Co-hydroprocessing of bio-oils to middle distillates”

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Training seminar 20. April 2021 (VTT organizer)

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 818120.

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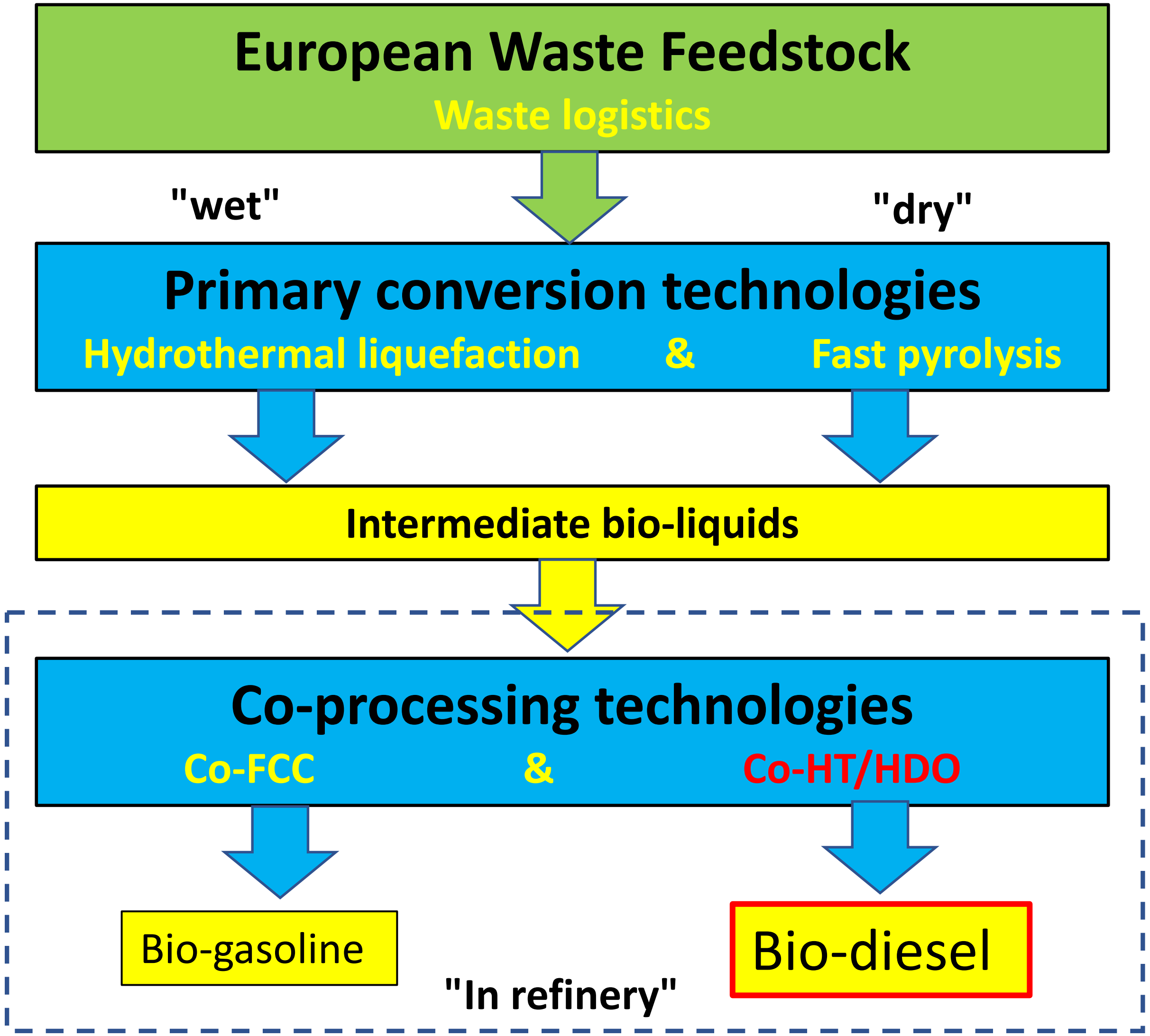
Co-HT/Co-HDO in the Waste2Road concept

WASTE2ROAD



Waste feedstock (examples):

- Organic municipal waste
- Food waste
- Black liquor
- Contaminated wood
- Sunflower husks
- Roadside grass
- Waste cooking oils

Co-HT/HDO
OMV
BTG (bioliquids)
SINTEF

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State-of-the-art

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Conventional hydroprocessing to fuels

Hydrotreating (HT)

- Remove hetero atoms & saturate carbon-carbon bonds
  - Sulfur, nitrogen, oxygen & metals removed
  - Olefinic and aromatic bonds saturated
  - Minimal cracking (loss)
- Minimal conversion - 10 - 20% typical
- Products suitable for **further processing** or final blending
  - Reforming, catalytic cracking, hydrocracking

In a conventional refinery it is located before the "Catalytic reforming and "(hydro)cracking" units - removing critical catalyst contaminants

Hydrocracking

- Severe form of hydroprocessing Break carbon-carbon bonds
- Drastic reduction in molecular weight
- Reduce average molecular weight and produce higher yields of fuel products
- 50%+ conversion
- Products more appropriate for diesel than gasoline

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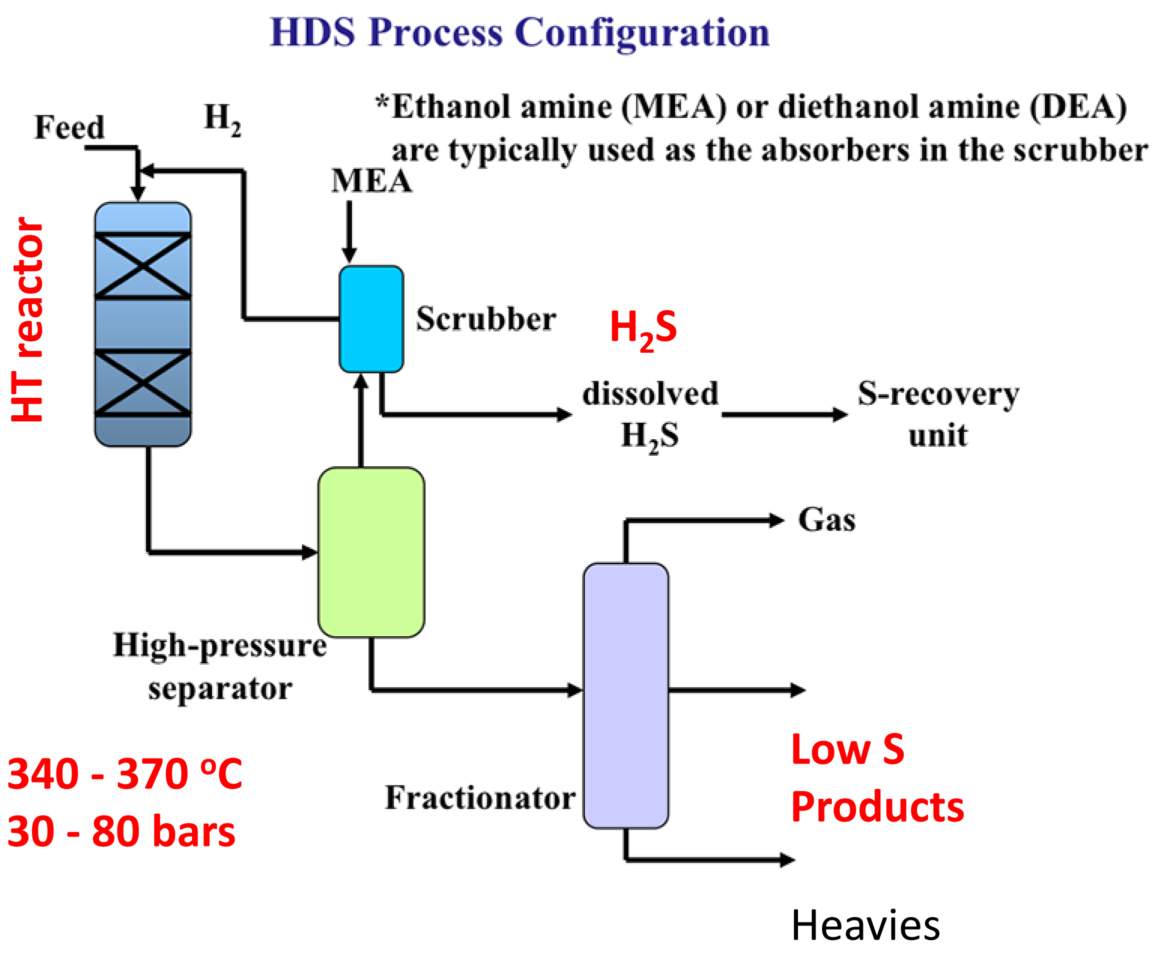
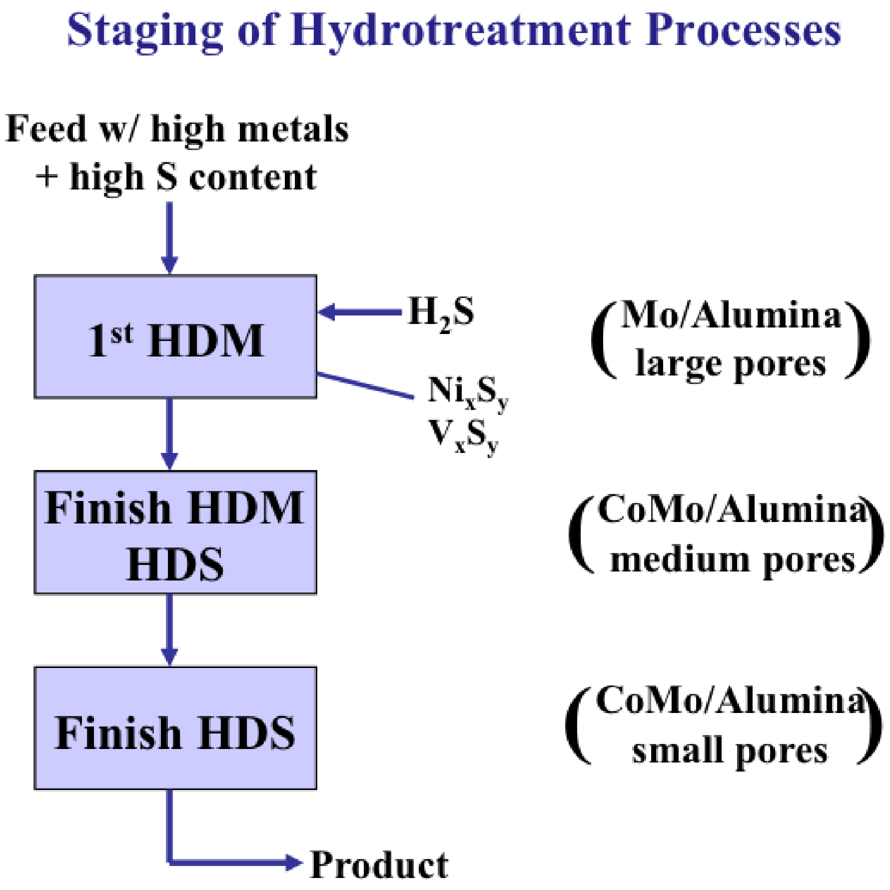
Conventional processing, "HDS"





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Commercial HT catalysts (sulphides)

Remarkably similar compositions!

Table 1. Catalysts Used in Hydrotreating/Hydrocracking Tests

supplier	catalyst id	active metals	weight %	support	form[a]
Harshaw	Ni-1404	Ni	68	proprietary	1/8-in T
Harshaw	CoMo0402	CoO/MoO_3	3/15	silica−alumina	1/8-in T
Harshaw	HT 400	CoO/MoO_3	3/15	γ-Al_2O_3	1/8-in E
Harshaw	HT 500	NiO/MoO_3	3.5/15.5	γ-Al_2O_3	1/8-in E
Harshaw	Ni-3266	Ni	50	silica−alumina	1/16-in E
Harshaw	Ni-4301	NiO/WO_2	6/19	γ-Al_2O_3	
Haldor Topsoe[b]	TK 710	CoO/MoO_3	2/6	Al_2O_3	3/16-in R
Haldor Topsoe[b]	TK 750	CoO/MoO_3	2.3/10	Al_2O_3	1/16-in E
Haldor Topsoe[b]	TK 770	CoO/MoO_3	3.4/14	Al_2O_3	1/16-in E
Haldor Topsoe	TK 751	NiO/MoO_3	3/13	Al_2O_3	1 mm E
Katalco	CoMo479	CoO/MoO_3	4.4/19	Al_2O_3	1/16-in E
Katalco	CoMo499	CoO/MoO_3	4.4/19	γ-Al_2O_3	1/16-in E
Katalco	KAT 4000	CoO/MoO_3	3.5/14	γ-Al_2O_3	1/32-in E
Shell	S411	NiO/MoO_3	2.67/14.48	Al_2O_3 [c]	1/20-in T
PNL/Linde	CoMo/Y	CoO/MoO_3	3.5/13.9	Y-zeolite/ Al_2O_3	1/16-in E
PNL/Grace	CoMo/SiAl	CoO/MoO_3	3/13	13%Al_2O_3 SiO_2	3/16-in T
Amoco	NiMo/Y	NiO/MoO_3	3.5/18	Y-zeolite/ Al_2O_3 [c]	1/16-in E
BASF	K8−11	CoO/MoO_3	4.3/11	MgO spinel/ Al_2O_3	1 mm E
Akzo	KF-742	CoO/MoO_3	4.4/15.0	γ-Al_2O_3	1.3 mm Q
Akzo	KF-840	NiO/MoO_3	3.9/19.6	Al_2O_3[c]	1.3 mm Q
Criterion	C-424	NiO/MoO_3	4/19.5	Al_2O_3[c]	1.3 mm Q
Strem	78−166	Pt	5	γ-Al_2O_3	P

[a] E = extrudates; R = ring; T = tablet; Q = quadrilobe extrudates; P = powder; and the size given is the o.d. [b] All three catalysts were used in a layered bed. [c] Includes phosphorus oxide.

Elliott, D.C., "Historical developments in hydroprocessing", 2007

State-of-the art also for renewable processing

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Existing renewable plants (commercial)

1. Generation (limited resources)

Production of "HVO diesel", Hydrogenated Vegetable Oil

Company Name	Location	Feedstocks	Capacity	Technology
Neste	The Netherlands	Vegetable oil and waste animal fat	1,000,000 tn/year	NExBTL
Neste	Singapore	Vegetable oil and waste animal fat	1,000,000 tn/year	NExBTL
Diamond Green Diesel	USA	Non-edible vegetable oils and animal fats	900,000 tn/year	Ecofining™
UOP/Eni	Italy	Vegetable oils, animal fats and used cooking oils	780,000 tn/year	Ecofining™
Neste	Finland	Vegetable oil and waste animal fat	380,000 tn/year	NExBTL
Renewable Energy Group (REG) Inc.	USA	High and low free fatty acid feedstocks	250,000 tn/year	Dynamic Fuels LLC
AltAir Fuels	USA	Non-edible natural oils and agricultural waste	130,000 tn/year	Ecofining™
UPM Biofuels	Finland	Crude tall oil	100,000 tn/year	UPM BioVerno

NOTES: Also, there are a number of companies co-processing vegetable oils with petroleum distillates such as Petrobras (Brazil), Cepsa (with several refineries in Spain), Preem (Sweden), Repsol (with several refineries in Spain) and British Petroleum (Australia).

Hydrodeoxygenaton + isomerization to reach fuel quality
(Esterification with CH3OH to FAME)

2. generation

Pyrolysis oil

BTG Bioliquids / Empyro / Netherlands "rotating cone"

BTG Bioliquids / Green Fuel Nordic / Finland

BTG Bioliquids / Pyrocell / Sweden (Autumn 2021)

VTT / Savon Voima Joensuu / Finland (earlier Fortum)

"fluidized sand"

Ensyn / Plants in Canada

Field is progressing

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W2R challenges

co-HT/co-HDO

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Chemical, physical and technical challenges in processing of renewables

- **High oxygen content;** Exothermic reactions and a high consumption of hydrogen
  - Might include a high H2O content
- **Materials;** The risk of corrosion due to a high acid number, a high chlorine content and the presence of oxygenated compounds, carboxylic acids
- **Contaminants;** Deposits causing pressure drop and catalyst deactivation due to the presence of components such as Si and P, and others
- **Product Quality;** The establish on the density and cold flow properties of the end product,
- **Feedstock supply;** The ability to secure a reliable supply of renewable feedstocks of sufficient quality

W2R solution is diversity in feedstock types and technology

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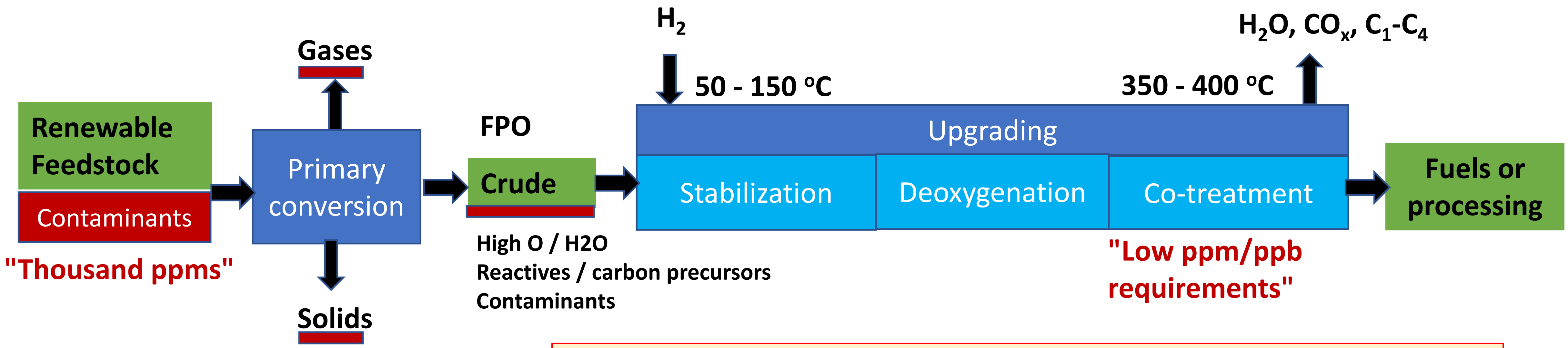
Upgrading needs and strategies (W2R)



Contaminants should be removed as far upstream as possible

- Catalyst protection
- Fuel quality

- How many upgrading steps are needed? - As few as possible
- What quality oil should be delivered to the refinery (O, contaminants), Crude?, Stabilized? Deoxygenated?
- Where should the H_2 be used (outside or inside refinery)? This is depending upon availability
- What are the sources for H_2?

- **Hydrotreatment** = Stabilization + Deoxygenation + co-treatment

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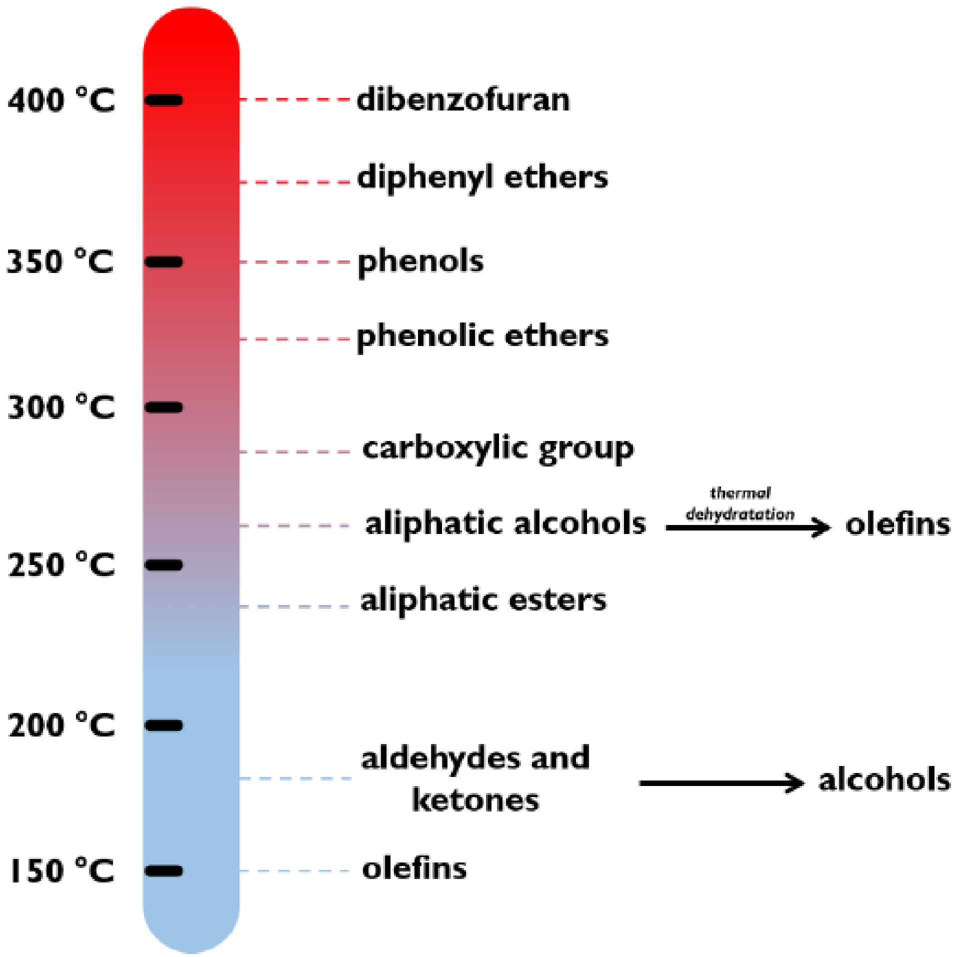
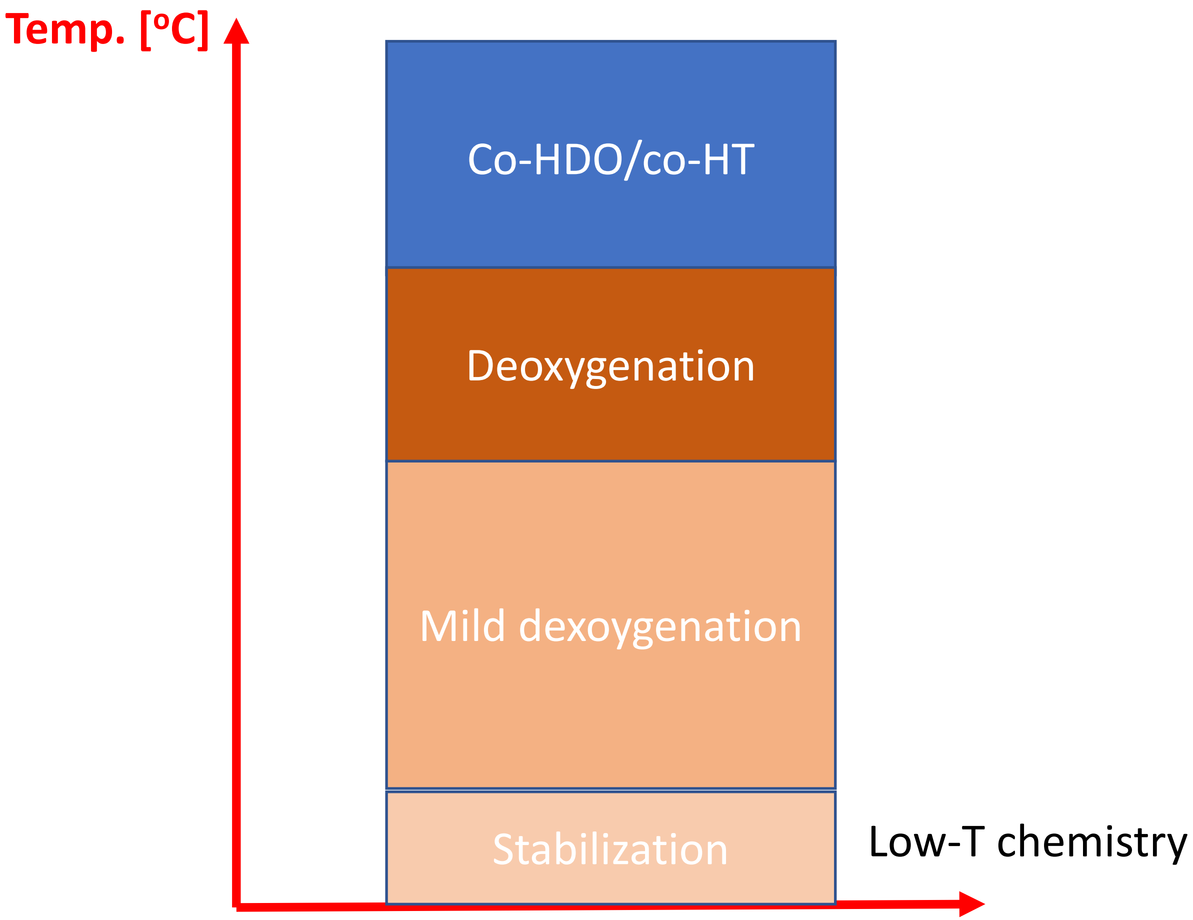
Reactivity scale of bio-oil components



Needed upgrading - wide T range



Bagnato G. et al., Catalysts, 2021

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Deactivation mechanisms & causes

General

- (i) Poisoning (blocking of active sites)
- (ii) Coking / carbonaceous
- (iii) Sintering
- (iv) Solid-state transformations
- (v) Masking or pore blockage (fouling)
- (vi) Leaching (loss of active phase)

Conventional oil HDS/HDN-processing

- Ni, V present (a.o.) **Demetallization**

Deactivation typically by

- Asphaltene formation
- Ni and V sulphides deposition
- V on the exterior, Ni interior

Typical poisons found in renewable feeds

Surface and pore blocking
Transport limitations

- Phosphorus (present in cell walls in form of phospholipids)
- Alkali metals like potassium or sodium (from soil as nutrients or counter ions of phospholipids)
- Iron (due to corrosion during transportation and storage in iron vessels)
- Silicon (from dust or soil)
- Chlorides (a counter anion)

Limiting regeneration and life-time

Removal; by adsorbents, ion exchange, etc.

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PO and HTL oils properties

TABLE 11-3 Properties of Wood-Derived Bio-Oil from Fast Pyrolysis and Liquefaction

Property	Pyrolysis oil	HTL oil
Elemental composition (%)		
Carbon (C)	58	73
Hydrogen (H)	7	8
Oxygen (O)	40	16
Nitrogen (N)	0.2	
Water content (wt%)	30	1
Viscosity (cP)	100[a]	15,000[b]
pH	2.5	
Heating value (MJ/kg)	19	34

[a]At 50 °C.
[b]At 61 °C.
Adapted from Ref. [6].

D. Elliott and G. Schiefelbein, *Liquid hydrocarbon fuels from biomass*, in American Chemical Society, Division of Fuel Chemistry Annual Meeting Preprints, 1989, vol. 34, pp. 1160–1166.

HTL oil rel. PO

- Higher C content
- Large heavy fraction above middle distillate range
- Lower H/C
- Lower O/C
- Lower H_2O
- Higher Viscosity

Challenges

- Flowability/processability
- Miscibility
- Catalytic O removal
- Also a CRACKING need

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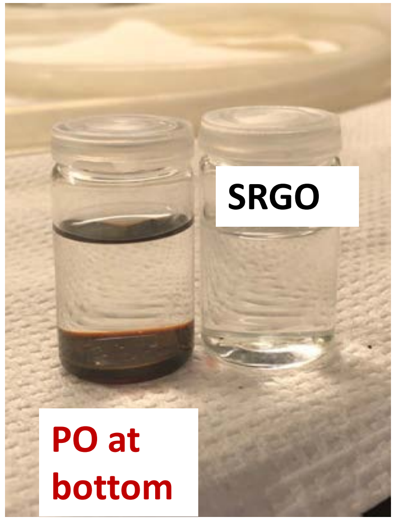
Oils compatibility / miscibility

WASTE2ROAD

30% PO in WCO

Compatibility

10% PO in SRGO



Abolutely no compatibility

10% HTLO in SRGO

A minor compatibility

10% WCO in SRGO

Compatibility at 10% level

10% HTLO in PO

Some compatibility

Needs processing adapted to reactivity

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Feedstock properties

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Primary feedstock and contaminants

Contaminated wood

- H_2O, 12 - 20 wt.%
- O, ca. 38 wt.%
- Ash, 0.02 - 0.17 wt.%
- Si, 790 - 8700 mg/kg
- Ca, 1700 - 4300 mg/kg
- Na, 350 - 1400 mg/kg
- K, 500 - 1300 mg/kg
- Mg, 230 - 590 mg/kg
- Fe, 210 - 1800 mg/kg
- Pb, 20 - 56 mg/kg
- Cu, 6 - 52 mg/kg

Paint, etc.

Food waste

- N, 1.3 - 3%
- Total solids, 50 - 300 g/kg
  - Partly insolubles
- Proteins, 78 - 13%
- Carbohydrates, 40 - 80%
- Lipids, 6- 10%
- Lignocellulosic matrix

Black liquor

- Na, 18 - 22 wt.%
- K, 1.8 - 4 wt.%
- S, 0.2 - 5 wt.%
- Cl, 0.4 - 5 wt.%
- Si, 0 - 4 wt.%
- Lignin
- Polysaccarides

Waste Cooking oil

- H_2O, ca. 100 ppmwt.%
- O, > 8.3 wt.%
- N, ca. 200 ppm-wt%
- S, ca. 20 ppm-wt%
- Polars, 99.75%
- Fatty acids
- Proteins

Feedstock variations - a challenge

Hydrocarbons? - Very little if any!

Ash

Metals and some organics

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Pyrolysis oils and HTL oil properties

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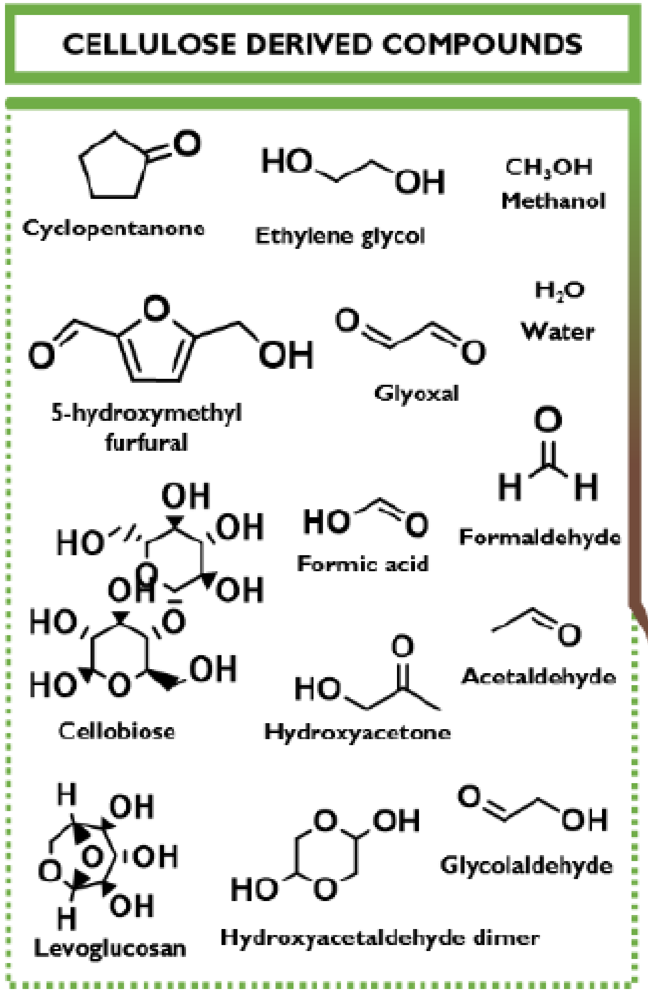
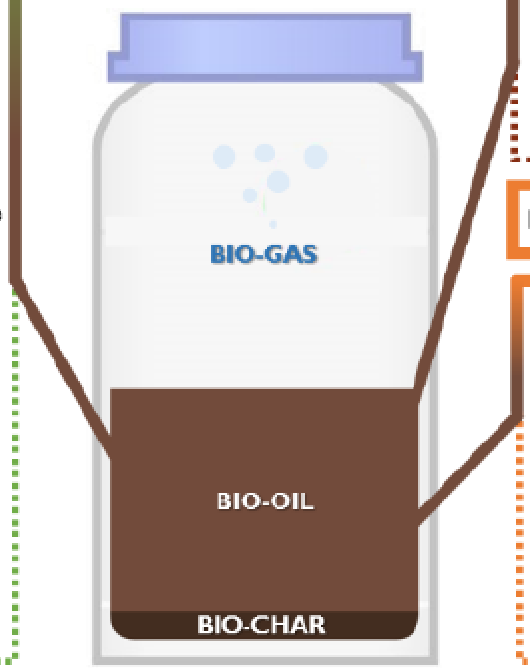
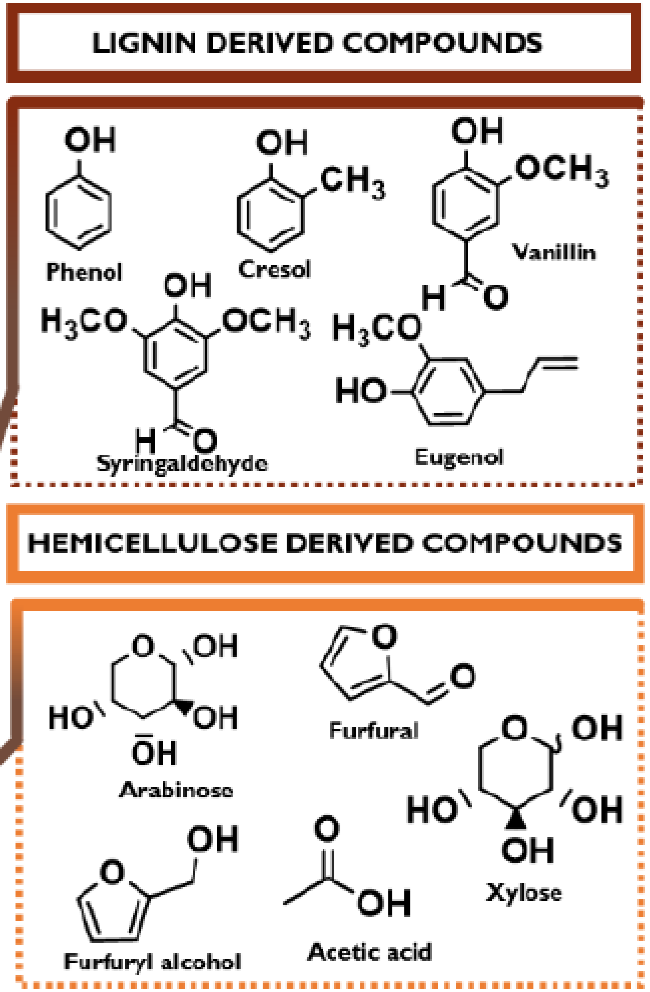
Pyrolysis bio-oil - A world of oxygen chemistry



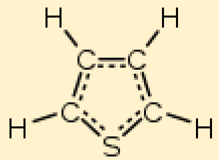
Incl. small reactives



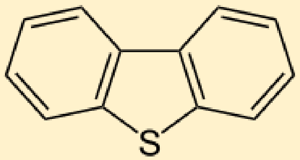


Conventional HT;

HDS



- Tiophene
- Benzothiophene
- Di-benzothiophene



Splitting of S by hydrogenolysis

Literature source: ?

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HTL properties

Table 2. Groups of chemicals of hydrothermal liquefaction bio-crude.

Main Components	Area% * Range	References
Phenolics	6%–65%	[14,20,39]
Esters	2%–44%	[14,27,39]
Aromatics and heterocyclics	6%–35%	[14,39]
Aldehydes	0%–18%	[14,20]
Carboxylic acids	2%–40%	[20,27,35]
Ketones	0%–38%	[20,27,35,40]
Alkanes	9%–13%	[35,40]
Nitrogenates	12%–23%	[35,40]

Note: *. Area % from gas chromatography-mass spectrometry results.

Ramirez et al., Energies, 2015

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Results examples

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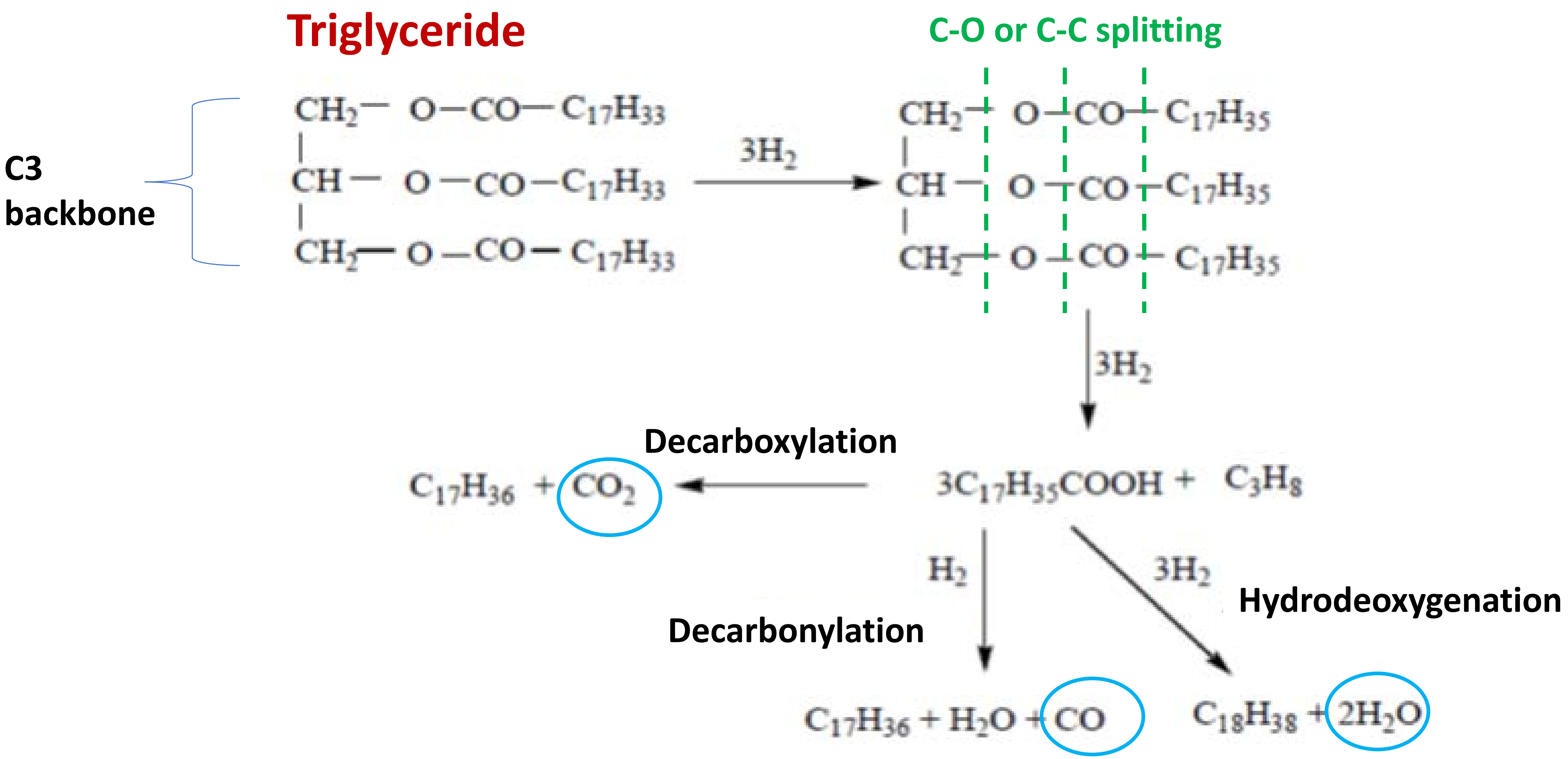
Waste Cooking oil / Main chemical pathways



Rogelia Boyas

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Complex oils / NiMoS / RSO + 5% SDPO

4refinery

SRGO periods - Rape seed oil periods - Cofeed og RSO & Stabilized Deox. Pyrolysis oils

DAYS		Sample id	Temp. [°C]	Pres. [bar]	LHSV [h^{-1}]	Density [g/ml]	S [wt.%ppm]	HDS [%]	N [wt.%ppm]	HDN [%]	O [wt.%]	HDO [%]
1	ref.	2-1 LGO	340	44	1	0,8471	1,9	96,0	5,7	99,5		
		2-2 RSO 1	340	44	1	0,7807	0,9	98,2	3,6	99,7	0,011	99,9
.		**2-3 RSO**	355	44	1	0,7798					0,085	99,2
.		**2-4 RSO**	370	44	1	0,7799	0,8	98,2	0,8	99,9	0,001	100,0
		2-5 RSO	355	38	1	0,7781					0,003	100,0
.		**2-6 RSO**	355	32	1	0,7782	0,2	99,6	1,0	99,9	0	100,0
.		**2-7 RSO**	355	44	2	0,7778	0,2	99,6	0,0	100,0	0	100,0
		2-8 RSO	355	44	3	0,7795	0,6	98,6	0,0	100,0	0,114	99,0
.		**2-9 RSO**	355	44	1	0,7784					0	100,0
.	ref.	2-10 LGO	340	44	1	0,8487	6,7	85,8	14,1	98,7		
		2-11 RSO	355	44	1	0,7814	0,9	98,1	0,6	99,9	0,003	100,0
.		**2-12 RSO**	355	44	1	0,7811					0,045	99,6
		2-13 Cofeed	355	44	1	0,7883	38,8	17,9	7,4	99,3	0,085	99,2
.		2-14 Cofeed	370	44	1	0,7872	29,2	38,2	10,7	99,0	0,042	99,6
.	ref.	2-15 LGO	340	44	1	0,8496	14,0	70,4	26,5	97,6		
16		**2-16 RSO 2**	355	44	1	0,7796					0	100,0

SRGO/LGO
S: ca. 1141 wt.% ppm
N: ca. 47 wt.% ppm

RSO
S: < 1 wt.% ppm
N: < 1 wt.% ppm

High degree of oxygen removal maintained during whole test

Theoretical 0.77 - 0.78 g/ml C_{17} HC
(Deep HDO established)

Lowered HDS and HDN in SRGO reference periods over time are indicative of deactivation processes (**see red circles**)

NiMoS / Light gases formation

4refinery

Day 1

Period	CO_2 [g/h]	CO [g/h]	CH_4 [g/h]	C_2 [g/h]	C_3 [g/h]	C_4 [g/h]	C_5 [g/h]	C_6 [g/h]	Sum gas prod. [g/h]
LGO									
Rape seed oil 1	2,62	0,45	0,07	0,10	1,08	0,01	0,00	0,00	4,34
RSO	1,97	0,48	0,13	0,12	1,12	0,01	0,01	0,00	3,84
RSO	1,96	0,57	0,17	0,14	1,11	0,02	0,01	0,01	3,98
RSO	2,30	0,55	0,10	0,12	1,19	0,01	0,01	0,00	4,27
RSO	2,72	0,63	0,08	0,13	1,29	0,01	0,01	0,00	4,86
RSO	3,37	0,88	0,11	0,16	1,84	0,01	0,01	0,00	6,38
RSO	3,85	1,14	0,09	0,16	2,12	0,01	0,00	0,00	7,38
RSO	2,01	0,48	0,10	0,12	1,12	0,01	0,00	0,00	3,85
LGO			0,00	0,00	0,01	0,01	0,00	0,00	0,03
RSO	2,44	0,51	0,09	0,13	1,09	0,01	0,01	0,00	4,28
RSO	2,44	0,48	0,08	0,14	1,05	0,01	0,01	0,00	4,21
RSO/SDPO	2,24	0,42	0,05	0,13	0,88	0,01	0,01	0,01	3,75
RSO/SDPO	1,94	0,49	0,08	0,16	0,88	0,02	0,01	0,01	3,59
LGO			0,00	0,00	0,01	0,00	0,00	0,00	0,02
Rape seed oil 2	2,24	0,53	0,14	0,08	1,15	0,01	0,00	0,00	4,16

Day 18

Theoretical (CO_2): ca. 4.2%
Observed: ca. 6%

Theoretical "C_3H_8" : ca. 5%
Observed "HCs" : ca. 4%

CO_2 (= loss)
CO (a poison)

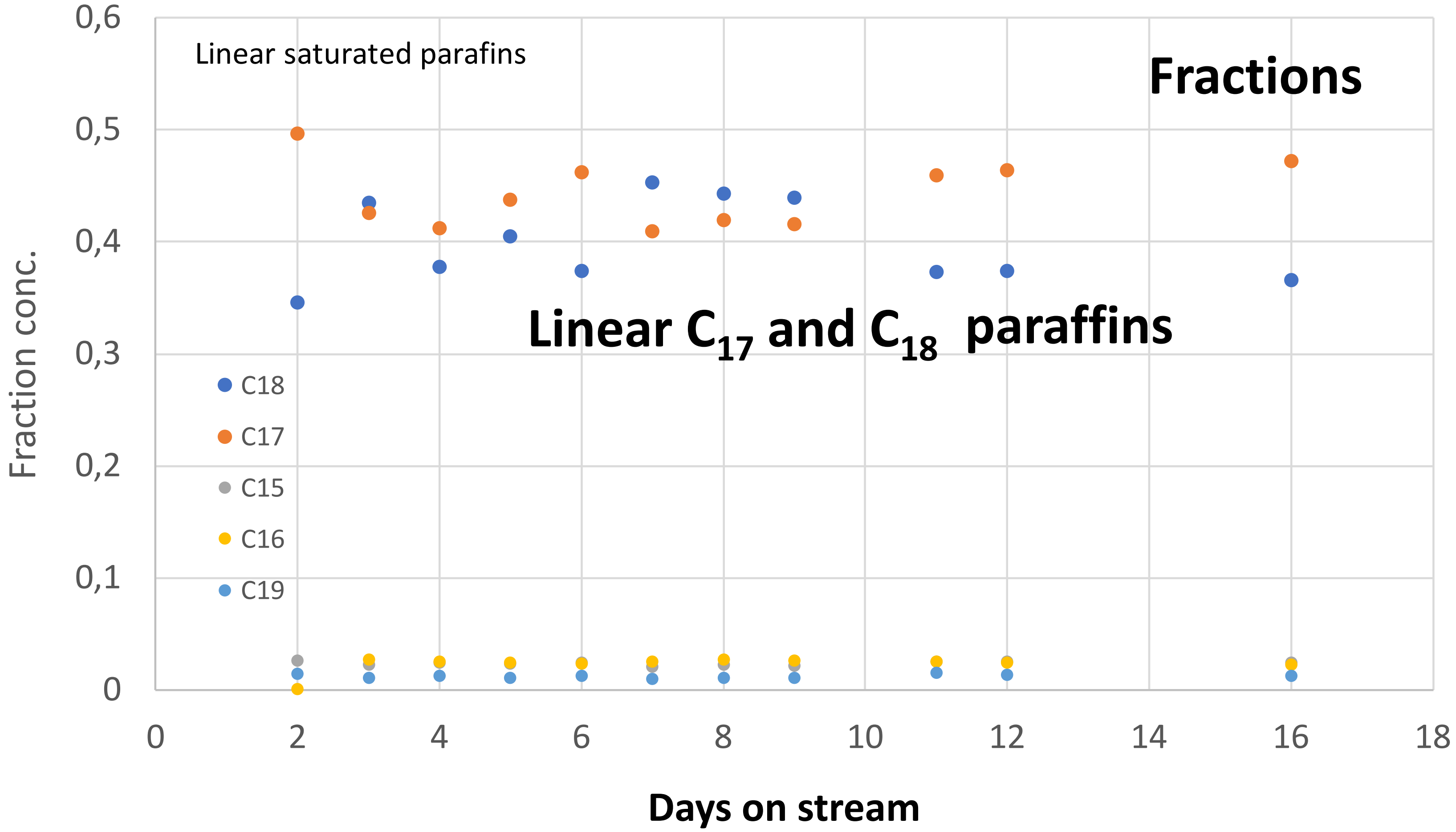
HCs (value, H_2)

C_3
Propane
Propene

Order
CO_2
C_3
CO
C_2
C_1
C_4

Liquid product composition from RSO

RSO reference periods (T, P, SV variations)



C-yield total: > 90%

Low Temperature, i.e. 340 °C favor high C_{17}/C_{18} ratio ("favor CO_2")

C_{15}, C_{16}, C_{19} not much affected by the performed parameter variations

Analysis by 2D-GC-MS

Conclusions & way forward

- Various types of waste feedstock have a potential for middle distillates production
- Co-feeding of renewable oils in conventional refineries is a rational strategy
  - Hydrotreating / (Hydro)cracking
- Critical aspects
  - Oils compatibility / contaminants & levels / reactives
- Cleaning technology;
  - Efficient deep contaminant removal is a critical aspect for upgrading
  - Number of processing steps should be minimized
- Robust technology;
  - Variability of feed composition is a challenge
- Catalysts materials;
  - New renewable dedicated non-sulfide based HT/HDO catalysts are desired

The W2R project is progressing the field of renewable processing

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Thank you for your attention!

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