Natural Resources Canada | Ressources naturelles Canada

Co-processing biocrudes from lignocellulosic biomass through hydrocracking: The importance of biocrude pre-treatment

Anton Alvarez-Majmutov, Sandeep Badoga, and Jinwen Chen

CanmetENERGY Devon, Natural Resources Canada

tcbiomass2024, Itasca, IL, September 10-12, 2024

Canada

The Canadian context

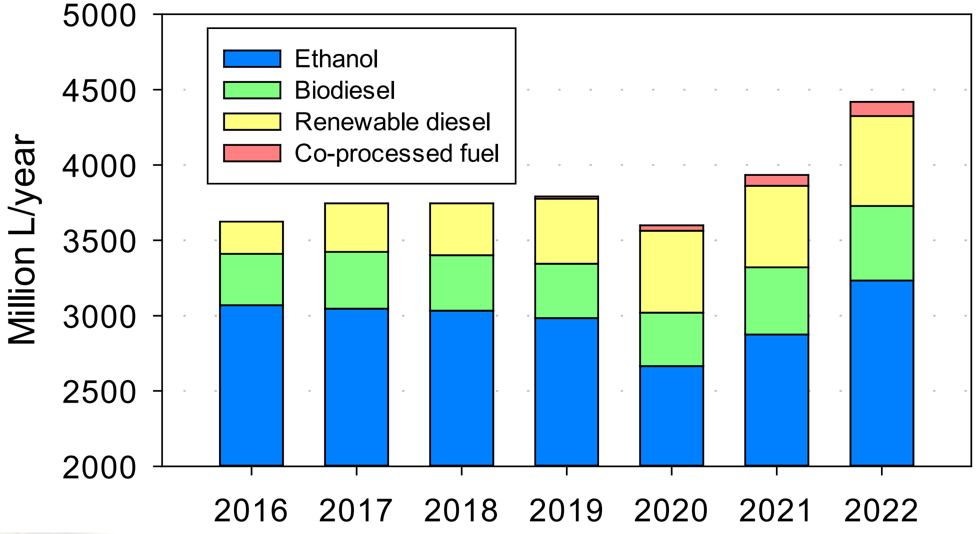
Canada's Renewable Fuel Regulations require that gasoline and diesel fuels have renewable content

- 5% in gasoline
- 2% in diesel
- No requirement yet for aviation fuels

Co-processing refers to the refining of biogenic feedstocks together with petroleum in an existing refinery

- In Canada, co-processed fuels are produced in British Columbia
- Made from lipid feedstocks

Biofuel consumption in Canada*



Biocrudes from thermochemical conversion of biomass are promising co-processing feedstocks

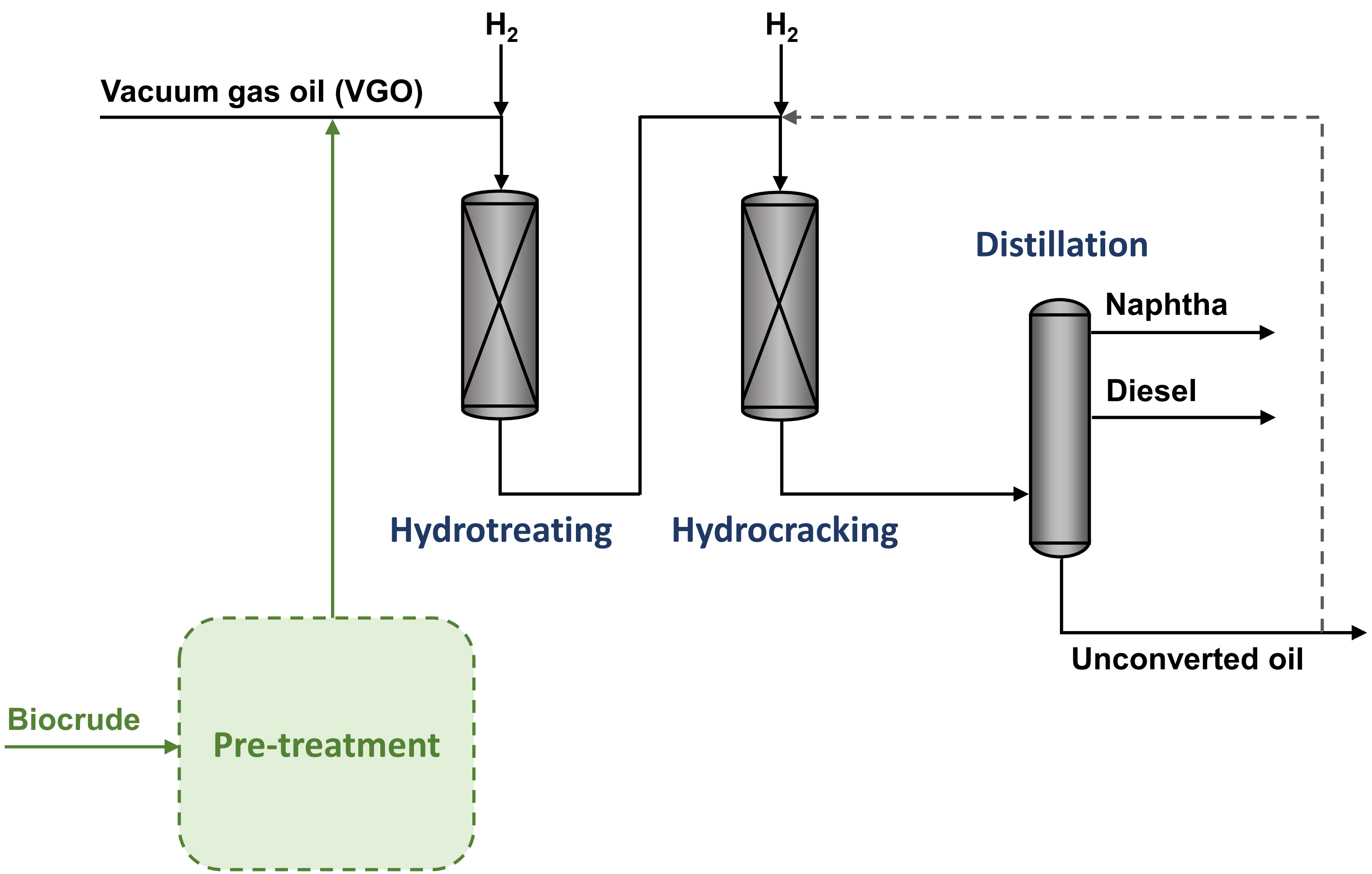
- Little commercial experience
- Technically challenging to refine

***Source: Biofuels in Canada 2023, Navius Research Inc.**

Co-processing biocrudes through hydrocracking

Drop-in locations in a refinery

- Fluid catalytic cracking (FCC) units
- Diesel hydrotreaters
- Hydrocracking
  - Relatively unexplored pathway
  - Potential to make not only gasoline and diesel, but also aviation fuel
  - Good for handling aromatic feedstocks



Why biocrude pre-treatment?

Challenges with biocrudes
(focus on hydrothermal liquefaction - HTL)

- Do not mix well with petroleum
  - Form aggregates that lead to plugging issues
- Thermally unstable
  - Tend to polymerize at refinery process temperatures (>300ºC)
- Affect refinery catalyst performance
  - Poisoning/deactivation

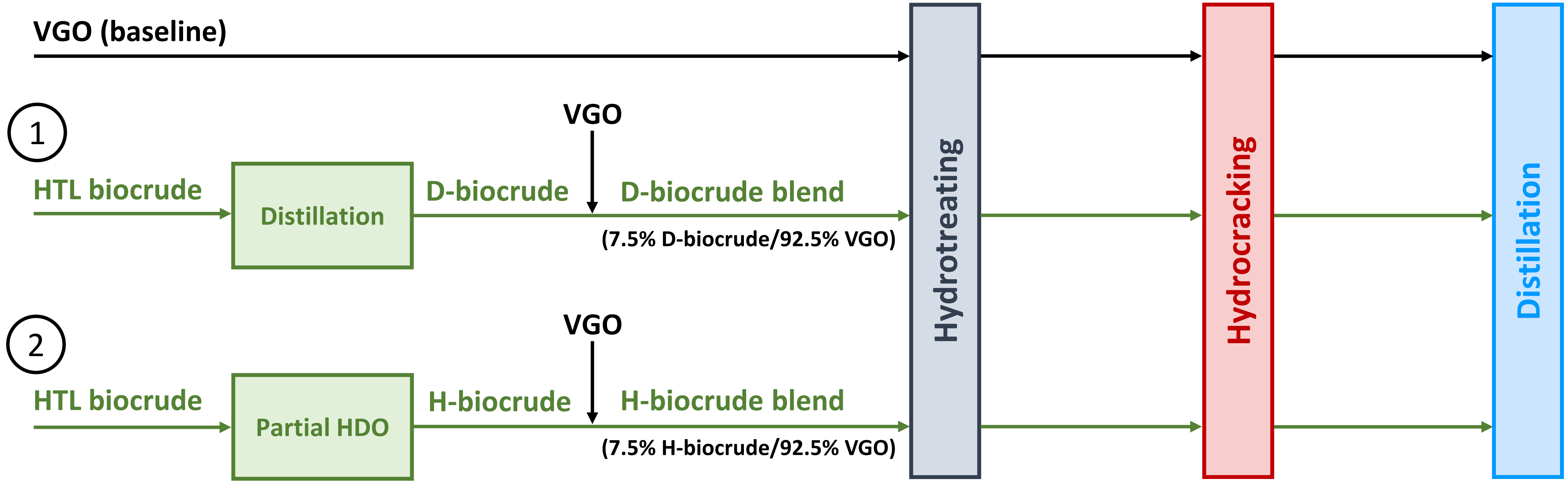
HTL biocrude/VGO blends

Pre-treatment options

- Fractionation (distillation)
  - Removes water and high-boiling material
  - Biocrude distillate shows better miscibility in oil and is more stable
- Partial hydrodeoxygenation (HDO)
  - Reduces oxygen content and stabilizes the biocrude
  - Improves miscibility in oil

Experimental plan

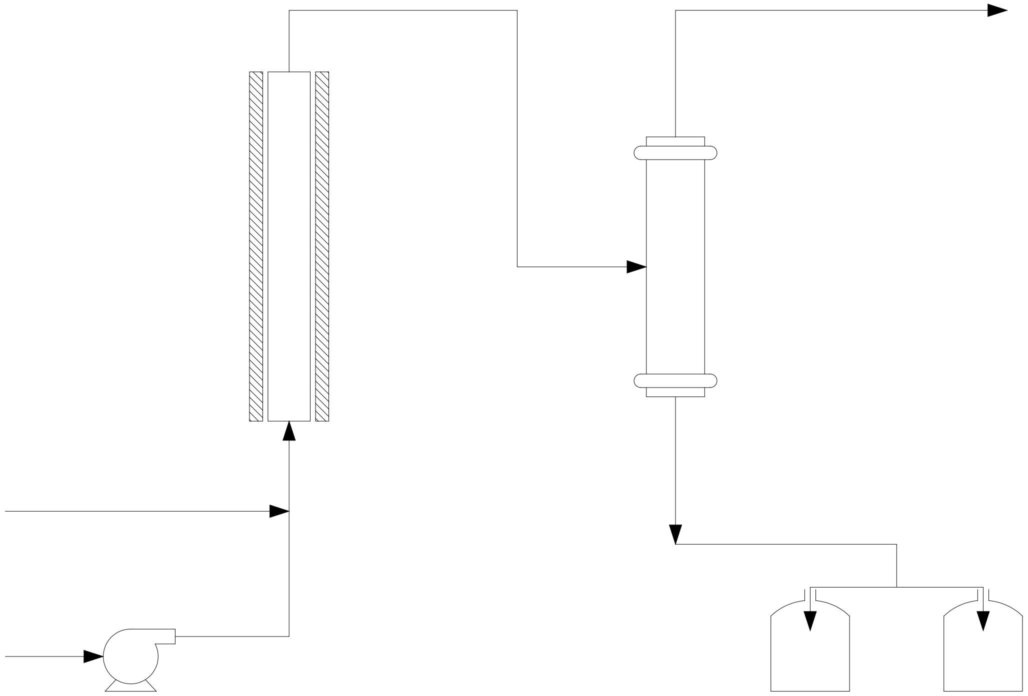
Goal: investigate the co-processing characteristics of HTL biocrude treated by distillation and HDO in the hydrocracking process



Feed materials

- Petroleum feed: VGO (343-525ºC) from Canadian bitumen
- Biogenic feed: HTL biocrude from a mix of spruce and pine wood

Co-processing pilot plant testing



10-30 mL/h continuous hydroprocessing unit

Catalysts

- Hydrotreating: NiMo-alumina catalyst
- Hydrocracking: zeolite bifunctional catalyst

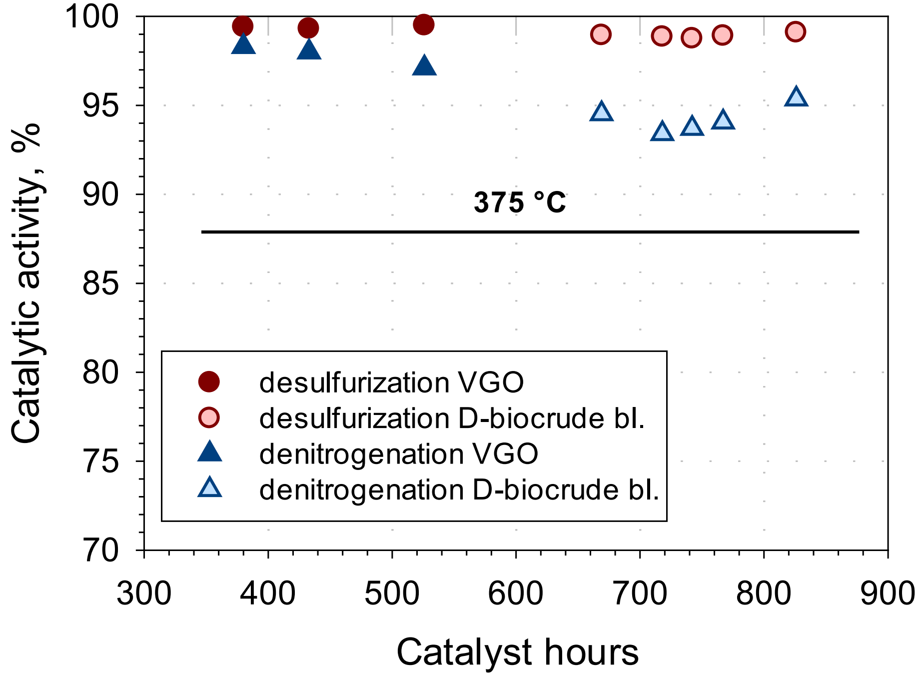
Feed properties

	(1)		(2)		
Property	**HTL biocrude**	**D-biocrude**	**HTL biocrude**	**H-biocrude**	**VGO**
distillation yield, wt%	-	63.4	-	-	-
density at 15.6°C, g/mL	1.0536	0.9925	1.0880	0.9910	0.9759
carbon, wt%	80.0	79.5	79.7	84.8	84.8
hydrogen, wt%	9.4	10.0	8.6	10.5	11.1
sulfur, wt%	<0.1	<0.1	0.1	<0.1	3.6
nitrogen, wt%	<0.1	<0.1	0.3	0.1	0.3
oxygen, wt%	10.5	10.6	11.3	3.6	0.5
Fractional composition					
distillate (<343°C), wt%	27.7	47.1	17.1	42.8	4.5
vacuum gas oil (343-525°C), wt%	34.7	49.6	31.9	28.7	86.5
vacuum residue (>525°C), wt%	37.6	2.7	51.0	28.5	9.0

Hydrotreating

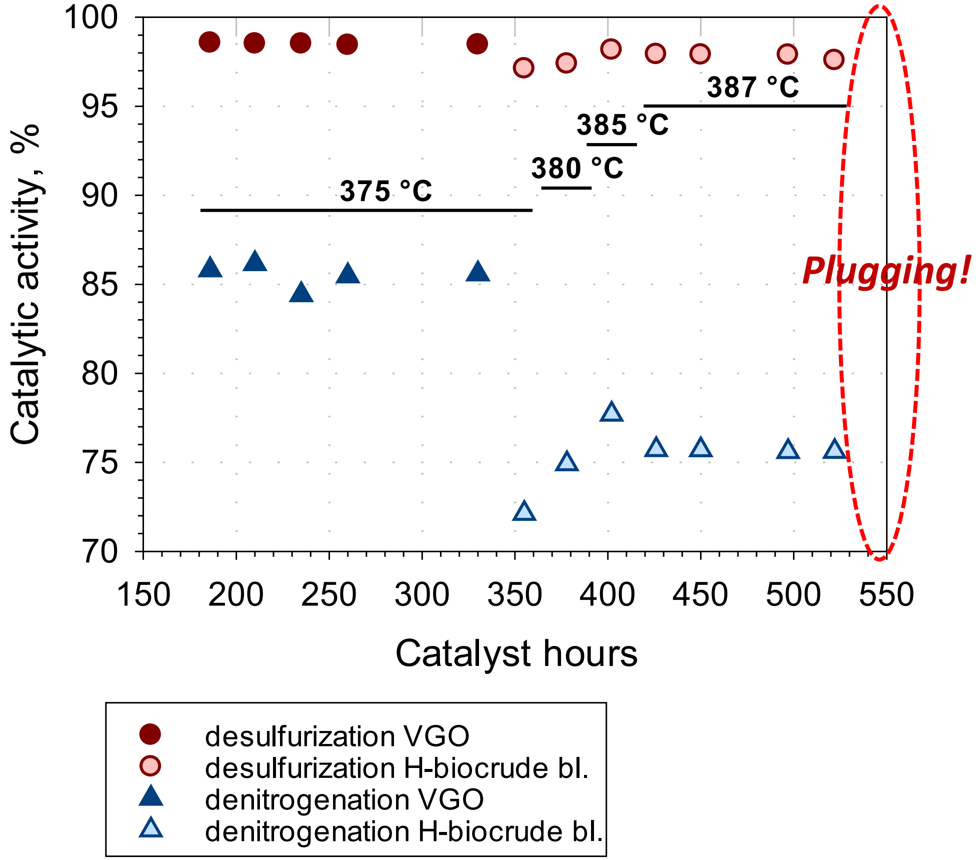
1 7.5% D-biocrude bl. hydrotreating activity

(D-biocrude 10.6 wt% oxygen)



2 7.5% H-biocrude bl. hydrotreating activity

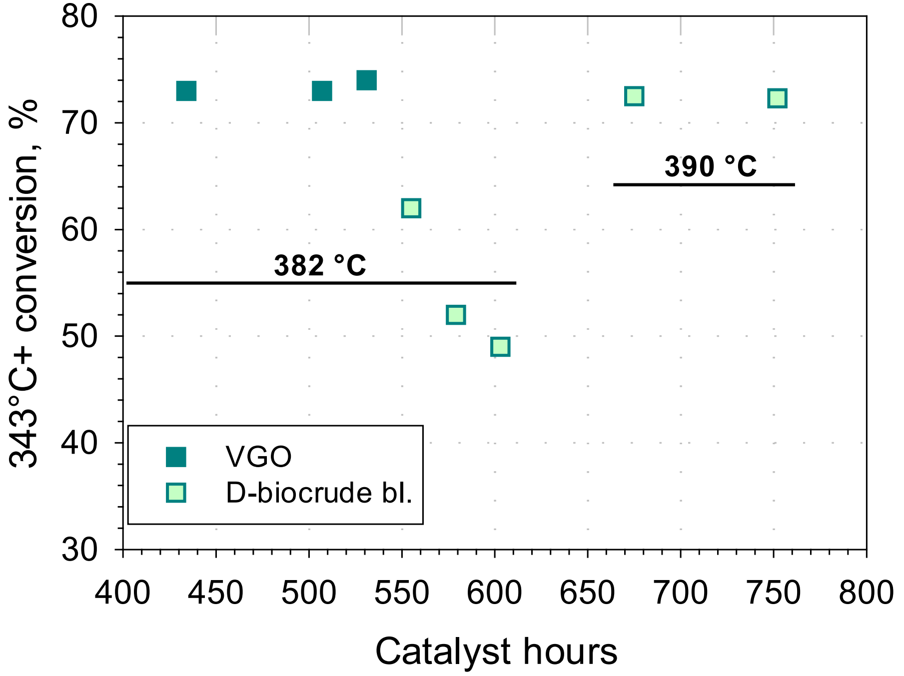
(H-biocrude 3.6 wt% oxygen)



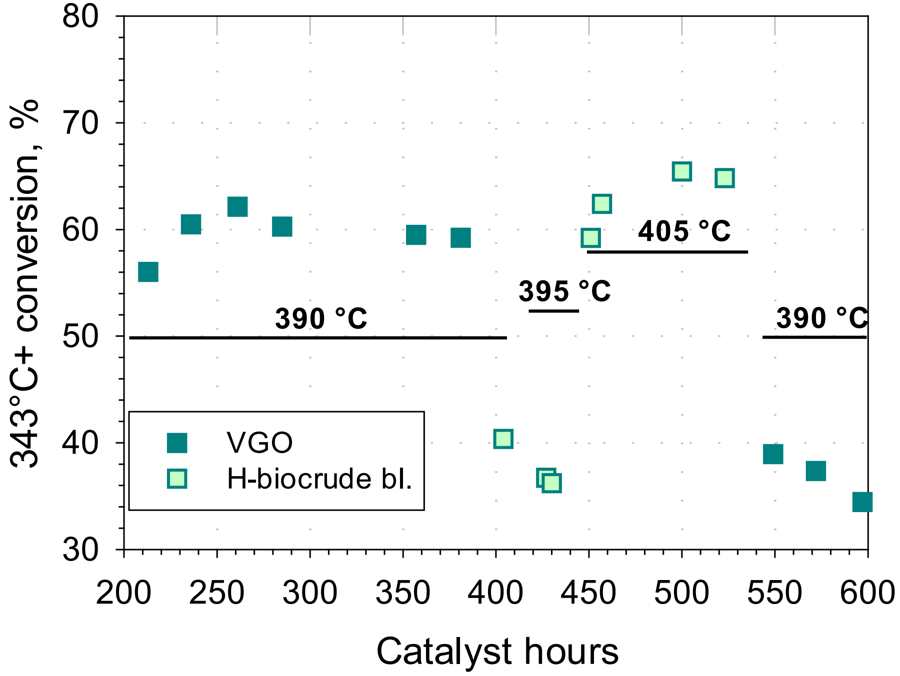
Pressure = 1,400 psi; LHSV = 1.5 h^{-1}; H_2/oil ratio = 800 NL/L

Hydrocracking

1 **7.5% D-biocrude bl. hydrocracking activity**
(D-biocrude 10.6 wt% oxygen)



2 **7.5% H-biocrude bl. hydrocracking activity**
(H-biocrude 3.6 wt% oxygen)



Pressure = 1,600 psi; LHSV = 1.5 h^{-1}; H_2/oil ratio = 800 NL/L

Hydrocracking (continued…)

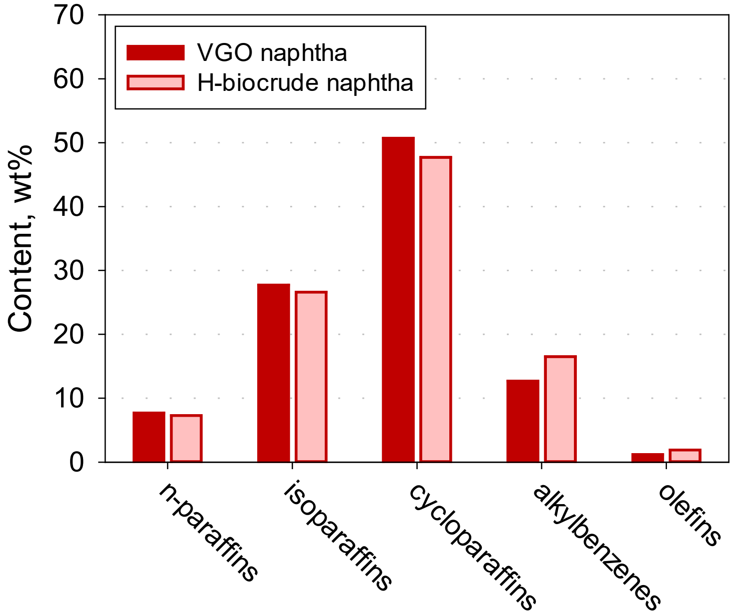
Overall product distribution* and hydrogen consumption

Parameter	VGO ①	7.5% D-biocrude blend	VGO ②	7.5% H-biocrude blend
hydrotreating temperature	base	+0 °C	base	+10-12 °C
hydrocracking temperature	base	+8 °C	base	+15 °C
gases (H_2S, C_1–C_4), wt%	7.0	6.9	6.9	7.2
naphtha (35–204°C), wt%	48.6	44.8	33.4	36.2
diesel (204–343°C), wt%	30.3	32.8	32.6	35.6
unconverted oil (>343°C), wt%	17.7	19.1	29.9	23.8
hydrogen consumption, scf/bbl	2,343	2,310	1,798	1,747

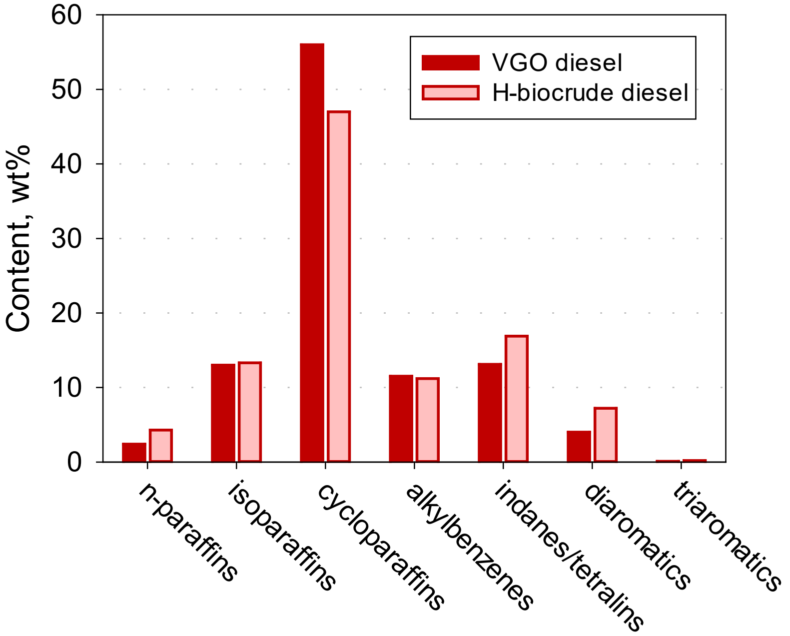
Liquid product yields estimated based on simulated distillation analysis

Co-processed fuel composition

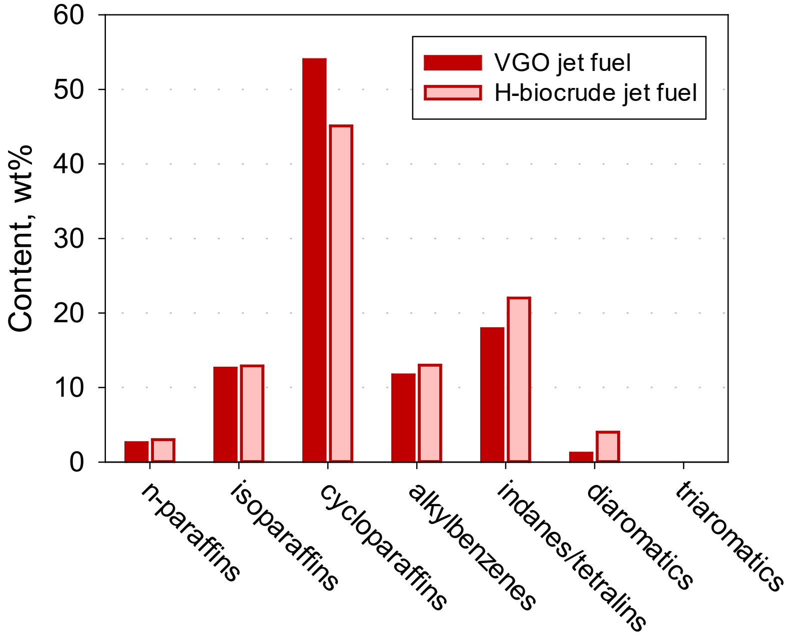
Naphtha from H-biocrude



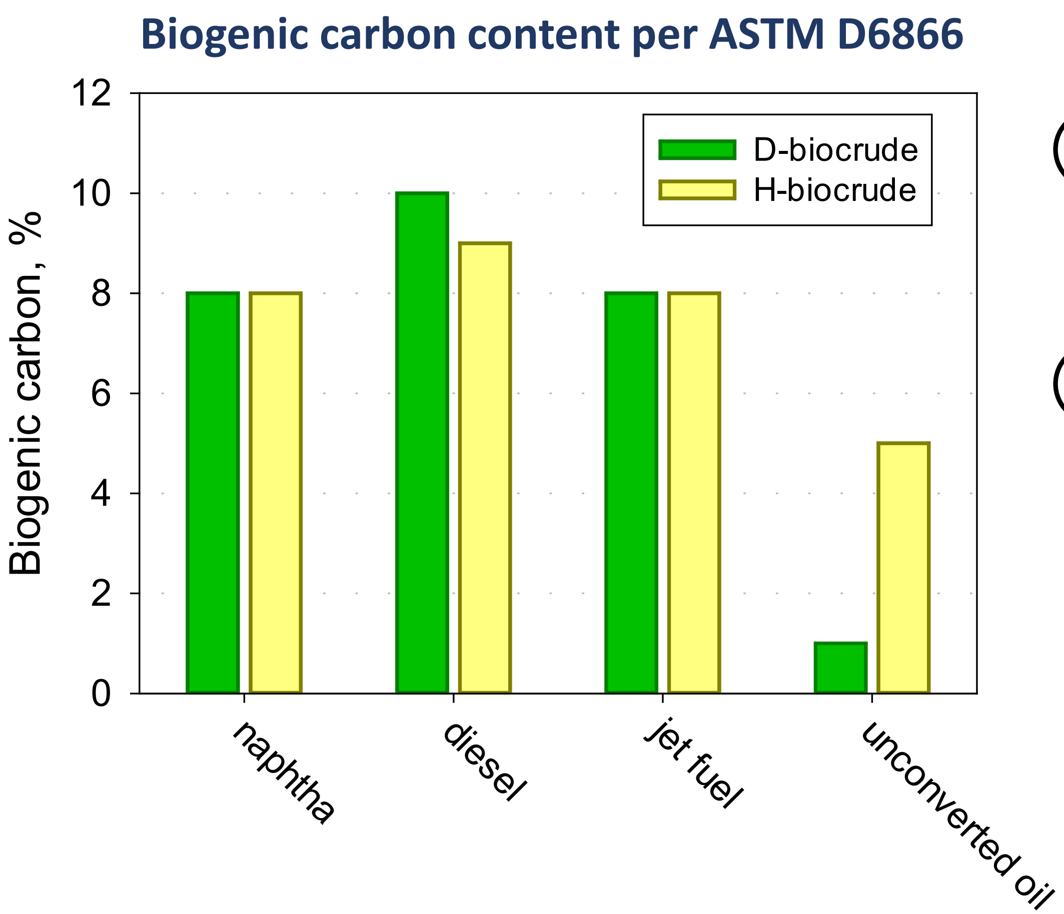
Diesel from H-biocrude



Jet fuel from H-biocrude



Biogenic carbon analysis



1. **D-biocrude co-processing:**
   - 83.6% of the biogenic carbon ends up in the naphtha and diesel products
   - 2.9% remains in the unconverted oil
2. **H-biocrude co-processing:**
   - 70.7% of the biogenic carbon ends up in the naphtha and diesel products
   - 14.7% remains in the unconverted oil

Key highlights

- Co-processing the biocrude treated by distillation had a lower impact on the hydrocracking process than the one treated by partial HDO
  - The removal of heavy material containing the most difficult oxygen species made a significant difference
  - Distillation residue not utilized in the co-processing
- The biocrude treated by HDO required higher co-processing temperatures to offset the effect of resistant oxygen compounds that survived HDO
- Both co-processing schemes were shown to stand on par with their corresponding VGO baselines in terms of hydrocracking product yields, and without consuming more hydrogen
- The co-processed fuel products were to some extent more aromatic than those from VGO
- Biogenic carbon was shown to be preferentially delivered to the desired products through this co-processing route

Acknowledgement

- CanmetENERGY Devon's Technical Services Team and Standard Analytical Lab
- Government of Canada's Office of Energy Research and Development (OERD) and the Canadian Forest Service (CFS)
- Industry partners

Anton Alvarez-Majmutov, Ph.D.
Biofuels and Process Modeling R&D Lead
Email: anton.alvarez-majmutov@nrcan-rncan.gc.ca
Telephone: +1 587-334-6268