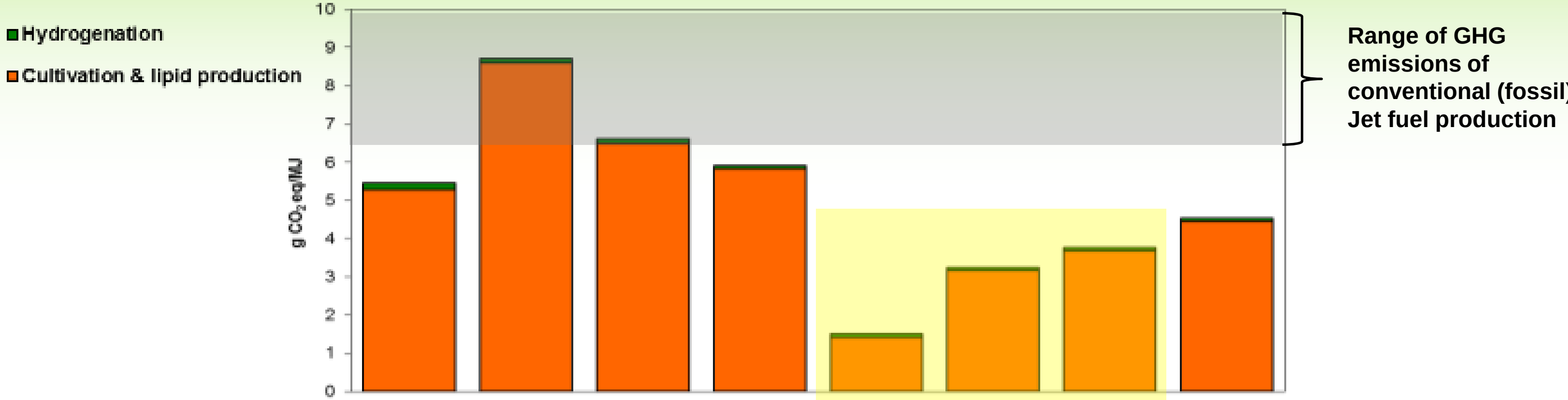
- Evaluate different microalgae species
  - *Stichococcus sp., Nannochloropsis sp., Botryococcus braunii*
- Develop technology for microalgal oil extraction and conversion to 3G-biofuels

ΕΣΠΑ 2007-2013

MICROALGAE-BIO-PRODUCTS

A. Karapatsia, et.al., 10th European Symposium on Biochemical Engineering Sciences and 6th International Forum on Industrial Bioprocesses, September 7-10, 2014, Lille, France

Overall HEFAs Production Carbon Footprint



	Plant oils				Microalgae oils			
	Sunflower	Rape	Palm	Coconut	Dunaliella sp.	Chlorella sp.	Nannochloropsis Oceanica	Trichodesmium erythraeum sp.
A. Cultivation & lipid production	5.288	8.609	6.489	5.835	1.410	3.160	3.676	4.450
B. Hydrogenation	0.171	0.122	0.113	0.085	0.089	0.085	0.082	0.073
Total (g CO_2-eq/MJ jet)	5.459	8.731	6.602	5.920	1.499	3.246	3.758	4.524

Sources:

[1] JRC Technical Report, 2014

[2] Spath, P.L., Mann, M.K. NREL report DE-AC36-99-GO10337, 2001

[3] Handler R.M., et.al.. Algal Research, 1, pp. 83-92, 2012

[4]. Medeiros, et.al. Journal of Cleaner Production, 96, pp.493-500,2015

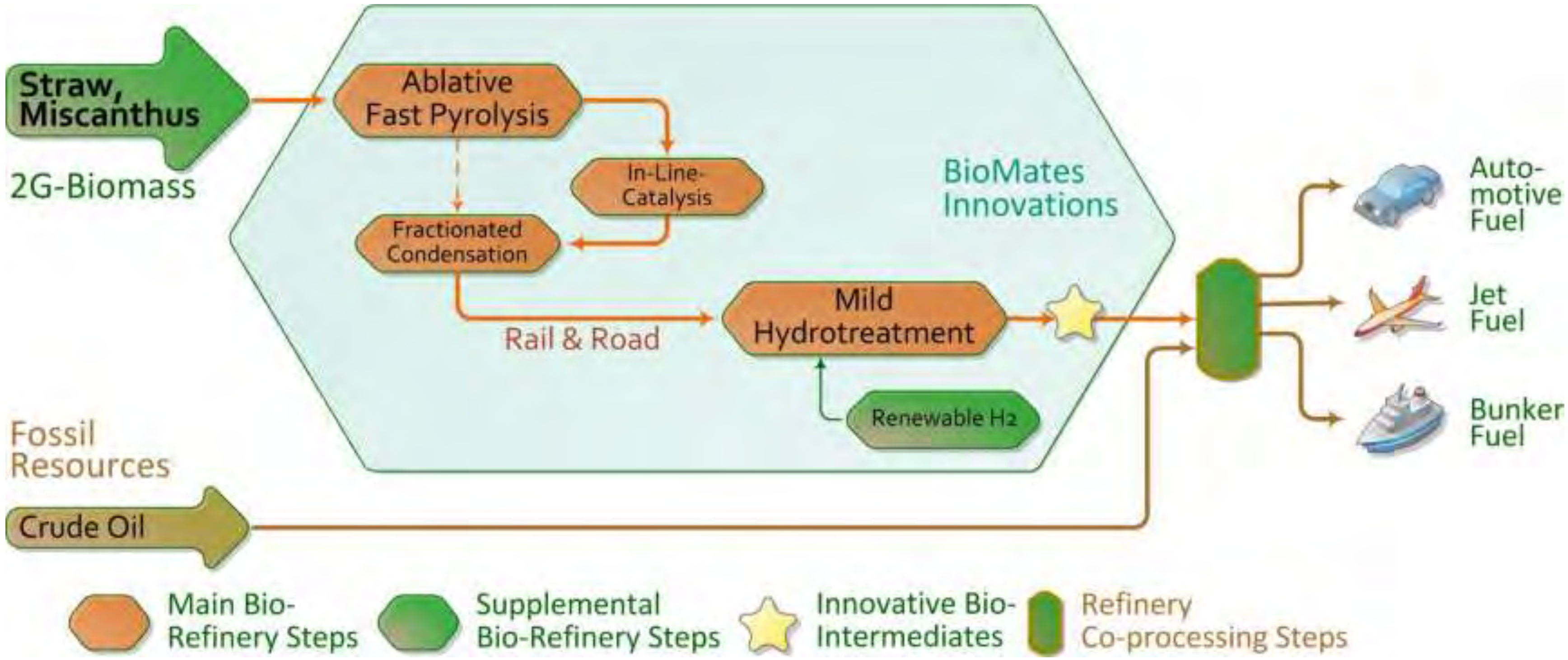
Limits & Opportunities of HEFAs

- High production costs
  - Mostly related with lipid cultivation/extraction
- Current low crude oil prices
- Low aromatics

- Favorable carbon footprint
  - For some (not all) lipid sources
- Potential lipid integration in underlying refineries ➲ Hybrid jet

Next Steps…

Horizon 20-20 project: Reliable Bio-based Refinery Intermediates - BIOMATES



www.biomates.eu

Grant # 727463

Thank you for your attention

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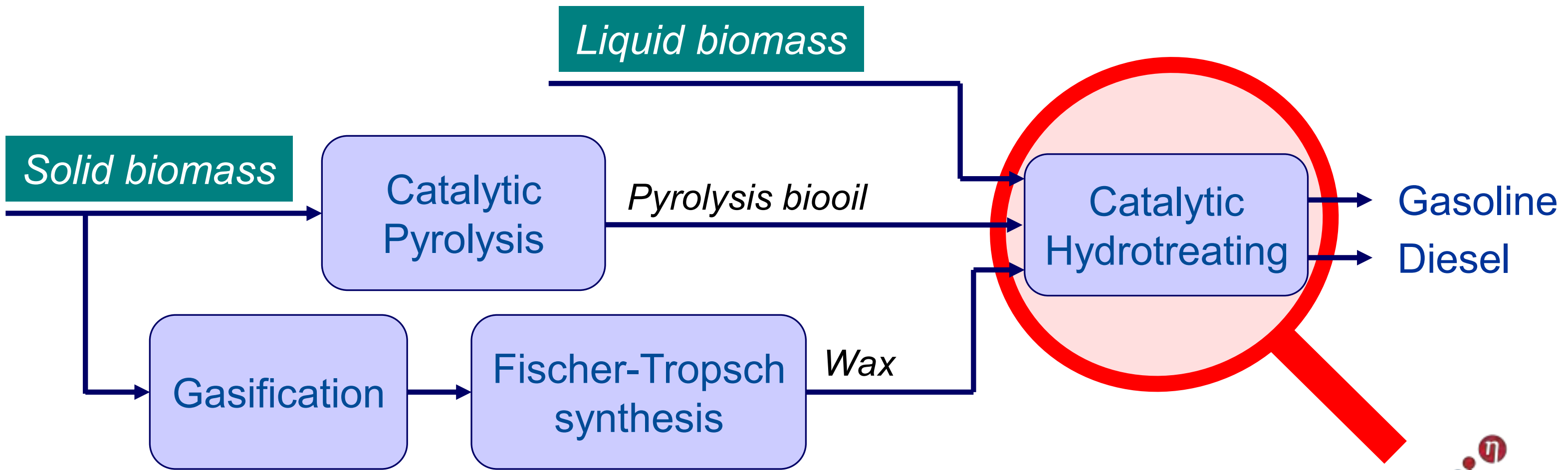
Extra Slides

Catalytic 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 <u>effective</u> technology for biomass upgrading



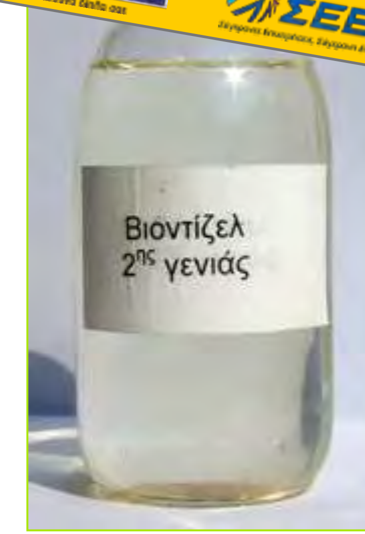
Waste Lipids Upgrading …

www.biofuels2g.gr

2nd Innovation Award
Η ΕΛΛΑΔΑ ΚΑΙΝΟΤΟΜΕΙ!
Eurobank EFG
ΣΕΒ

+ H_2

catalyst



Potential to cover 9,5% of Greek diesel demand

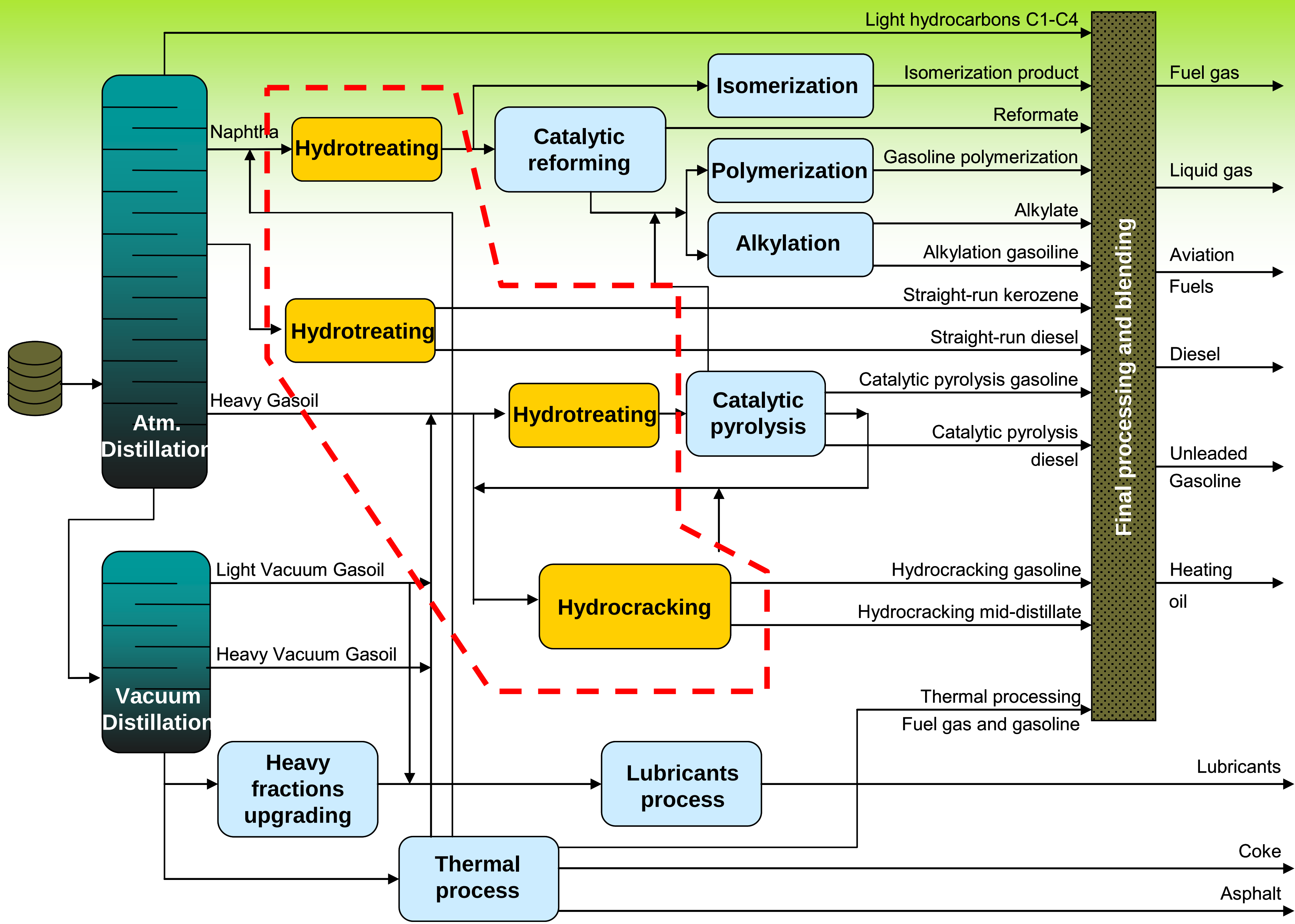
✓

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

?

- Large-scale units require large investments

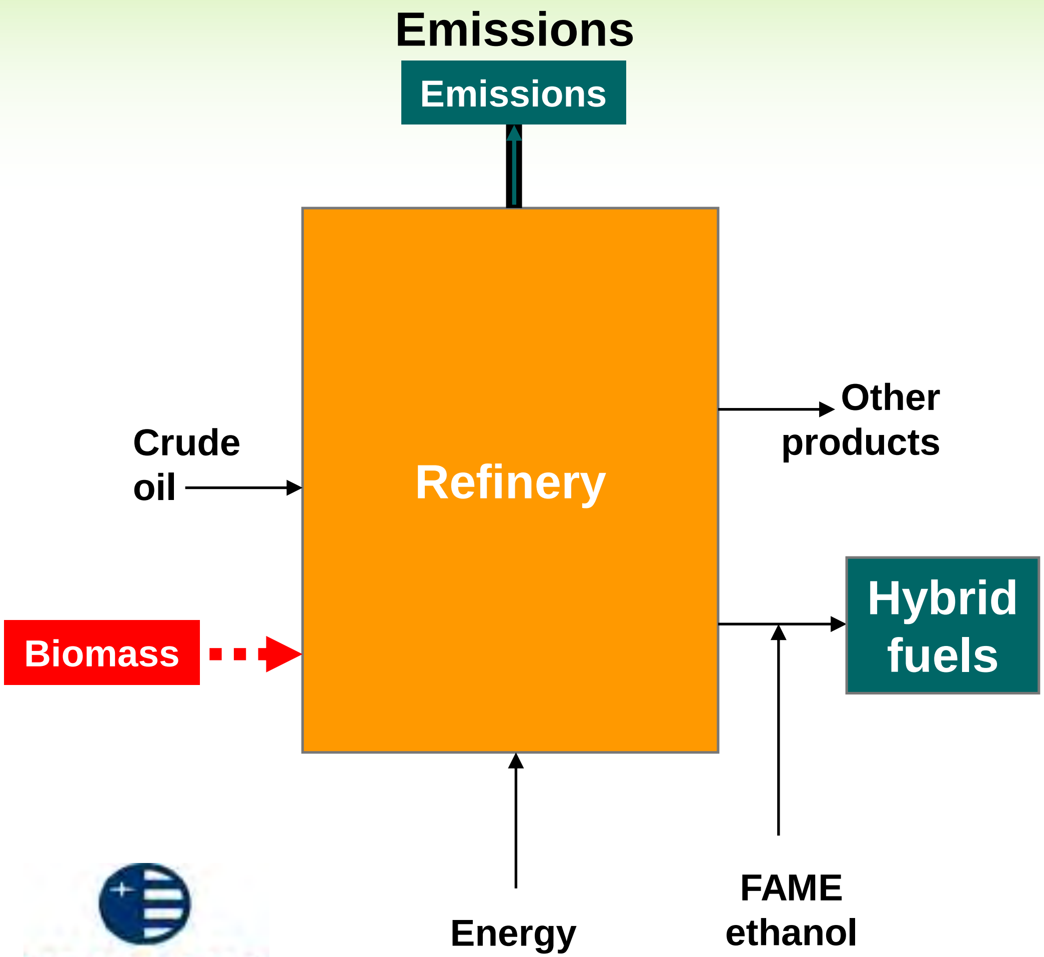
- *Bezergianni, S. et al. (2014) Fuel* ***118****:300*
- *Bezergianni, S.,et al. (2012), Fuel,* ***93****:638*
- *Bezergianni, S., et al. (2011), Ind.Eng.Che.Res.,* ***50****(7):3874*
- *Bezergianni, S., et al. (2010), Biores. Techn.,* ***101****(19):7658*
- *Bezergianni, S., et al. (2010), Biores. Techn.* ***101****(17):6651*



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

Is it possible to integrate biomass in refineries?

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)

HELLENIC PETROLEUM

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www.sustaindiesel.gr

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Technical Feasibility Assessment

❶ Evaluation of hydrotreating catalyst

❷ Determine optimal operating conditions

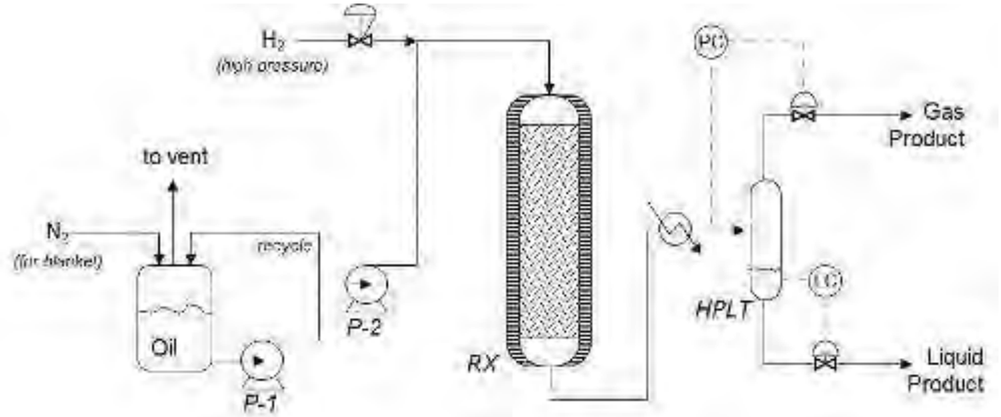
– T, P, H_2/oil, LHSV

❸ Determine max WCO mixing ratio

❹ Evaluate hybrid diesel

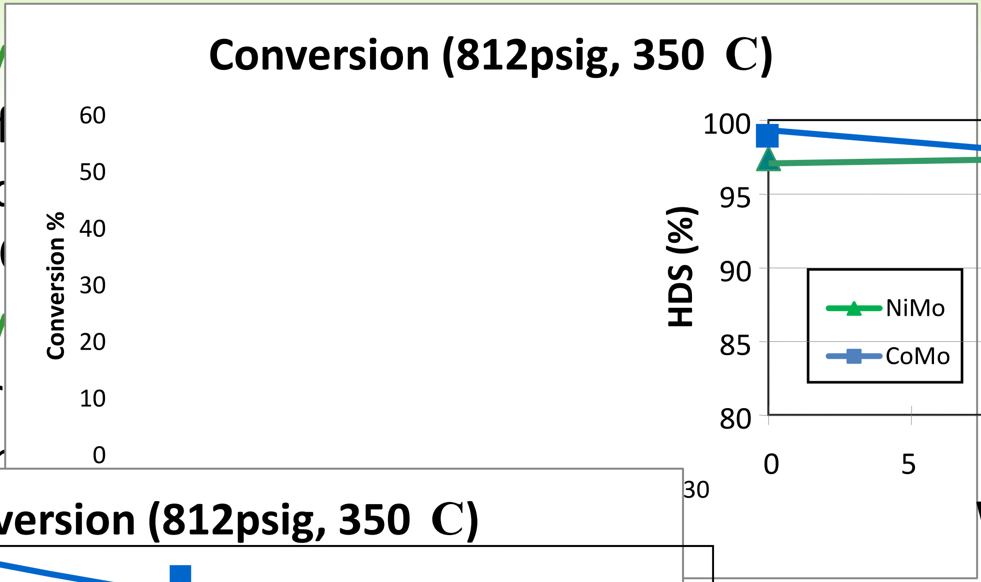
– GHG emissions

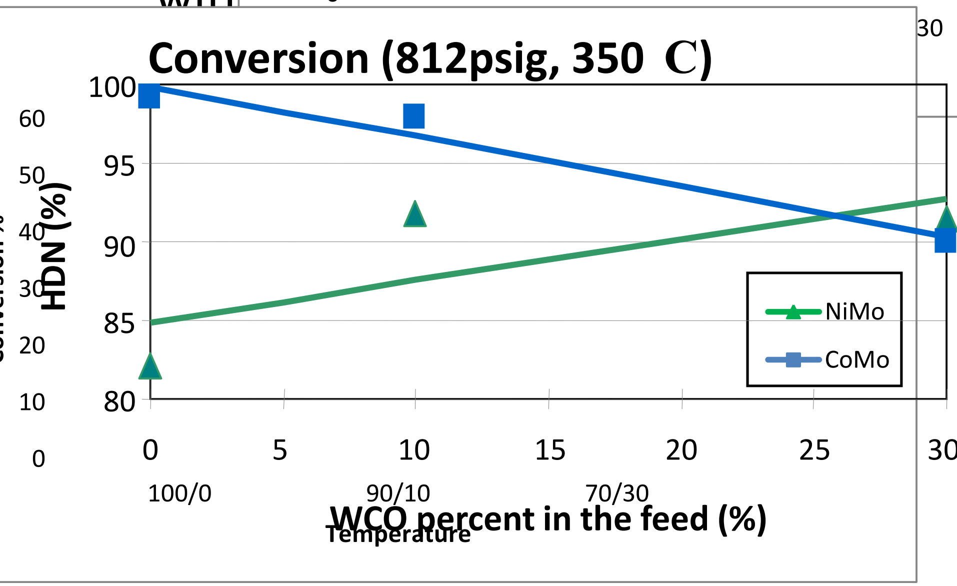
– engine performance



Catalyst Evaluation
Heteroatom Removal

- **NiM**
  perf
  feed
  WC
- **NiM**
  incr
  with



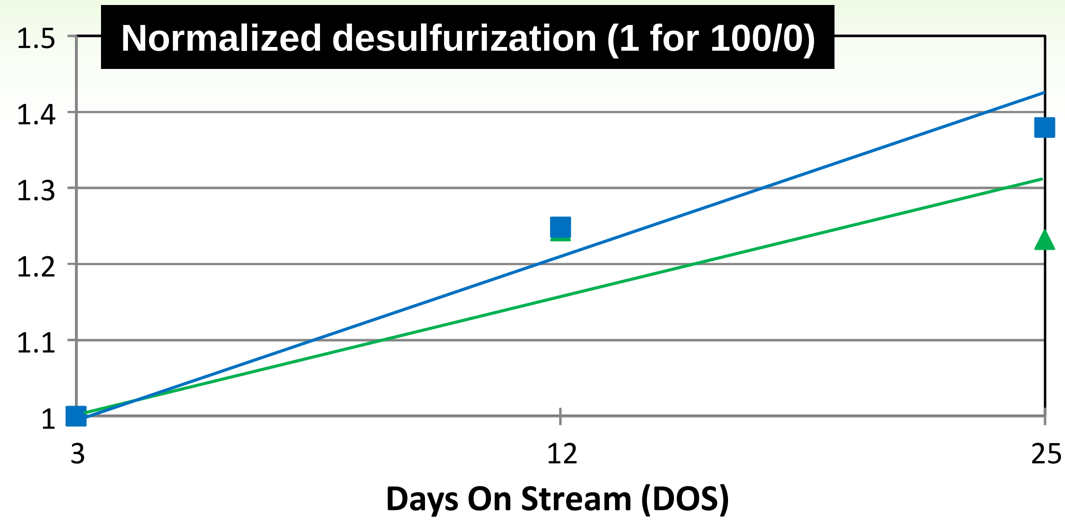


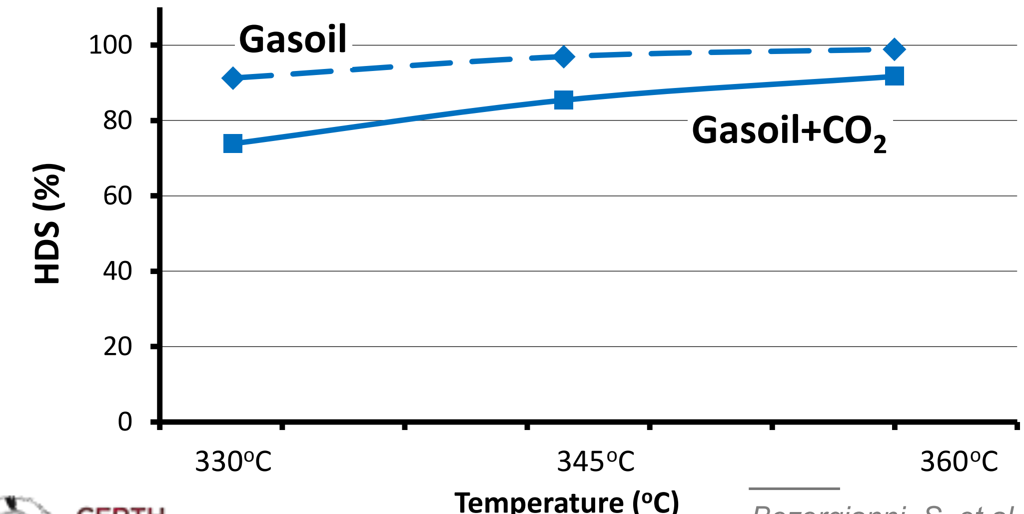
WCO addition does not decrease product quality when NiMo catalyst is used

S. Bezergianni et al. (2014), Fuel, 125:129

Catalyst Evaluation
Deactivation Rate

- Catalyst deactivation rate is extremely important for catalyst selection
- Deactivation rate determined based on desulfurization efficiency at different DOS
- WCO by-product CO_2 has a suspending role in HDS/HDN



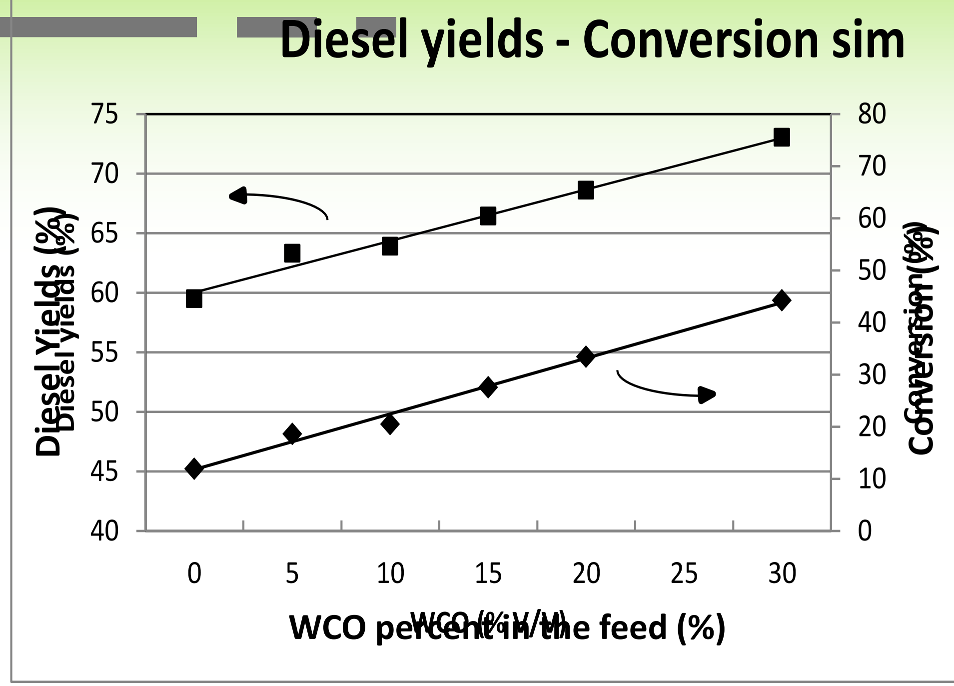


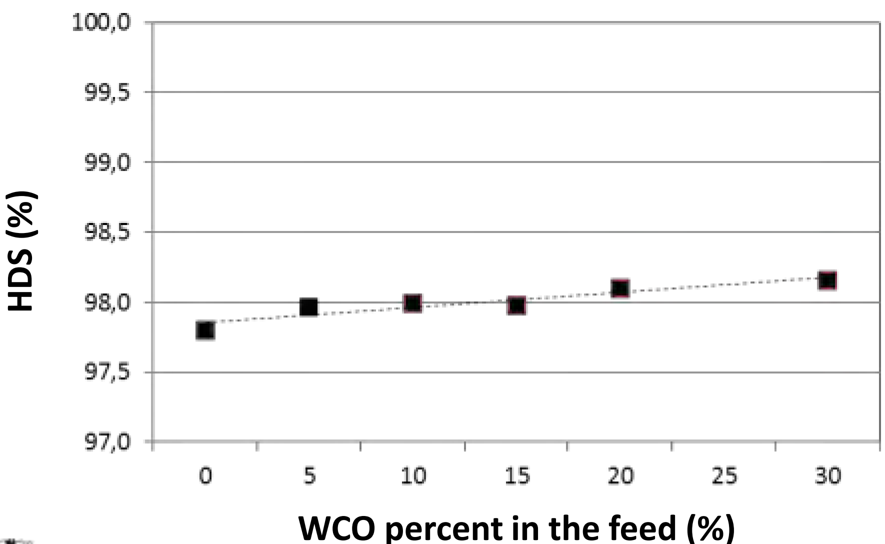
NiMo deactivation rate is 3 times smaller than CoMo

Bezergianni, S. et al. (2015) Canadian J. Chem. Eng. 93:1017

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 is not limited by WCO



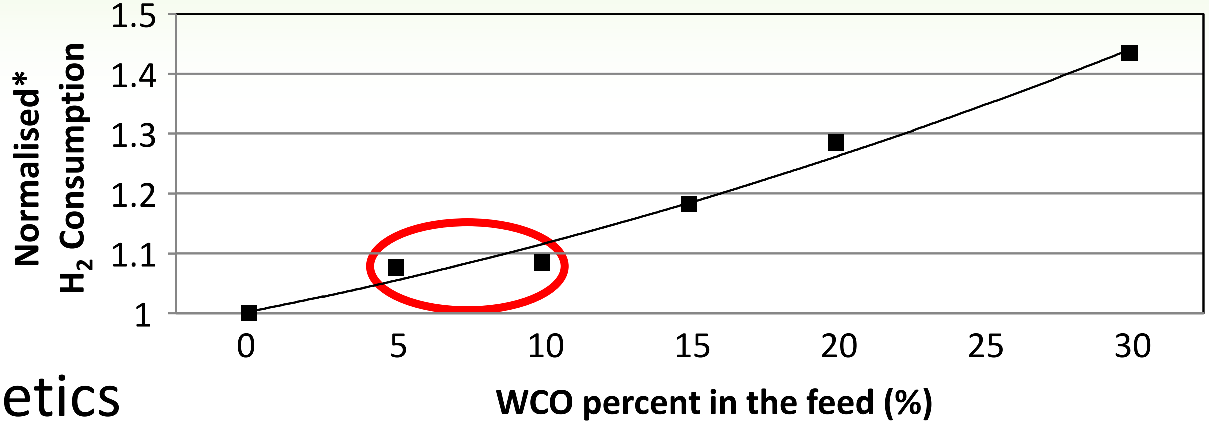


Biomass integration favors diesel yields and renders low S diesel

Bezergianni, S. et al (2014), Fuel, 136:366

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
  - 5-10% WCO → 7.5-8.5 % increase in H_2 consumption



No more than 10% H_2 consumption increase for less than 10% WCO

Quality Assessment
Hybrid vs. Market Diesel

Properties	Units	Hybrid diesel	Market diesel
Density	kg/m^3	825,8	829,2
Flash point	°C	61	67
Sulpur	wppm	8,2	5,8
Viscosity (40°C)	cSt	2,996	3,066
Cetane index		59,1	58,3
Cetane number		56,7	55,7
Water	wppm	100	60
CFPP	°C	-2	0
Polyaromatics	%w/w	1,1	1,4
Lubricity	μm	181	174
Recovery 95% v/v	°C	353	353,2
Recovery at 250°C	%v/v	26,8	25,8

Environmental Performance Assessment

Fuel* type	gCO_2 eq/MJ
Market diesel	16.97
Hybrid diesel (WCO co-processing)	9.32
Diesel with WCO-based HVO	14.15

** All fuels have a total 7% v/v bio-content*

Expected reduction of GHG emissions by 45%

Co-processing of biomass in refinery is environmentally and economically more sustainable allowing extended integration of biomass in transportation sector.

Bezergianni, S. et al (2015), Proceedings of GCGW-15

Stand-alone Biomass Upgrading vs. Co-processing

Stand-alone biomass upgrading	Biomass co-processing
• Produces drop-in biofuels (FAME, ethanol, HVOs, etc) – Technical limitations may be associated with end-use • Requires infrastructure ➲ large CAPEX • Utility intensive processes (fuel, NG, H_2 etc) • Ambiguous environmental benefits	• Renders hybrid fuels (decarb gasoline, jet, diesel) – Fully compatible with fossil counterparts • Utilizes existing infrastructure ➲ low CAPEX • Employs underlying utilities of refineries • Clear reduction of CO_2 emissions during production

Conclusions

- Catalytic hydrotreatment is a key technology 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)
  - Optimal way of integrating biomass in transportation sector from an environmental and economic point of view

Biomass & Biofuels

BIOMASS

- Energy crops
  - Sunflower, rapeseed, cotton, corn, barley, soy, sweet- sorghum, sugar-beet etc
- Lignocellulosic material
  - Wood, paper industry waste, forestry waste etc
- Animal fats
- Agricultural and municipal waste
- Waste cooking oil/fats
- Algae
- ….

BIOFUELS

Fuels produced from biomass

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FAME Biodiesel
Most Common Biofuel in EU

- Fatty Acid Methyl Esters, FAME
  - Produced via transesterification of fatty acids
- Lipid feedstocks / Triglycerides
  - Rape-seed oil, sunflower oil, cotton oil, tallow, waste cooking oil etc
  - Require dedicated cultivated areas ➲ Food vs. Fuel
- Properties
  - ✚ Environmentally friendly (reduced SO_x, CO, aromatics)
  - ✚ Higher cetane number and lubricity
  - — Reduced cold flow properties
  - — Low oxidation stability
  - — Tend to decompose ➲ hydroperoxides, acids, cetones
- Utilized as mixture with conventional diesel
  - B5 to B20 (higher FAME content renders problems in warmer countries)
  - No major engine modifications required

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Bioethanol
Most Popular Biofuel Worldwide

- Sugar and starch feedstocks
  - – Sugar-cane, sugarbeet, sweet-sorghum, corn, potato, etc
  - – Require dedicated cultivated areas ➲ Food vs. Fuel
- Properties
  - ✚ Similar combustion with gasoline
  - ✚ Reduction of emissions
  - ✚ Higher octane number
    - » Employed as octane booster
  - ✚ Increase engine performance
  - ▬ Requires high purity ethanol in gasoline mixtures (99.5-99.9%)
- Utilized in mixtures with gasoline
  - – Most common E10, ideal E85 (FFVs)