“Engine fuels production via hydrotreatment of hydrothermal liquefaction bio-crude oil and pyrolysis bio-oil”

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YES or NO to Fuels?

- **Fuels are interlinked with growth and development**
  - ➢ **Agriculture, industry, technology**

- **However, the increasing demand on fossil fuels has negative implications:**
  - ➢ **Dependence from oil-producing countries**
  - ➢ **Intense fluctuation of fuel prices**
  - ➢ **Reduction of natural resources**
  - ➢ **Green house effect & Climate change**

Biofuels are Part of the Solution

Can boost national economy

- Create new employment opportunities
- Reinforce other industries
  - Sugar industry, Paper industry etc.

Follows environmental EU commitment

- Paper, Kyoto Protocol (2012)
- RedGreen, green house gas emissions
- Reduction of total carbon footprint

Can contribute to the reduction of atmospheric pollution

- CO, SOx, HC, PM

Reduces dependence of oil imports

- Countries can produce their own biofuels

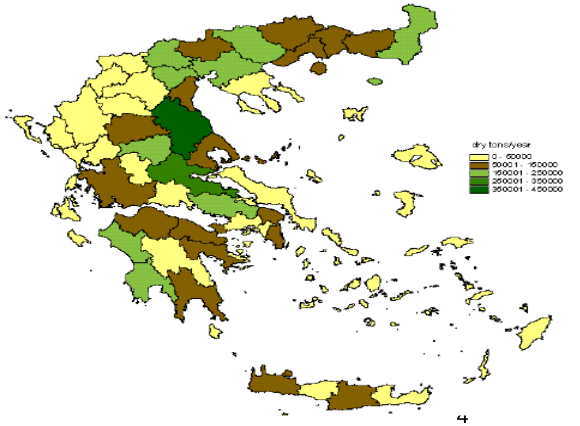
Wheat Straw Waste

Wheat straw waste: Promising feedstock for 2nd generation biofuels production

Two main thermochemical processes can be applied

Pyrolysis

Hydrothermal Liquefaction



Main Objective - Feedstocks

- **Research target:** “ 2nd generation Engine fuel production”
- Two feedstocks were investigated
  - ➢Pyrolysis bio-oil
  - ➢HTL bio-crude

- Both oils produced from wheat straw wastes
- The Oils have different upgrading challenges

Pyrolysis bio-oil

Phenols

Carboxylic acids

Aldehydes

Ketones

Methoxyphenols

Properties	Units	Pyrolysis bio-oil	HTL bio-crude
Density at 15°C	gr/ml	1.024	1.002
S on dry basis	wppm	596	175
H on dry basis	wt%	6.50	8.38
C on dry basis	wt%	42.13	55.87
O on dry basis	wt%	29.41	22.56
Viscosity at 40°C	cSts	156	NA
TAN	mgKOH/g	79.92	88.24
H_2O dissolved	wt%	21.86	13.05
HHV	MJ/kg	20	27
Pour point	°C	-3	21
MCR	wt%	15.7	13

HTL bio-crude

Alcohols

Carboxylic acids

Esters

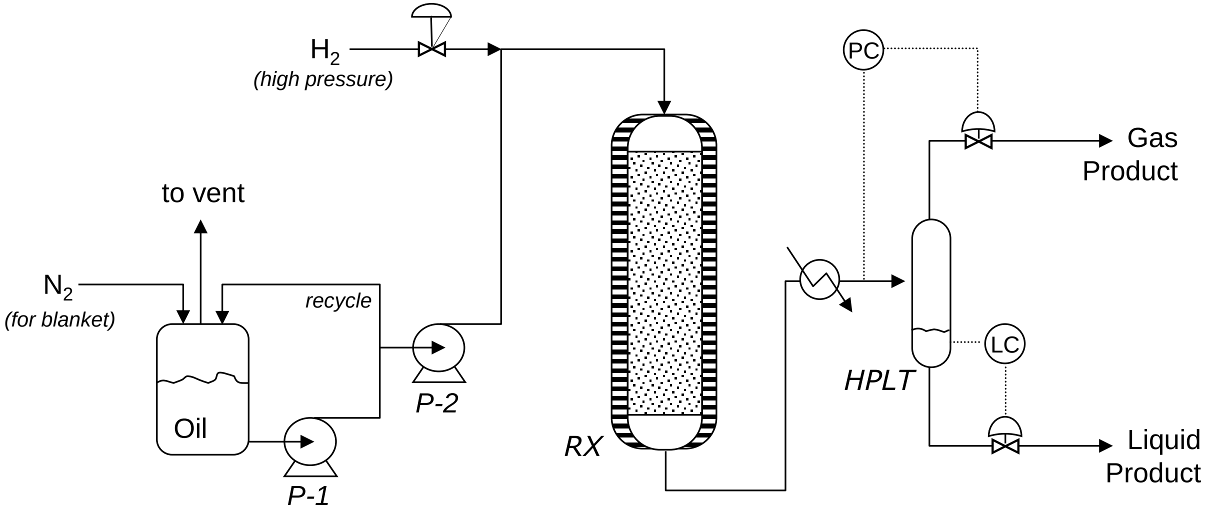
Aldehydes

Oxyphenols

Aromatics

Experimental Procedure

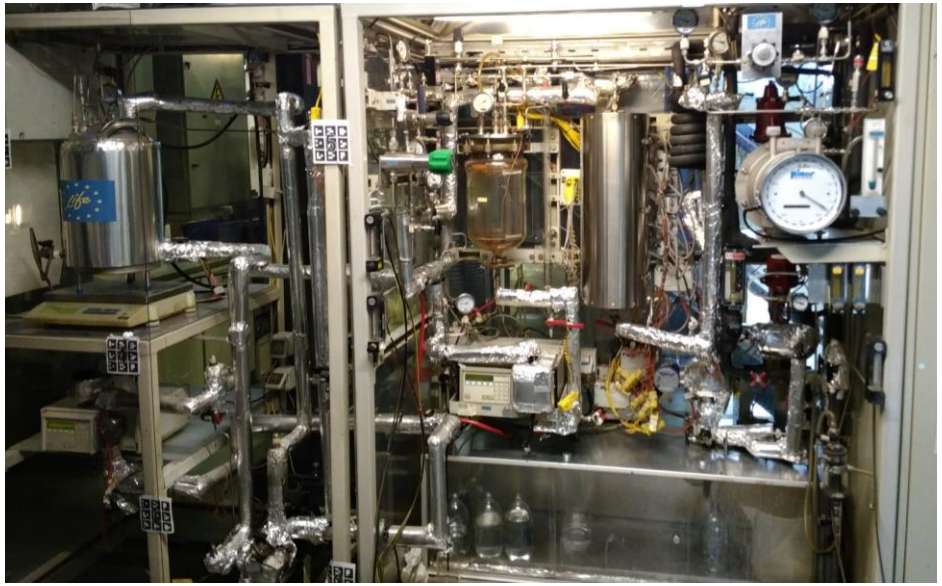
- Hydrotreatment experiments were conducted in TRL 3 HDT unit at CERTH
  - ➢Continuous flow
  - ➢Capacity 60 ml/hr
- Commercial hydrotreating NiMo/γ-Al_2O_3 catalyst
- Effect of operating parameters
  - ➢Reaction temperature
  - ➢H_2 supply



HDT Operating window tested

Parameters	Units	Cond. 1	Cond. 2	Cond. 3
Temperature	°C	330	360	330
Pressure	psi	1000	1000	1000
H_2/Oil ratio	scfb	5000	5000	3000
LHSV	hr^{-1}	1	1	1

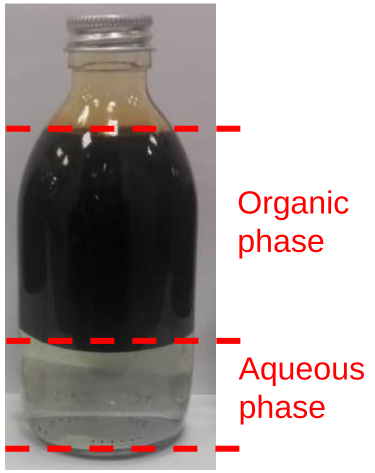
TRL 3 Hydrotreating unit



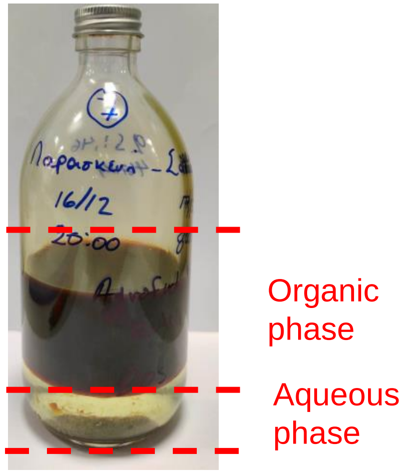
Results – Elemental Composition

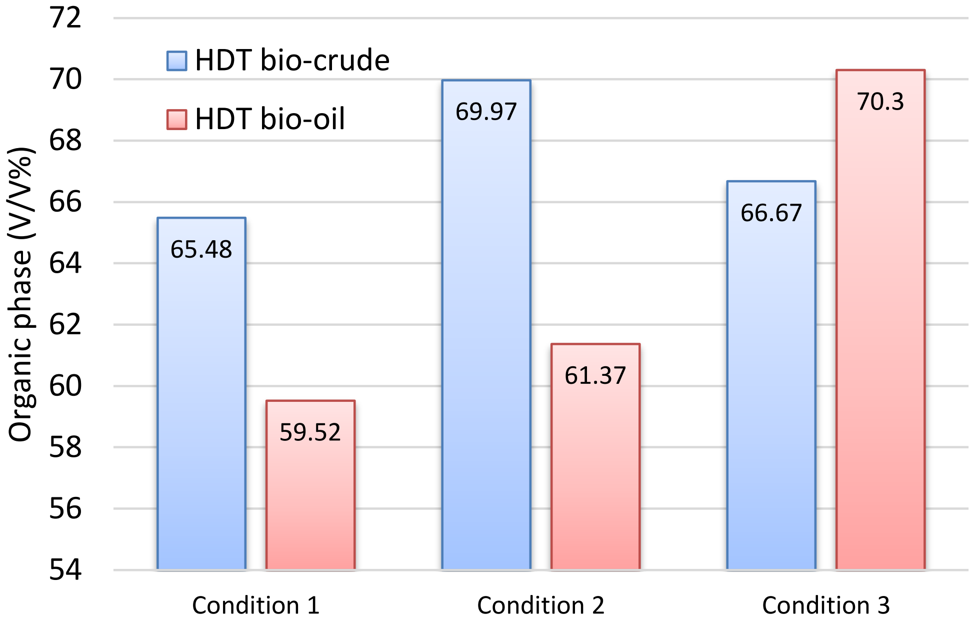
- Oxygenates were totally removed via aqueous phase
  - ➢Organic phase have almost zero oxygen and water content
- Higher temperatures lead to higher aqueous phase yields
  - ➢More severe hydrodeoxygenation reactions
- HDT of bio-crude lead to higher organic yields compared to HDT of bio-oil

HDT Bio-oil



HDT Bio-crude



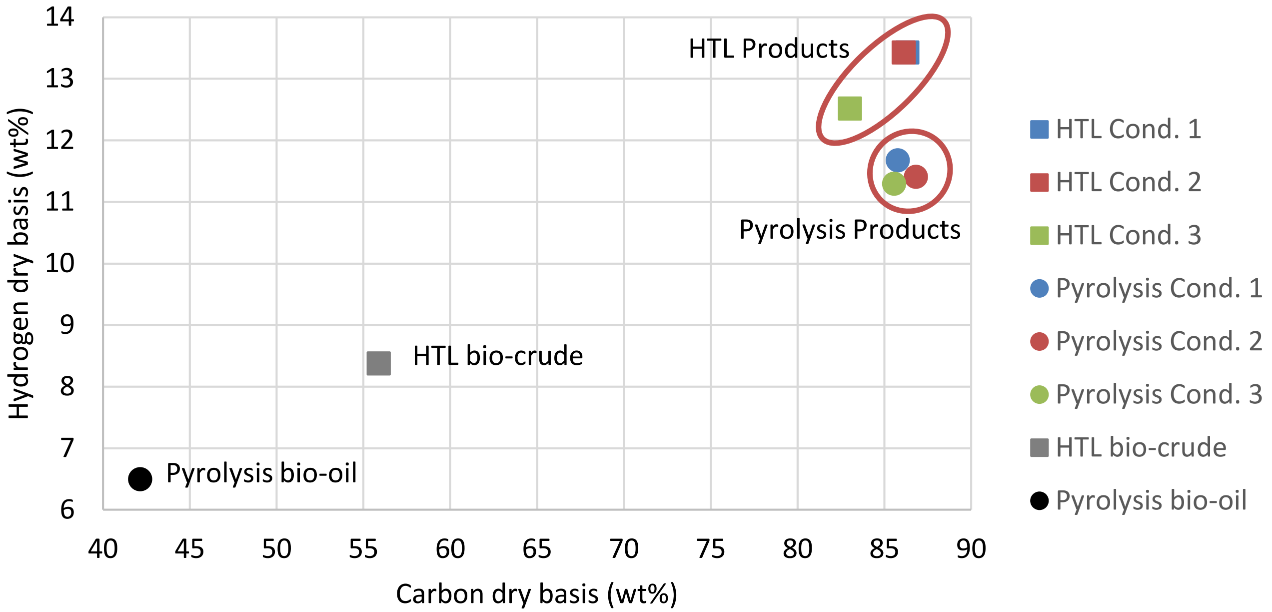


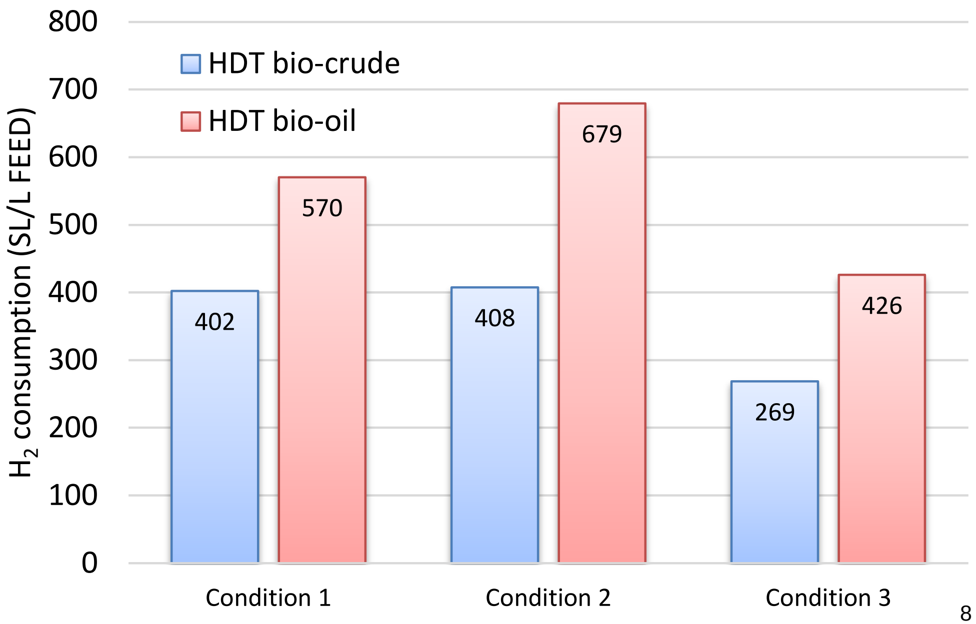
Properties	Units	Pyrolysis bio-oil	HTL bio-crude
Density at 15°C	gr/ml	0.91-0.94	0.84-0.87
S on dry basis	wppm	30-80	10-80
H on dry basis	wt%	11.3-11.7	12.5-13.4
C on dry basis	wt%	85.5-86.8	83.0-86.1
O on dry basis	wt%	1.70-2.99	0.00-3.34
Viscosity at 40°C	cSts	4.9-14.6	5.3-13.3
TAN	mgKOH/g	0.00-0.87	0.18-6.0
H2O dissolved	wt%	0.001-0.02	0.002-0.65
HHV	MJ/kg	42.8-43.5	43.4-45.9
Organic phase	v/v %	65-70	59-70
Aqueous phase	v/v %	32-34	38-45

Results – Elemental Composition

- HDT increase the hydrogen content resulting in high energy organic product
  - ➢60% higher H content in bio-crude products
  - ➢79% higher H content in pyrolysis bio-oil products
- HDT Bio-crude has higher H/C ratio compared to HDT bio-oil
  - ➢HDT bio-crude higher energy content

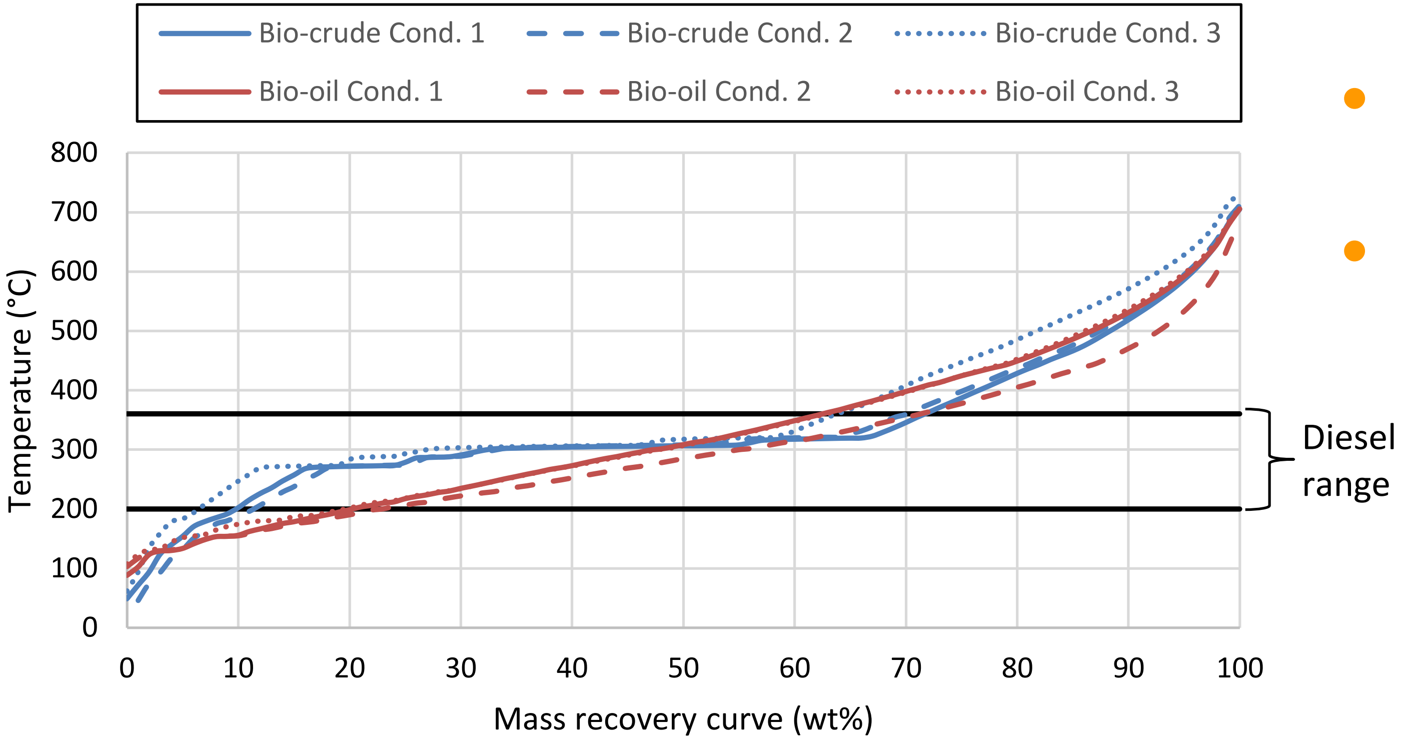
- Increase of hydrogen supply result in higher H/C ratio
- HDT of bio-oil has higher H_2 consumption compared to HDT of HTL bio-crude





Results - Mass recovery curve - Product Yields

- Instability of HTL bio-crude and pyrolysis bio-oil, is a result of their heavy hydrocarbon molecules
- Hydrocracking and saturation of these heavy molecules improve stability
- Increase of T, raise the rate of hydrocracking and H_2 consumption
- Gasoline and diesel range hydrocarbons are produced



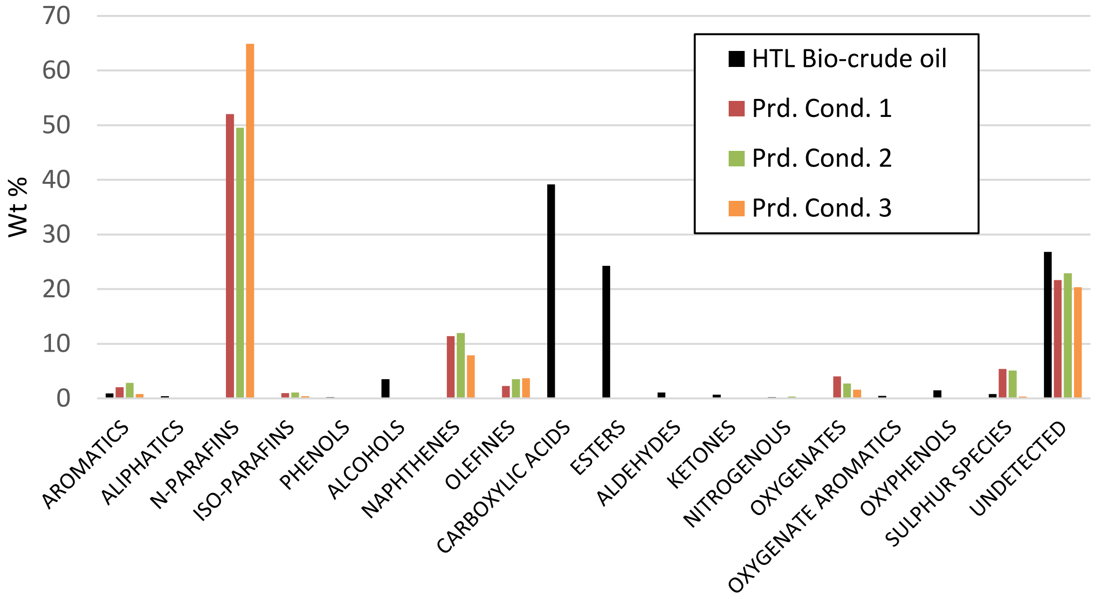
- HTL bio-crude optimum condition 1
  - 10 wt% gasoline, 62 wt% Diesel and 28 wt% heavy fuel
- Pyrolysis bio-oil optimum condition 2
  - 20 wt% gasoline, 43 wt% diesel and 37 wt% heavy fuel

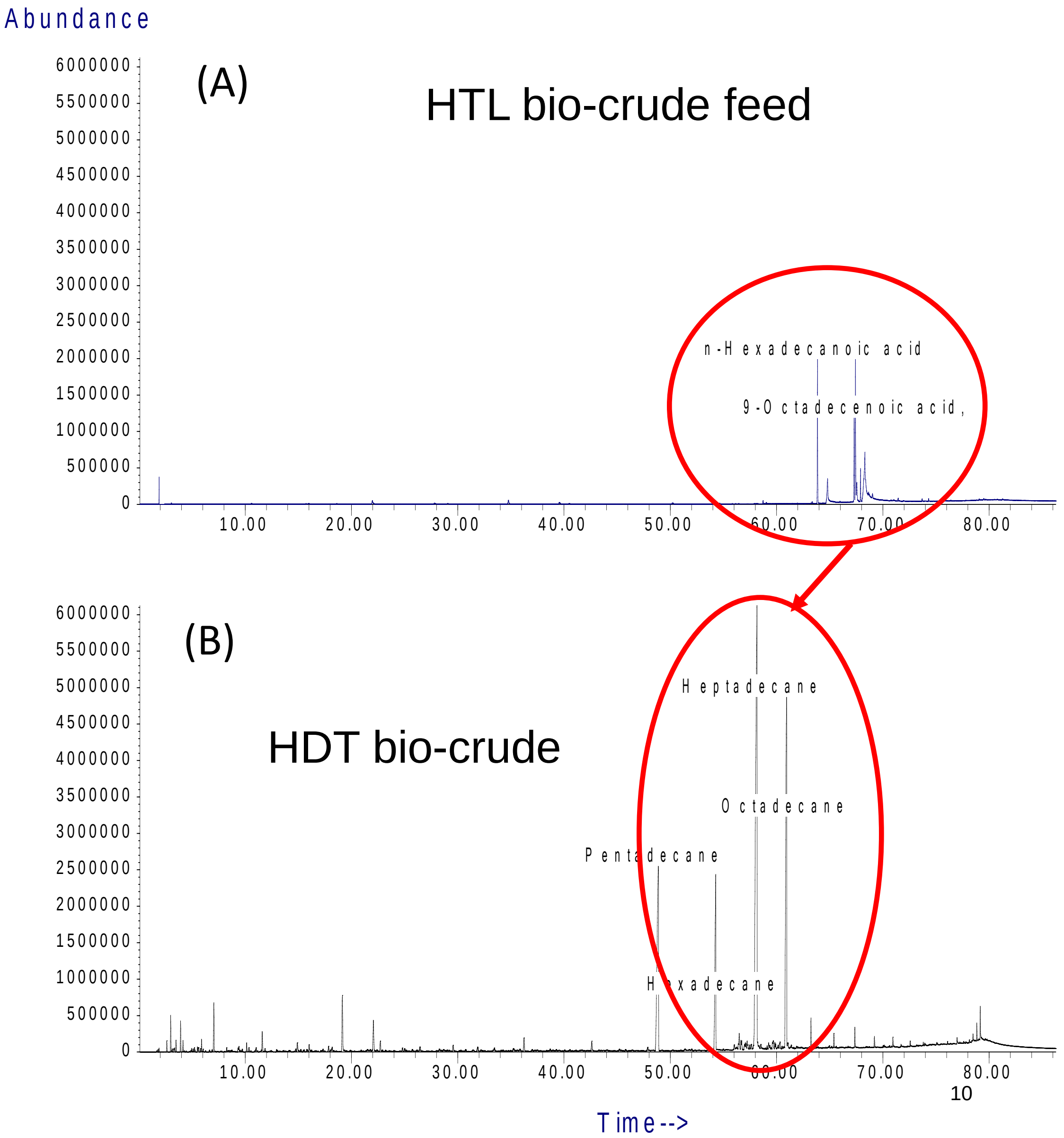
GC-MS Chromatograph Results
HDT Bio-Crude

- HDT reduced the oxygen- and nitrogen-containing compounds
- Organic liquid consists mainly from:
  - ➢~50 wt% n-paraffins and high percent of saturated (Naphthene 7.88 - 11.94 wt%) and unsaturated (Olefines 2.29 - 3.67 wt%) hydrocarbons

$$Palmitic\ acid\ (CH3(CH2)14COOH) \rightarrow Heptadecane\ (C17H36)$$

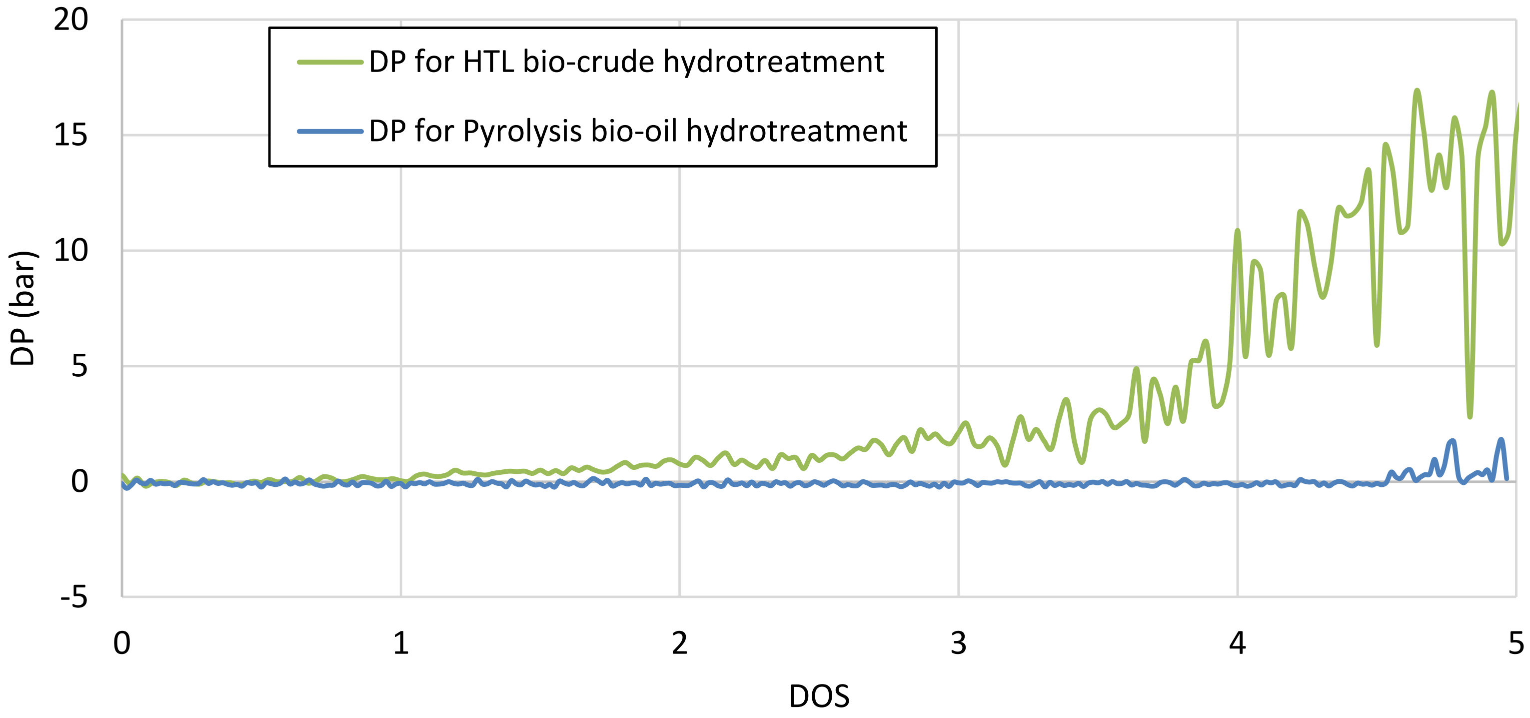
$$Oleic\ acid\ (CH18H34O) \rightarrow Octadecane\ (C18H38)$$





Catalyst Deactivation

- Catalyst deactivation is mostly caused by cocking, sintering, poisoning and metal deposition
- Fast catalyst deactivation, expressed via DP build-up, was observed
- For HTL bio-crude: the DP build up produced linearly with time on stream, starting from the 2nd DOS
- For pyrolysis bio-oil, the DP was steady for 4 DOS and increased rapidly at the end of DOS 4



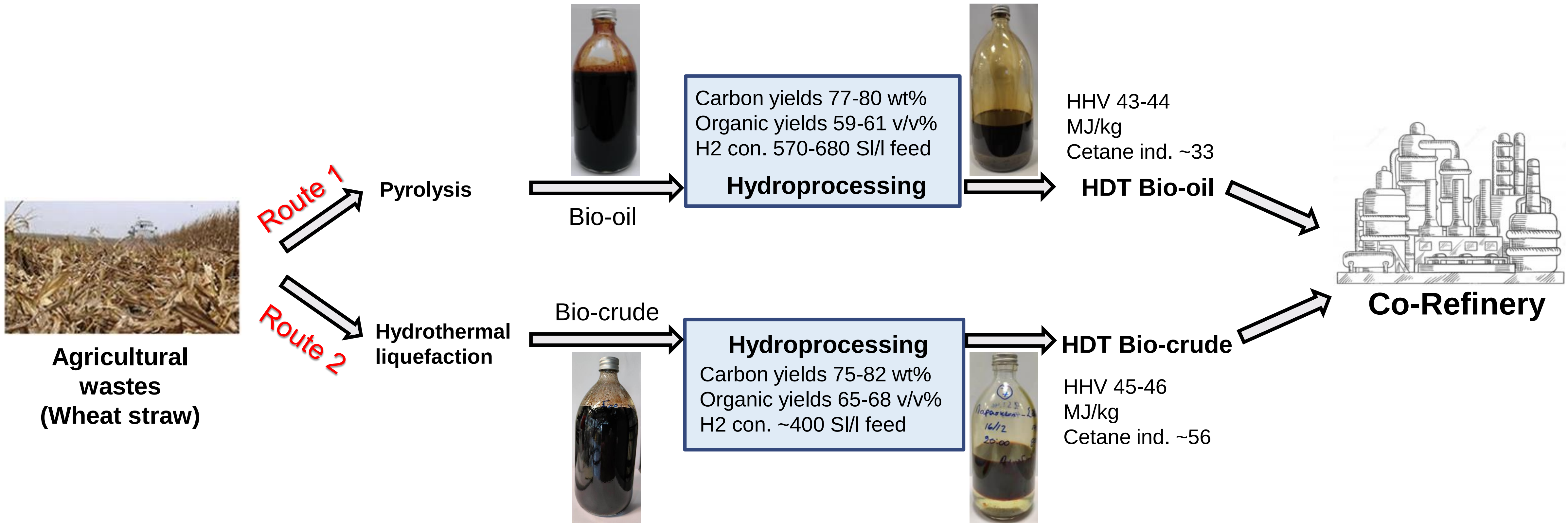
Conclusions

- Hydrotreatment of pyrolysis bio-oil has led to an almost zero oxygen and water content product with high energy density
- The carboxylic acids of HTL bio-crude, especially the palmitic and oleic, were fully converted to the corresponding Heptadecane and Octadecane hydrocarbons leading to an almost zero oxygenate product
- Hydrotreatment of HTL bio-crude is characterized by lower hydrogen consumption and higher carbon yields, compared to hydrotreatment of pyrolysis bio-oil
- Refinery intermediate products were successfully produced from both routes
- Hybrid fuels can be produced via co-processing of HDT oil with petroleum fractions



Summarize

“Stabilization of hydrothermal liquefaction bio-crude and flash pyrolysis bio-oil by removing the oxygenate compounds via hydrotreatment”



Conclusion: Route 2 via hydrothermal liquefaction lead to a better quality product with less hydrogen consumption and higher organic and carbon yields

HydroProcessing HyPro group

Thank you for your attention

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