Producing Renewable Biofuels through Co-processing/Co-refining – Bioenergy/Biofuels R&D at CanmetENERGY Devon

Jinwen Chen and Anton Alvarez-Majmutov

Natural Resources Canada

CanmetENERGY Devon

Oil Patch Drive, Devon, Alberta, Canada

Presentation at BEN Virtual Bioenergy Symposium
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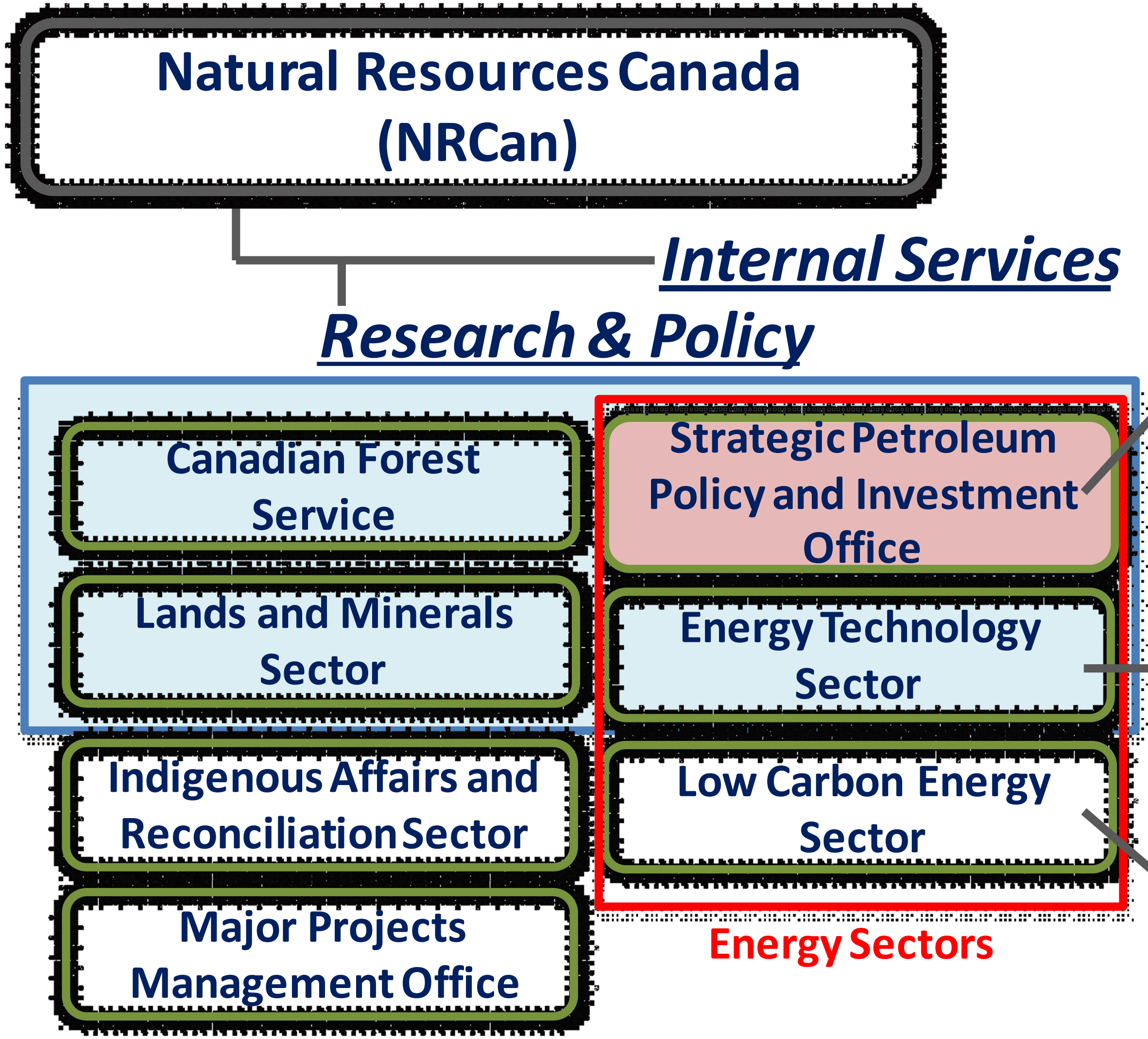
Who Are We?



SPPIO

- Focused on the strategic priorities of Canada's oil and gas sector in both international and domestic markets.
- Centre of expertise on petroleum policy and research and development activities .
- Includes CanmetENERGY Devon and Petroleum Resources Branch

ETS

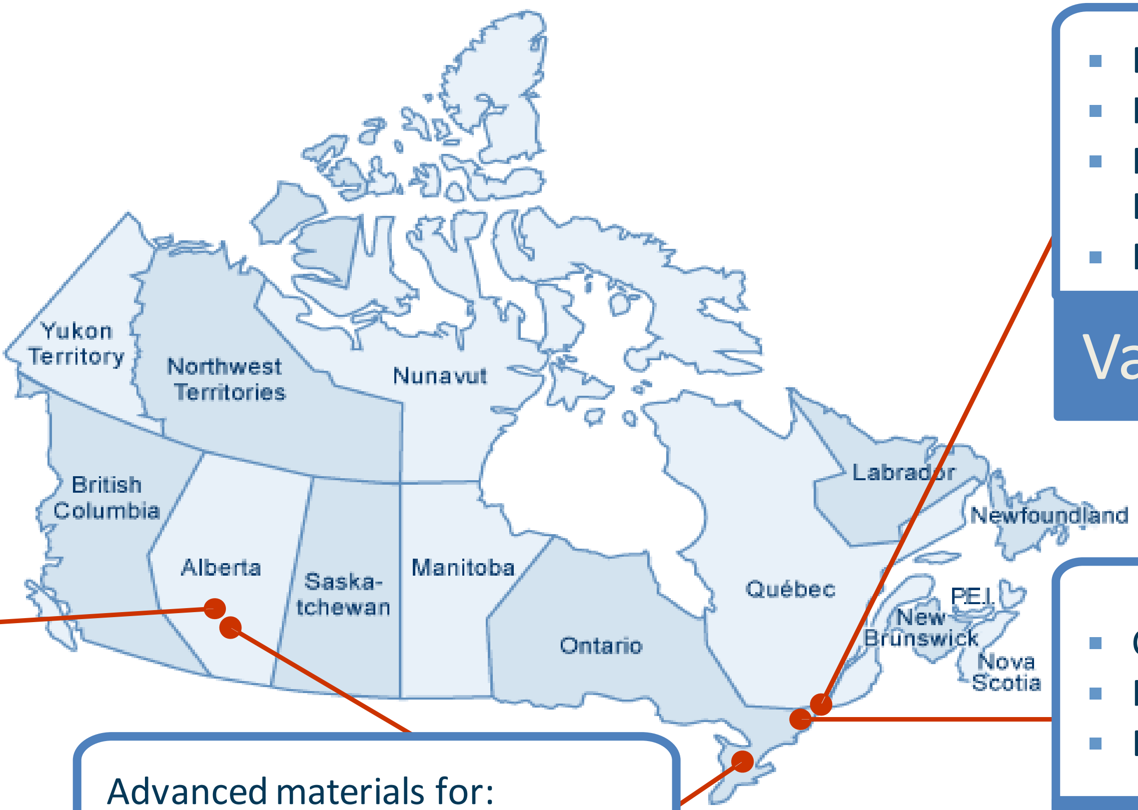
- Lead research and development to provide clean energy solutions connected to energy policy and innovation .
- 3 Canmet Labs and Office of Energy Research and Development

LCES

- Lead strategic energy policy, international energy files, electrification, renewable energy and energy efficiency.

NRCan Canmet Labs

Expertise in 4 Canmet labs that support science and clean technology development.



- Downstream & Renewables
- Upstream & Environment

Devon, AB

Advanced materials for:

- Energy end-use
- Energy production
- Energy Distribution (pipelines)
- Safety and Security

Hamilton and Calgary

- Buildings and Communities
- Industrial processes
- Renewable & Distributed Energy
- RETScreen International

Varennes

- Clean fossil fuels
- Renewables
- Energy end-use

Ottawa

CanmetENERGY Devon

Mandate: Provide national leadership for the **fossil fuel** portfolio to drive **sustainable energy development** and use, and the mitigation of related **environmental impacts** with particular emphasis on unconventional oil and gas.

Upstream and Environments

- Water Quality/Treatment
- Oil Spill Science
- Reclamation
- Extractive Technologies (Hydrocarbon Recovery)
- Value-Added Processes
- Digital Innovation & Modelling

Downstream and Renewables

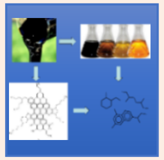
- Partial Upgrading & Processability
- **Renewables & Bioenergy/Biofuels**
- Petroleum Refining, Hydroprocessing
- **Process Modeling, LCA**
- **Advanced Chemistry and Characterization**
- Artificial Intelligence
- **Analytical Lab Services**

Operations

- Technical Services
- Business Services
- Science & Policy Integration
- People & Development
- Facilities
- Planning & Performance

Downstream and Renewables - Our Research Areas

Upgrading/refining Technologies



Bioenergy/Biofuels

Renewable Low-Carbon Fuels

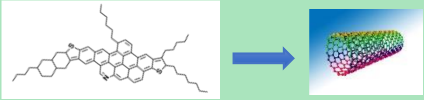
Processability for Refining/biorefining/ co-refining

Modeling, Simulation, Life Cycle Analysis

- Reduce air impacts and GHG emissions
- Improve product quality, competitiveness and access to new markets
- Gain in-depth fundamental understanding
- Inform governments and support policy development

Advanced Chemistry and Characterization

Bitumen Beyond Combustion and Valorization



Analytical Service

Drivers of Bioenergy and Biofuels Research

- Canada's goal for net-zero emission by 2050
- Canada's commitment on GHG reduction (Paris Agreement) 30% below 2005 levels by 2030
- Government initiatives and regulations:
  - Mission Innovation (IC4), Clean Tech Impact, Clean Growth Program, Impact Canada, GoA/AI Clean Resources Programs……
  - Clean Fuel Standard, regulations on renewables in fuels
- Canadian advantages:
  - Biofuels have a smaller carbon footprint than fossil fuels
  - Rich biomass resources - forest residues, agricultural products and wastes
  - Canadian refineries import renewable fuels for downstream blending
- Stand-alone biorefineries requires large capital investment. **Co-processing** renewable oils with petroleum in refineries is attractive and practical

CanmetENERGY Bioenergy/Biofuel R&D Program

Federal government

- NRCan/OERD/PERD
- NRCan/CFS/FIP
- NRCan North America Energy Collaboration Program
- NRCan's other labs
- OEE/ECCC

Provincial/international governments

- Alberta Innovates
- CCITF
- CCITF Facilities
- Alberta Climate Change Office
- BC government
- PNNL, NREL of USDOE

Bioenergy/Biofuel R&D Program

Industry

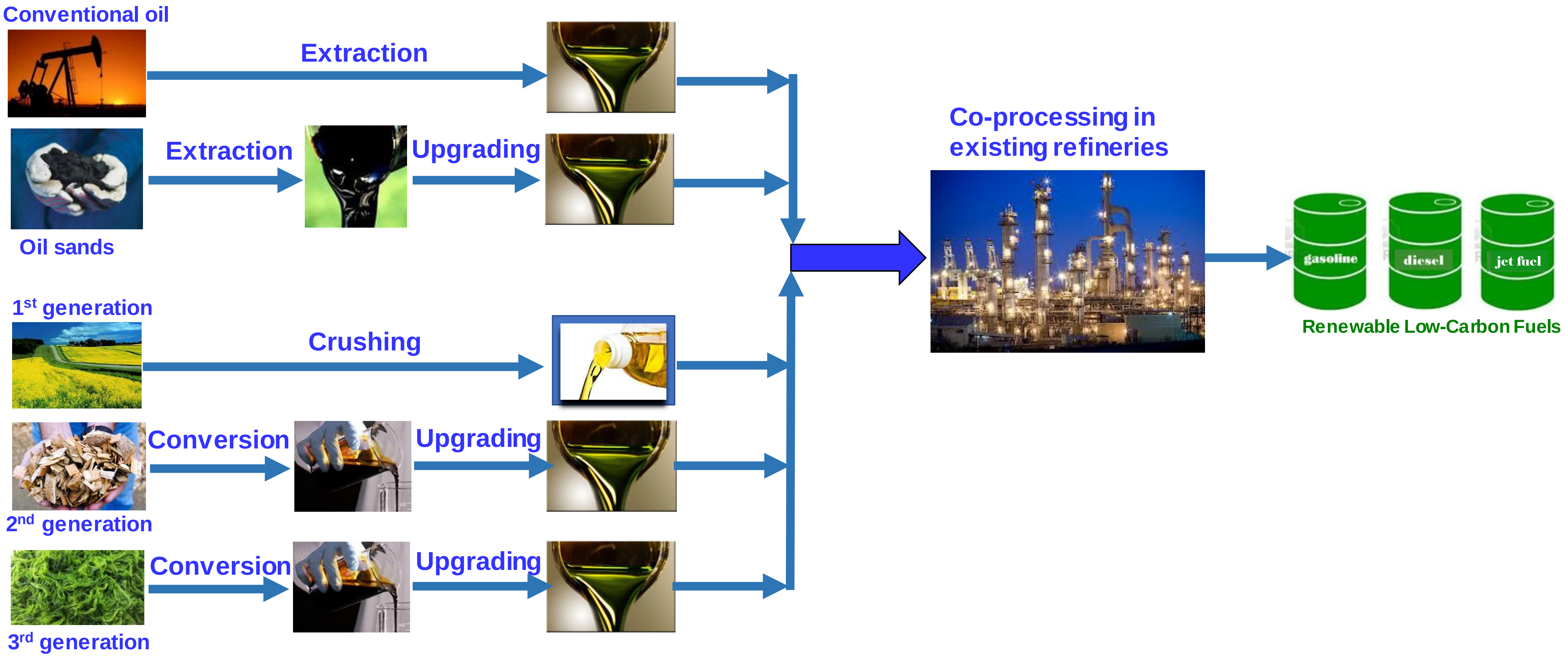
- Suncor Energy; Parkland Refinery
- Steeper Energy; NuLife Green Tech
- Susteen/Fraunhofer
- Licella/Canfor; SBI BioEnergy
- Carbon Engineering
- Forge Hydrocarbon
- Westjet

Academia and R&D Org.

- University of Alberta
- Alborg University
- Washington State University
- Canada-China Bioenergy Center (C-CBC)
- National Polytechnic Institute of Mexico
- Mexican Institute of Petroleum

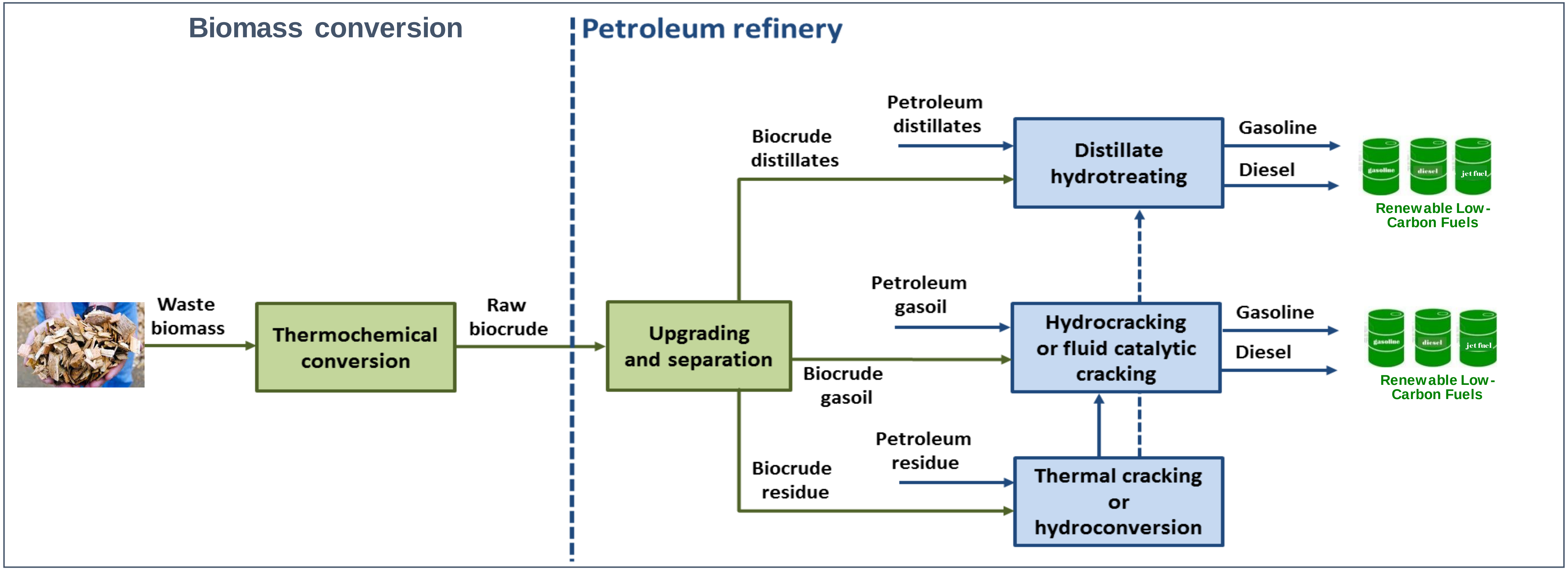
Biofuel technology development → production → consumption → regulation

Co-processing Bio-oils/Biocrudes in a Petroleum Refinery



Co-processing Biocrudes from Biomass

Integrating Biocrudes from Biomass into a Petroleum Refinery



Co-processing Biocrudes in a Petroleum Refinery

Objectives:

- Bio-oil/biocrude upgrading/pre-treatment
- Co-processing different bio-oil/biocrude feedstocks, in different refinery units
- Impacts on refinery operation and product quality
- Equipment fouling and corrosion
- Advanced chemistry and chemical composition
- Processability, compatibility and stability .
- Analytical and characterization methods, and quality matrix
- Techno-economic assessment and life cycle GHG emissions

Natural Resources Canada
Ressources naturelles Canada
Canada

R&D Activities – Distributed among Different Projects

Biocrude upgrading/pre-treatment

- Chemical/catalytic upgrading
- Physical separation (distillation, SDA etc.)
- Additives, other methods/approaches

Biocrude chemistry and characterization

- Identification and quantification of chemical functional groups
- Speciation (GC-VUV, -MS, GC×GC, HPLC)
- Biogenic carbon quantification and tracking along processing chain
- Methods validation

Biocrude co-processing with petroleum

- Hydroprocessing, fluid catalytic cracking
- Catalyst deactivation and mitigation
- Hydroconversion
- Coking/thermal processing for residue
- Process modeling and simulation, LCA

Processability/compatibility/stability

- Miscibility and stability of biocrudes
- Particle agglomeration and precipitation
- Fouling and corrosion caused by biocrudes and blended feedstocks

Our Early R&D with First-Generation Bio-oils for Co-processing

Biogenic Feedstocks:

- Canola oil (raw & de-gummed), other vegetable oils

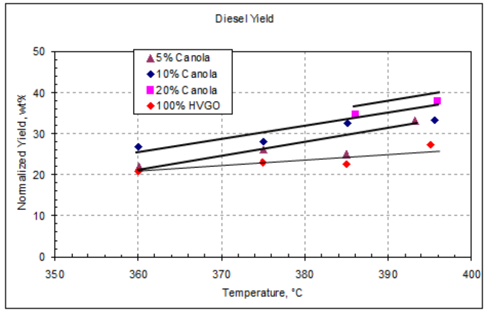
Petroleum Feedstocks:

- Heavy gasoil (HGO), heavy vacuum gasoil (HVGO)
- Light cycle oil (LCO)
- Other petroleum fractions

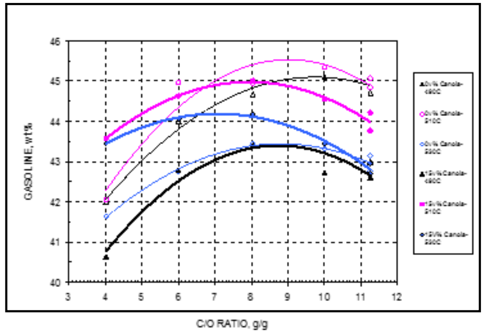
Process Performance and product quality:

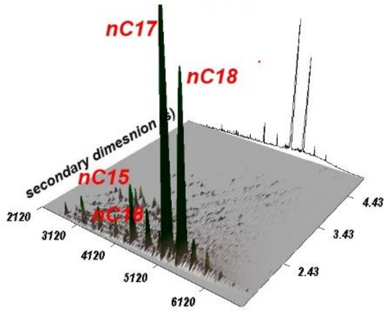
- Conversions and product yields
- Process operating conditions
- Sulfur and nitrogen contents
- Hydrocarbon type compositions
- Product properties (octane/cetane numbers, density, viscosity etc.)
- Cold flow properties

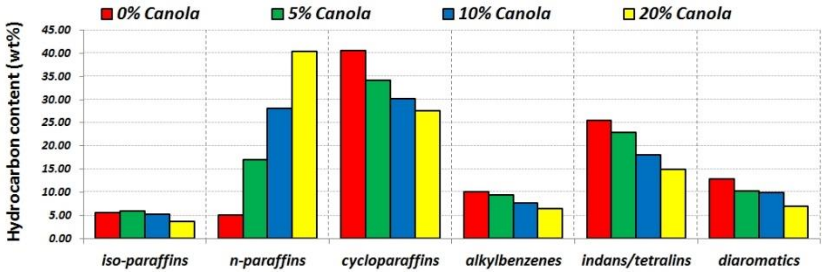
Diesel Yields (Hydroprocessing)



Gasoline Yields (FCC)







Selected Publications from Early R&D

Hydroprocessing

- Wang, H., Farooqi, H., Chen, J., “Co-hydrotreating light cycle oil-canola oil blends”, Front. Chem. Sci. Eng., 9(3), 336-348, 2015
- Chen, J., Farooqi, H., Fairbridge, C., “Experimental Study on Co-hydroprocessing Canola Oil and Heavy Vacuum Gas Oil Blends”, Energy & Fuels, 27,3306-3315, 2013
- Al-Sabawi, M., Chen, J. “Hydroprocessing of Biomass-Derived Oils and Their Blends with Petroleum Feedstocks: A Review”, Energy & Fuels, 26, 5373-5399, 2012

Fluid catalytic cracking

- Ng, S, H., Al-Sabawi, M., Wang, J., Ling, H., Zheng, Y., Wei, Q., Ding, F., Little, E. “FCC coprocessing oil sands heavy gas oil and canola oil. 1. Yield structure”, Fuel, 156, 163-176, 2015.
- Al-Sabawi, M., Chen, J., Ng, M. “Fluid Catalytic Cracking of Biomass-Derived Oils and Their Blends with Petroleum Feedstocks: A Review”, Energy & Fuels, 26, 5355-5372, 2012

Our Current R&D with Second-Generation Bio-oils for Co-processing

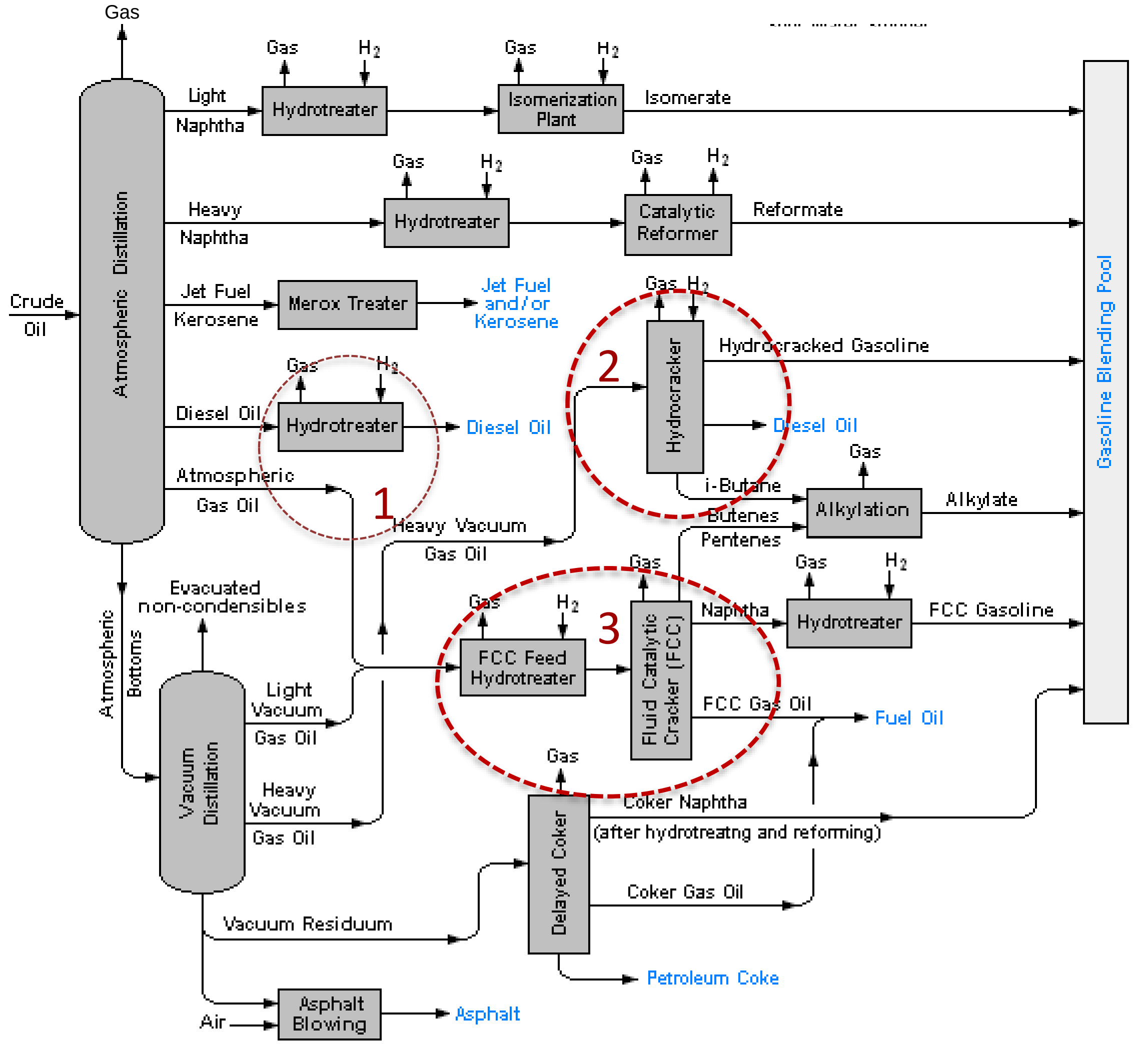
Our Current R&D focuses on second-generation of bio-oils and biocrudes

- Pyrolysis oils
- HTL biocrudes
- TCR biocrudes
- Bio-oils and biocrudes from other conversion technologies

from:

- Forest by-products/wastes
- Agriculture by-products/wastes
- Food industry by-products/wastes
- Municipal solid wastes
- Other resources

Co-processing – Potential Drop-in Points in a Refinery

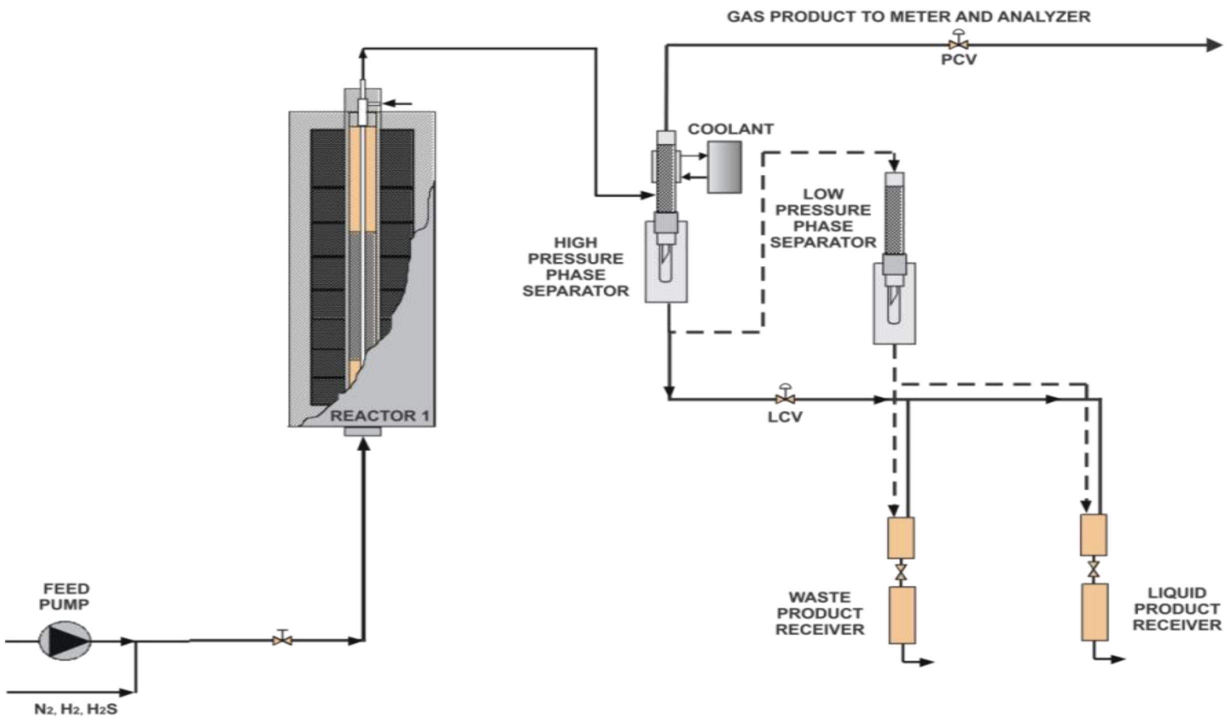


- Crude oil is first distilled into fractions
- Each fraction is processed separately
- Heavy fractions cracked into lighter ones
- Potential biocrude insertion points:
  - Diesel hydrotreating
  - **Hydrocracking**
  - **Fluid Catalytic Cracking (FCC)**

Source: https://en.wikipedia.org/wiki/Oil_refinery

Co-Processing Canola Oil through Hydrotreating

Fixed-bed hydroprocessing unit



Chen, J.; Farooqi, H.; Fairbridge, C. Energy & Fuels 2013, 27, 3306

Pilot plant setup

- Continuous flow fixed-bed reactor unit
- Commercial NiMo/Al_2O_3 catalyst

Testing conditions

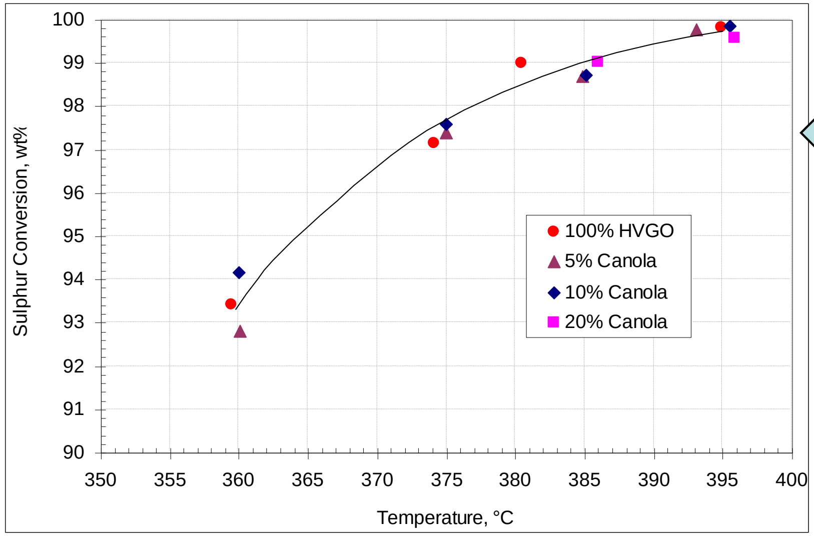
- Temperature: 360-395°C
- LHSV: 1.0-2.5 h^{-1}
- Pressure: 80-110 bar
- H_2/oil ratio: 800 NL/L

Feedstocks

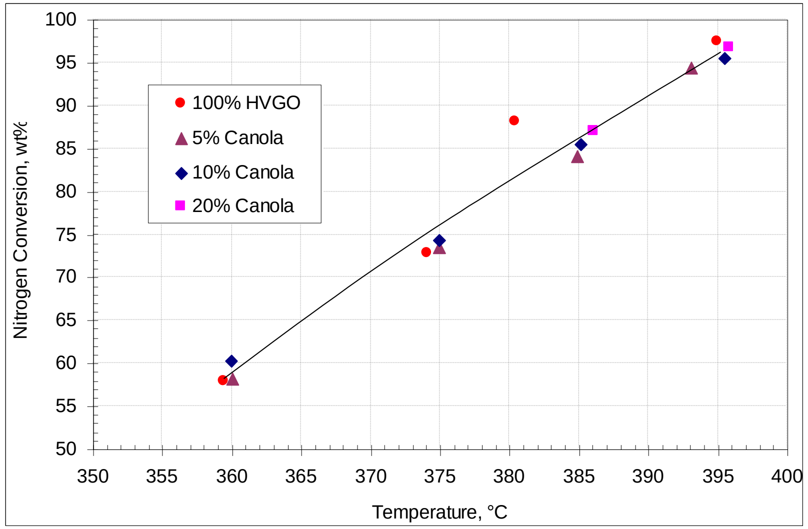
- Heavy vacuum gas oil (HVGO)
- Raw canola oil: 5, 10, 20% in HVGO

Co-Processing Canola Oil – Test Results

Sulfur conversion

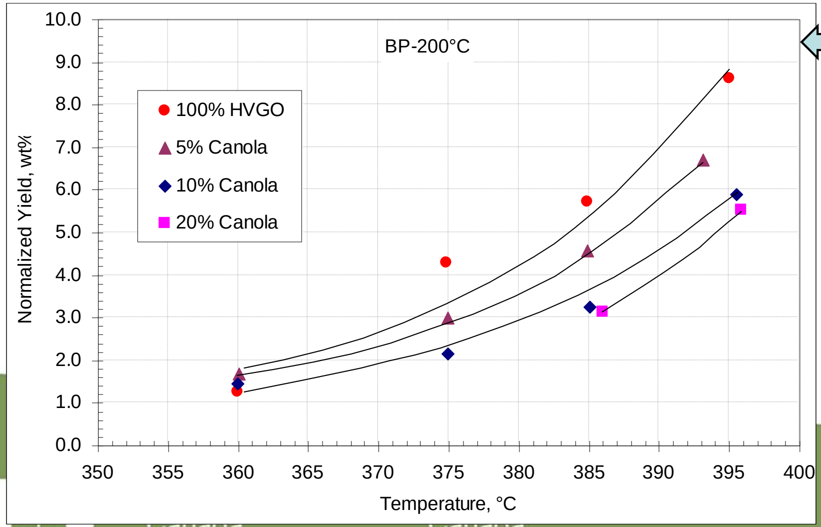


Nitrogen conversion



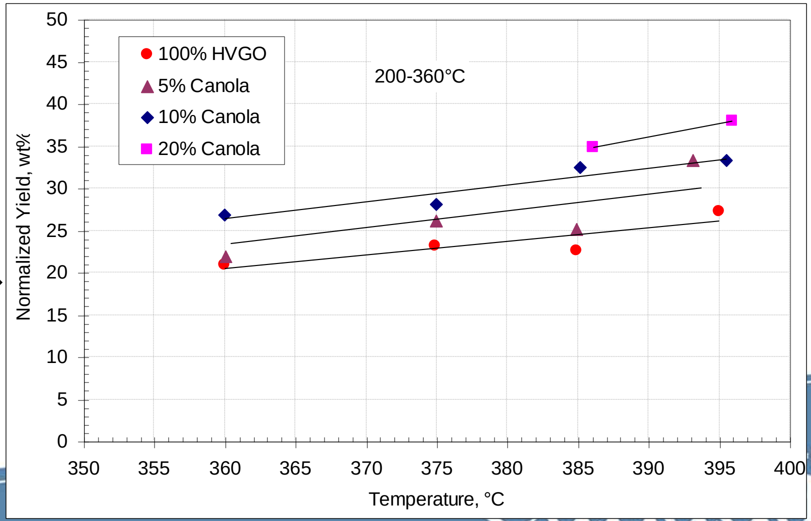
Sulfur and nitrogen removals are not significantly affected by the addition of canola

Gasoline yields



Gasoline yield drops with the addition of canola

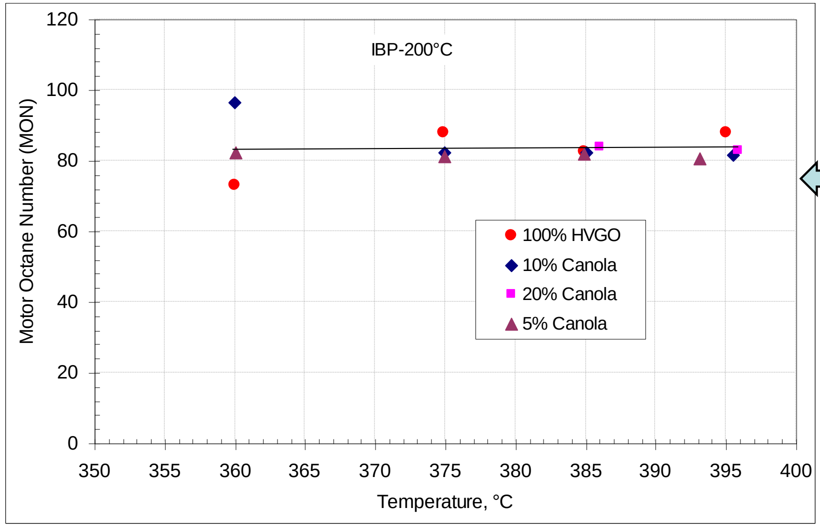
Diesel yields



Diesel yield increases with the addition of canola

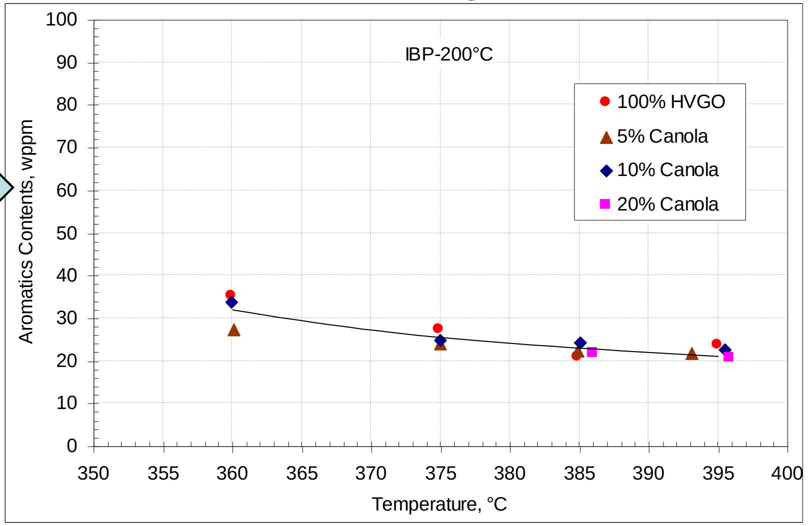
Co-Processing Canola Oil – Test Results

Gasoline Octane Number

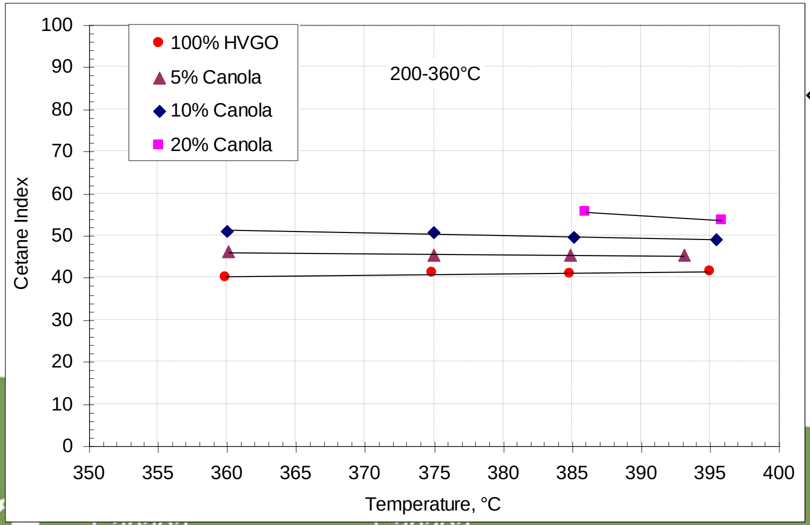


Aromatics content and octane number in gasoline do not change with the addition of canola

Aromatics in gasoline



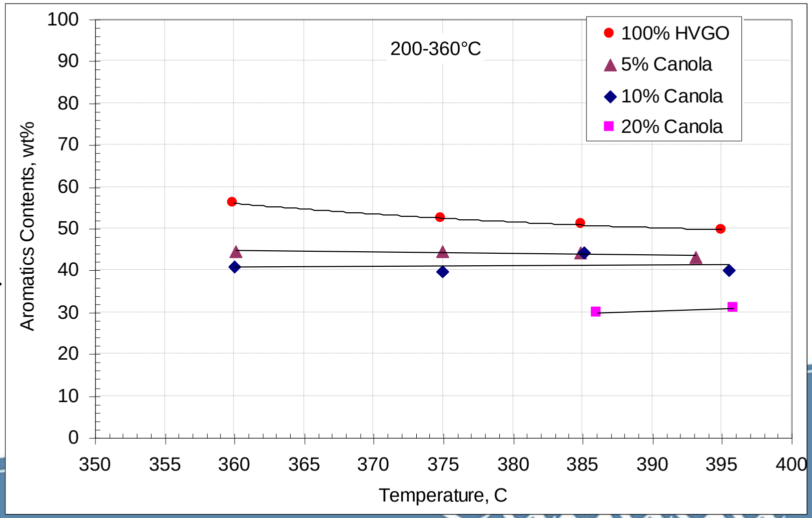
Diesel Cetane Index



Diesel cetane index increases with the addition of canola oil

Aromatics content in diesel decreases with the addition of canola oil

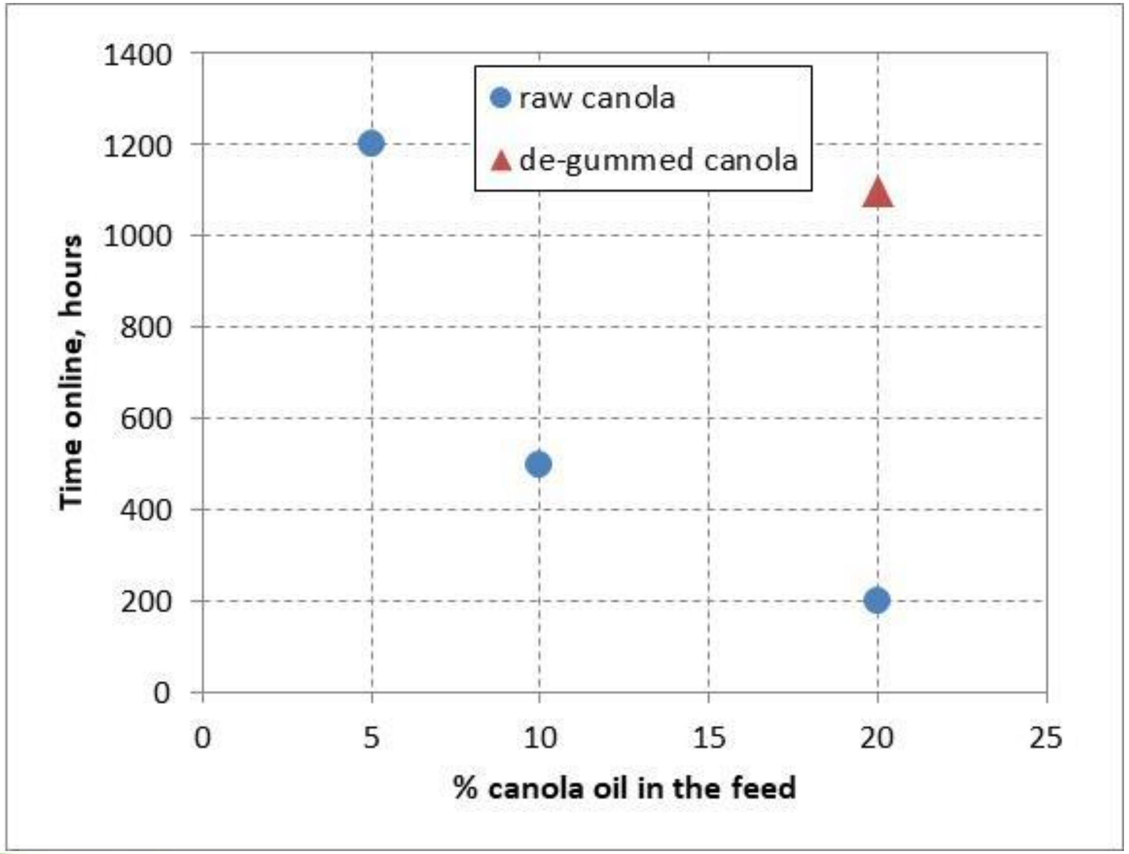
Aromatics in diesel



Co-Processing Canola Oil – Operational Issues

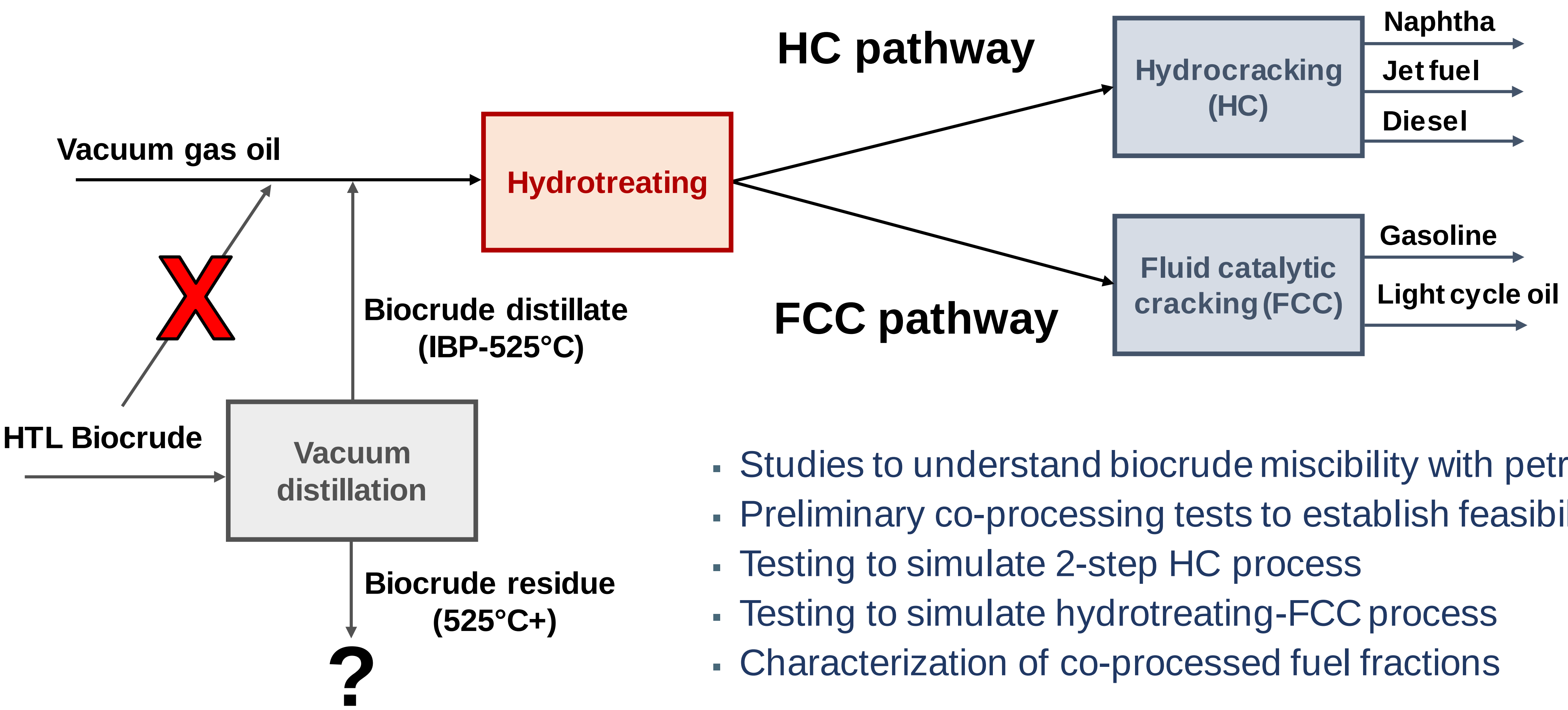
Reactor plugging/fouling experienced at certain concentrations of canola oil

Time on-line before reactor plugging



- With the 5% canola oil feed it was possible to run the unit for over 1200 hours online without any signs of plugging
- The 10% and 20% canola oil feed blends caused complete reactor plugging at 200 and 500 hours online, respectively
- Canola de-gumming enabled 1100 hours online without any signs of plugging

Co-Processing HTL Biocrude from Woody Biomass



- Studies to understand biocrude miscibility with petroleum
- Preliminary co-processing tests to establish feasibility
- Testing to simulate 2-step HC process
- Testing to simulate hydrotreating-FCC process
- Characterization of co-processed fuel fractions

HTL Biocrude Characterization

Property	HTL Biocrude
Density at 15.6°C, g/mL	1.054
Sulfur, wt%	0.01
Nitrogen, wt%	0.08
Oxygen, wt%	10.52
SARA analysis	
Saturates + Aromatics, wt%	11.0
Polars, wt%	44.0
n-C_5 insolubles, wt%	45.0
Fractional composition	
Naphtha (IBP-204°C), wt%	6.0
Gas oil (204-525°C), wt%	56.0
Residue (525°C+), wt%	38.0

5% biocrude in VGO

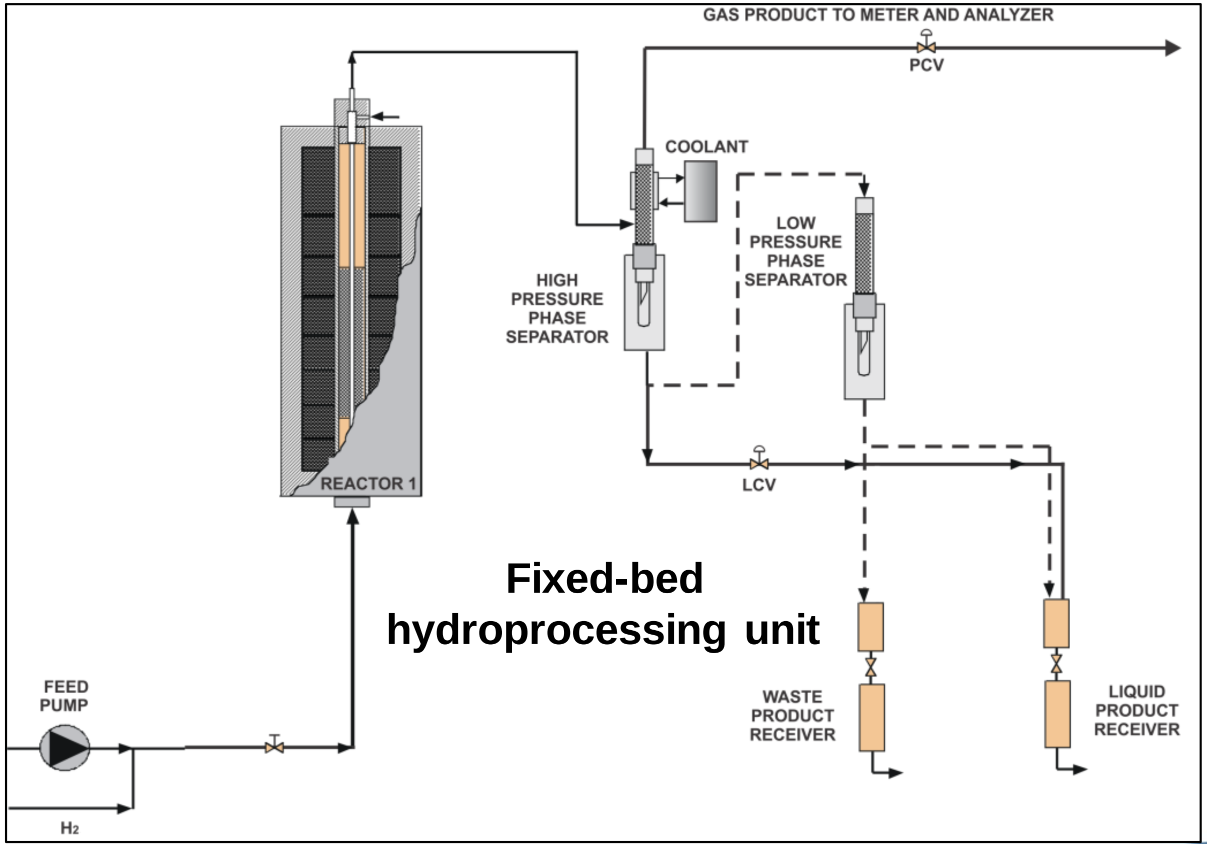
Deposits

Exploratory Co-Processing Tests – Hydrotreating

Understand impact on hydrotreating performance and establish operating window

- Base feed: VGO (343-525°C) from bitumen
- Co-processing blends: 0, 5, 10, 15% biocrude

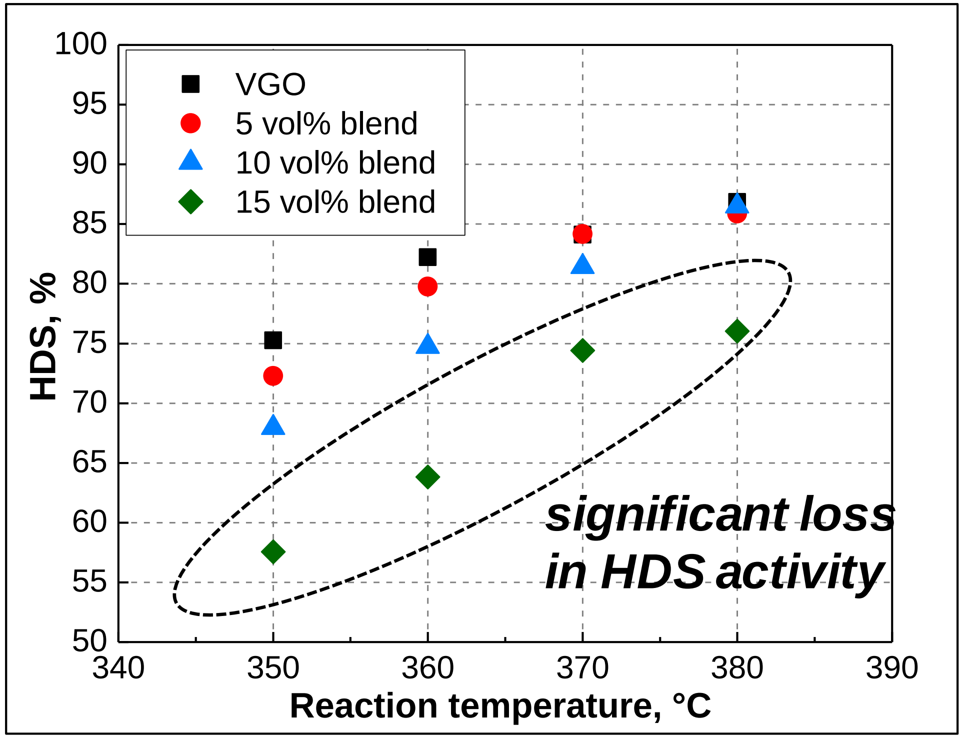
Property	VGO
Density at 15.6°C, g/mL	0.9759
Sulfur, wt%	3.6
Nitrogen, wt%	0.3
Oxygen, wt%	0.5
SAP analysis	
Saturates, wt%	32.9
Aromatics, wt%	54.1
Polars, wt%	13.0



Fixed-bed hydroprocessing unit

Exploratory Co-Processing Tests (continued…)

Hydrodesulfurization (HDS) profiles



LHSV = 1.5 h^{-1}, P = 69 bar , H_2/oil = 800 NL/L

Major observations

- Loss in HDS becomes significant at co-processing ratios above 10 vol% biocrude
- High temperature can offset the effect of oxygen on HDS
- Similar hydrogen consumption levels

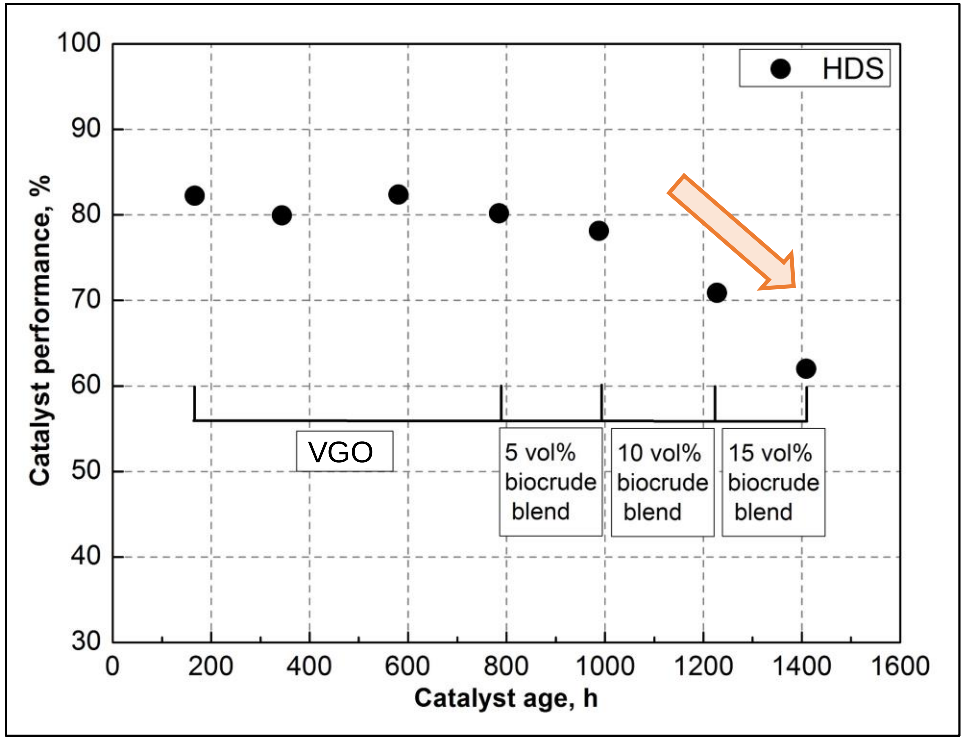
Xing, T.; Alvarez-Majmutov, A.; Gieleciak, R.; Chen, J. Energy & Fuels 2019, 33, 11135

Exploratory Co-processing Tests (continued…)

Major observations

- Catalyst deactivation an issue at >10 vol% biocrude
- Recommendation to use co-processing ratios below 10 vol% biocrude and temperatures above 370°C

Catalyst age monitoring by check-back tests using pure VGO at 360°C



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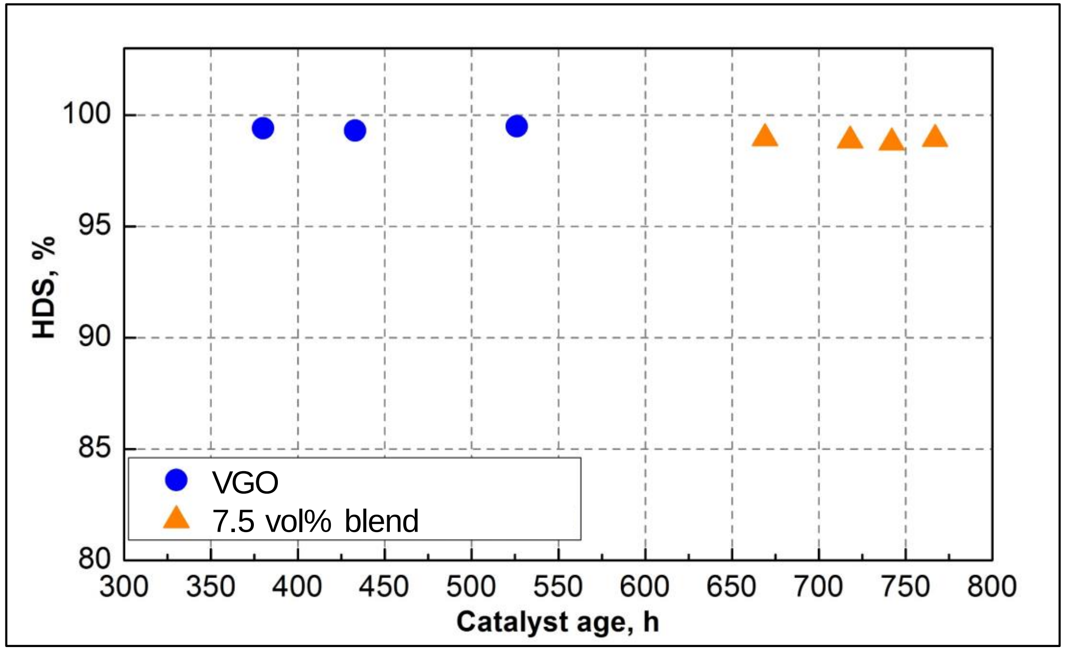
Xing, T.; Alvarez-Majmutov, A.; Gieleciak, R.; Chen, J. Energy & Fuels 2019, 33, 11135

HC Pathway – Hydrotreating Step

Prepare hydrotreated VGO and co-processing blend (7.5 vol% biocrude) for hydrocracking step

HDS profile during production run



$T = 375°C$, $LHSV = 1.5\ h^{-1}$, $P = 97$ bar, $H_2/oil = 800$ NL/L

	VGO	7.5 vol% blend
Liquid product properties		
Density at 15.6°C, g/ml	0.9020	0.9025
Sulfur, wppm	200	410
Nitrogen, wppm	46	92
Oxygen, wppm	<1000	1530
Hydrogen consumption, scf/bbl	1,074	1,099

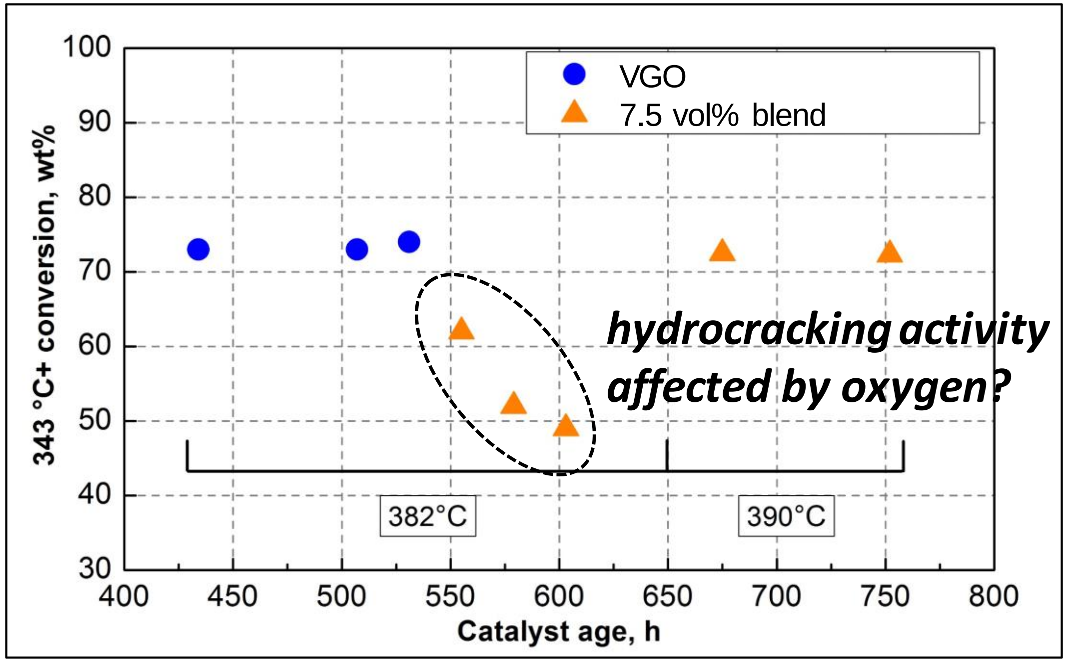
Similar performance, except for oxygen removal

Badoga, S.; Alvarez-Majmutov, A.; Xing, T.; Gieleciak, R.; Chen, J. Energy & Fuels 2020, 34, 7160

HC Pathway – Hydrocracking Step

Produce hydrocracked product to distil out naphtha, diesel, and jet fuel fractions

343°C+ conversion profile during production run



LHSV = 1.5 h^{-1}, P = 110 bar , H_2/oil = 800 NL/L

	VGO	7.5 vol% blend
Overall product distribution		
Gas (H_2S, C_1-C_4), wt%	7.0	6.9
Naphtha (IBP-204°C), wt%	48.6	44.8
Diesel (204-343°C), wt%	30.3	32.8
Unconverted oil (343°C+), wt%	17.7	19.1
Total	103.6	103.6
Hydrogen consumption, scf/bbl	2,343	2,310

Similar overall product yield structure and hydrogen consumption

HC Pathway – Biogenic Carbon Distribution

Biogenic carbon (bc) measurements by radiocarbon analysis ASTM D6866

Sample	% bc	g bc per 100 g feed
7.5 vol% blend	8	6.7
Hydrocracked products		
Naphtha fraction	8	3.0
Diesel fraction	10	2.6
Unconverted oil fraction	1	0.2
Jet fuel fraction	8	1.7

84% bc in the feed is retained in the naphtha and diesel fractions

Only 3% bc ends up in the unconverted oil fraction

In a jet fuel scenario, the jet fuel fraction would capture 26% bc

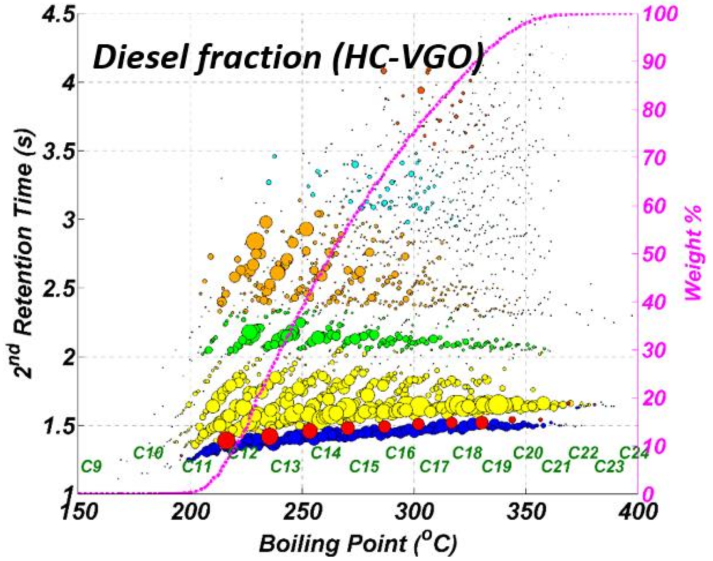
Badoga, S.; Alvarez-Majmutov, A.; Xing, T.; Gieleciak, R.; Chen, J. Energy & Fuels 2020, 34, 7160

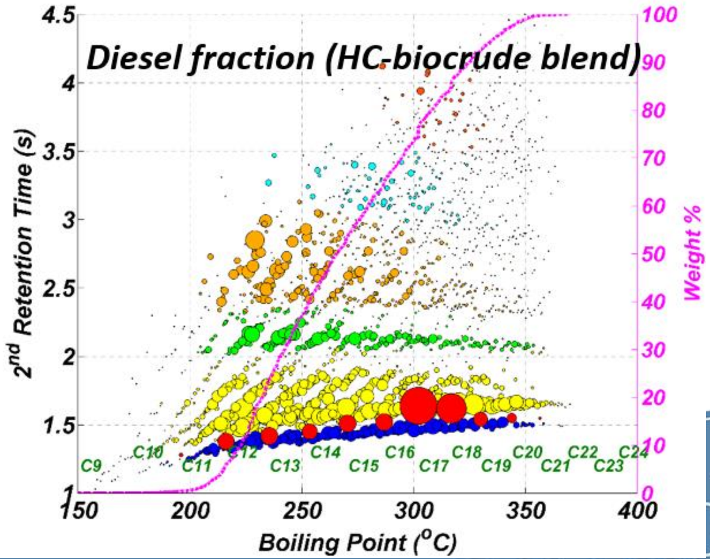
HC Pathway – Hydrocarbon Composition

Hydrocarbon type characterization by GC×GC and GC-VUV

Hydrocarbon class	Diesel - VGO	Diesel - biocrude blend
n-paraffins, wt%	2.9	6.5
Isoparaffins, wt%	15.7	15.1
Cycloparaffins, wt%	57.8	52.5
Alkylbenzenes, wt%	10.0	10.4
Indans/tetralins, wt%	11.0	12.3
Diaromatics, wt%	2.5	3.1
Triaromatics, wt%	0.1	0.1

Co-processed diesel slightly more paraffinic and higher in tetralins and di-aromatics

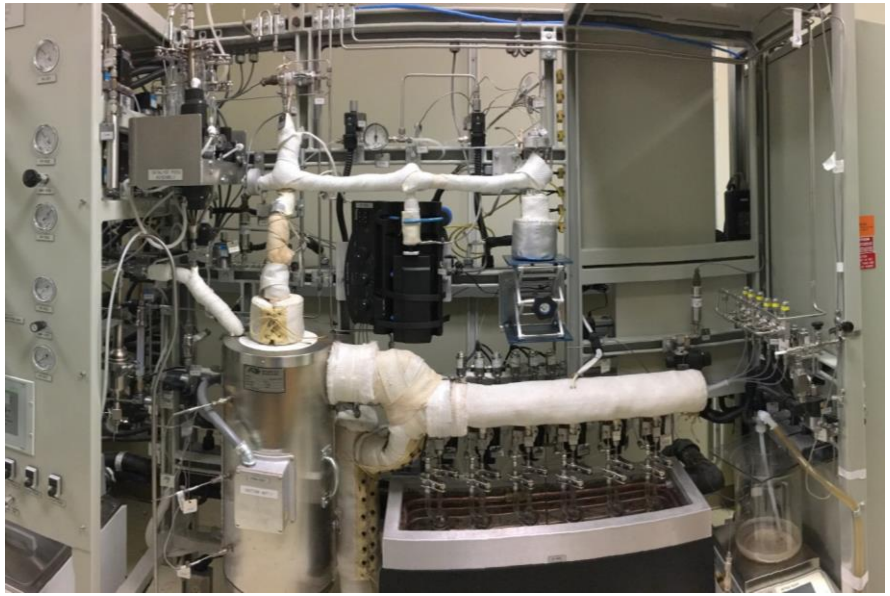


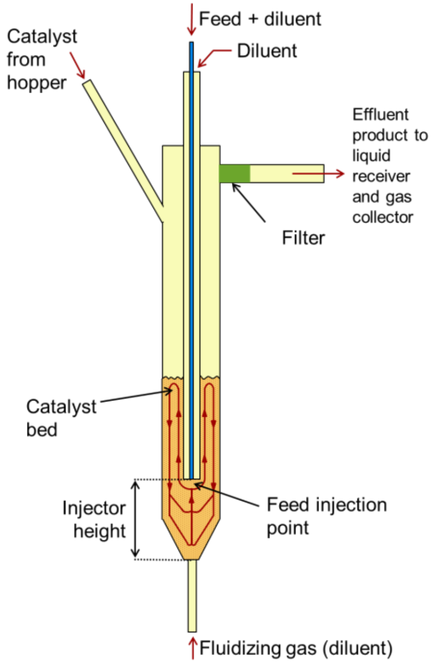


FCC Pathway

FCC testing with hydrotreated VGO and biocrude blends

Advanced Cracking Evaluation (ACE) Unit





- Feedstocks: hydrotreated VGO and 5, 10, 15 vol% biocrude blends
- Refinery equilibrium catalyst
- Reactor temperature: 510°C
- Catalyst-to-oil (CTO) ratio : 4-10 g/g
- Regeneration temperature: 715°C

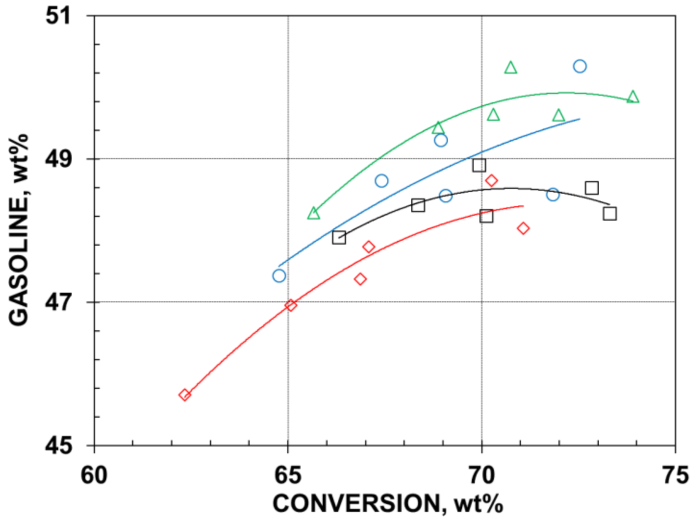
FCC Pathway – Feedstocks

Properties of hydrotreated feedstocks at 360°C

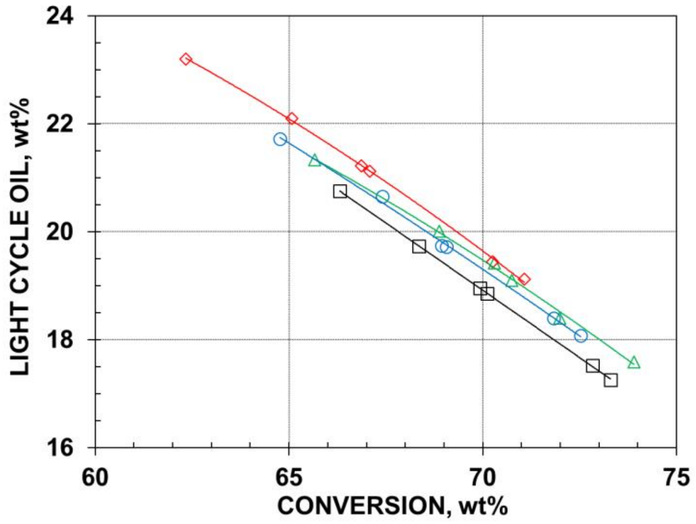
Property	HT-VGO	HT-5 vol% blend	HT-10 vol% blend	HT-15 vol% blend
Density at 15.6°C, g/mL	0.9295	0.9278	0.9286	0.9317
Sulfur, wt%	0.6	0.6	0.8	1.1
Nitrogen, wppm	817	883	921	954
Oxygen, wt%	<0.1	<0.1	0.1	0.2
SAP analysis				
Saturates, wt%	50.0	49.3	51.5	47.2
Aromatics, wt%	44.8	45.4	43.8	45.9
Polars, wt%	5.2	5.3	4.7	6.9

FCC Pathway – Product Yields

Gasoline



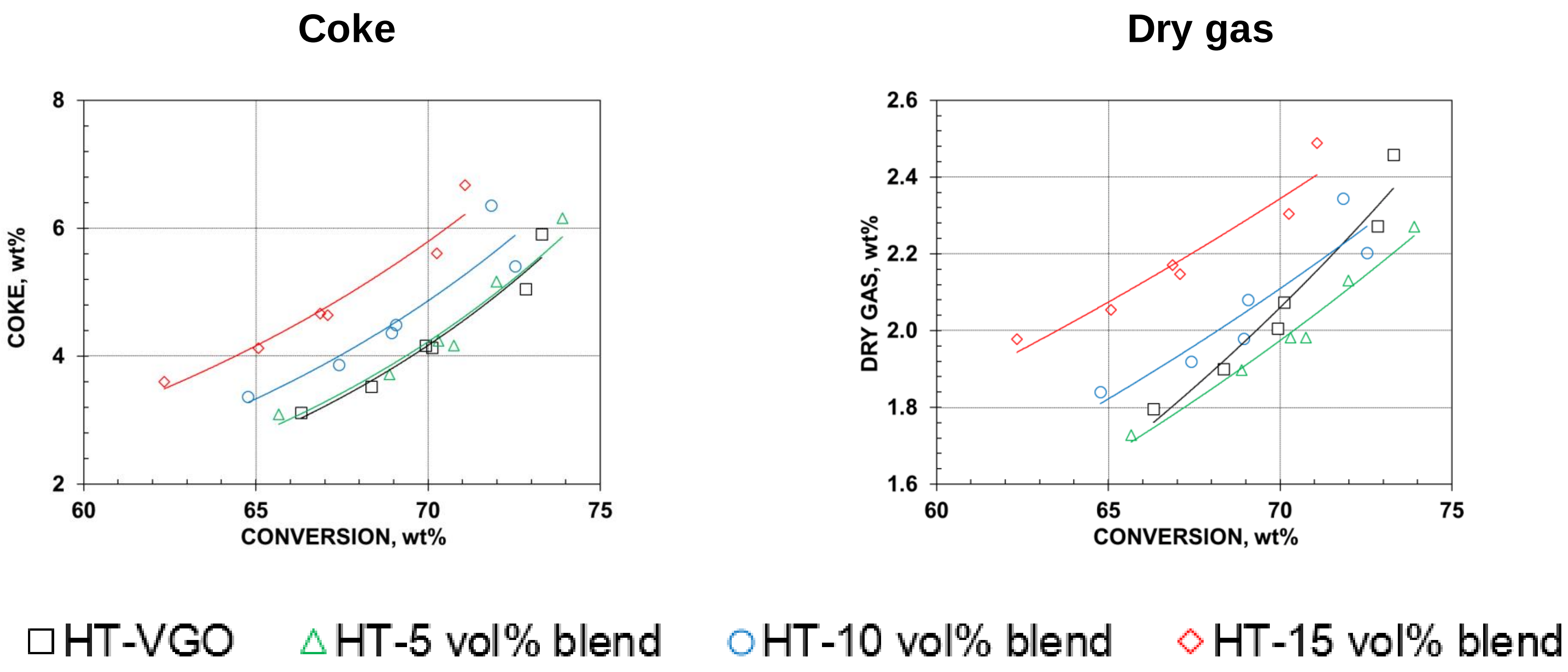
Light cycle oil (LCO)



□ HT-VGO △ HT-5 vol% blend ○ HT-10 vol% blend ◇ HT-15 vol% blend

- The 5% blend shows the highest selectivity towards gasoline, while the 15% blend the lowest
- The three blends appear to yield more LCO than the base feed

FCC Pathway – Product Yields (continued…)



- The 10 and 15% blends give higher coke and dry gas yields

FCC Pathway – Biogenic Carbon Distribution

Biogenic carbon (bc) measurements by radiocarbon analysis ASTM D6866

Sample	% bc	g bc per 100 g feed
Hydrotreated feed blends		
5 vol% blend	5	4.4
10 vol% blend	9	7.8
15 vol% blend	14	12.1
FCC total liquid product		
5 vol% blend	5	3.5
10 vol% blend	10	7.0
15 vol% blend	15	10.4

80-90% bc in the hydrotreated feed blends is retained in the total liquid product from FCC

Current Activities

Biocrude pre-treatment to enhance co-processing

- Solvent extraction (based on the concept of solvent deasphalting in oil refining)
- Partial hydrodeoxygenation

Biocrude chemistry & quality metrics

- Adapt existing hydrocarbon analysis methods for use in biocrude characterization
- Standard protocols to assess blending compatibility
- Biocrude quality specs for co-processing

Techno-economic and environmental modeling

- Build process models informed by pilot plant data
- Cost and carbon intensity modeling of co-processed fuels

Our Collaborators, Partners and Clients

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Leadership in ecoInnovation

Canada
Natural Resources Canada
Canadian Forest Service

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Carbon Engineering

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For further information please contact:

Dr. Jinwen Chen

Director

Downstream and Renewables

CanmetENERGY Devon

Natural Resources Canada

Jinwen.Chen@canada.ca

Telephone: 780 987 8763

Dr. Anton Alvarez-Majmutov

Research Scientist, Team Lead

Downstream and Renewables

CanmetENERGY Devon

Natural Resources Canada

Anton.Alvarez-Majmutov@canada.ca

Telephone: 780 987 8348

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