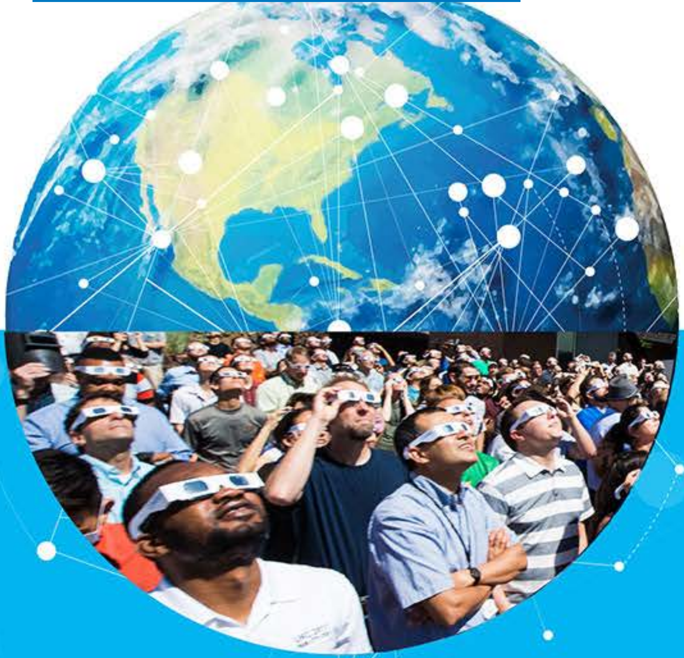


Renewable Diesel Production through Stand-Alone and Co-Hydrotreating of Catalytic Fast Pyrolysis Oil

Xiaolin Chen, Kristiina Iisa, Kellene Orton,
Calvin Mukarakate, Michael Griffin
Catalytic Carbon Transformation & Scaleup Center

3.7.2023

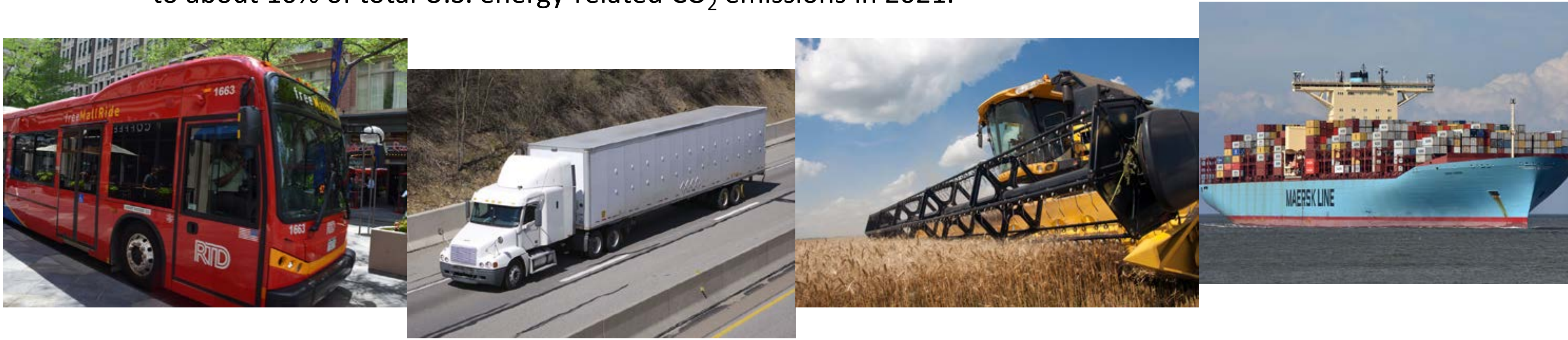
Photo by Dennis Schroeder, NREL 46840

Contents

1 Background and Objective
2 Strategy
3 CFP Oil
4 Co-hydrotreating
5 Stand-alone Hydrotreating
6 Conclusion
7 Acknowledgement

Background

- Petroleum diesel has been broadly utilized in **heavy-duty** transportation applications.
- Approximately 47 billion gallons of petroleum diesel fuel were consumed by the U.S. transportation sector in 2021, which resulted in about 472 million metric tons of CO_2 emission.
- This amount was equal to about 26% of total U.S. transportation sector CO_2 emissions and equal to about 10% of total U.S. energy-related CO_2 emissions in 2021.



It is urgent to develop solutions to reduce petroleum diesel-derived carbon emissions.

Source: U.S. Energy Information Administration (EIA)

Background

Feedstock: oilseed crops
- Edible materials
- Limited availability

Renewable diesel or green diesel (hydrotreated vegetable oil, HVO)

- ASTM D975
- Produced through hydrotreating triglycerides (oil and fats).
- Existing refinery infrastructures
- Can be used in 100% concentration
- Existing diesel engines

Traditional biodiesel (fatty acid methyl ester, FAME)

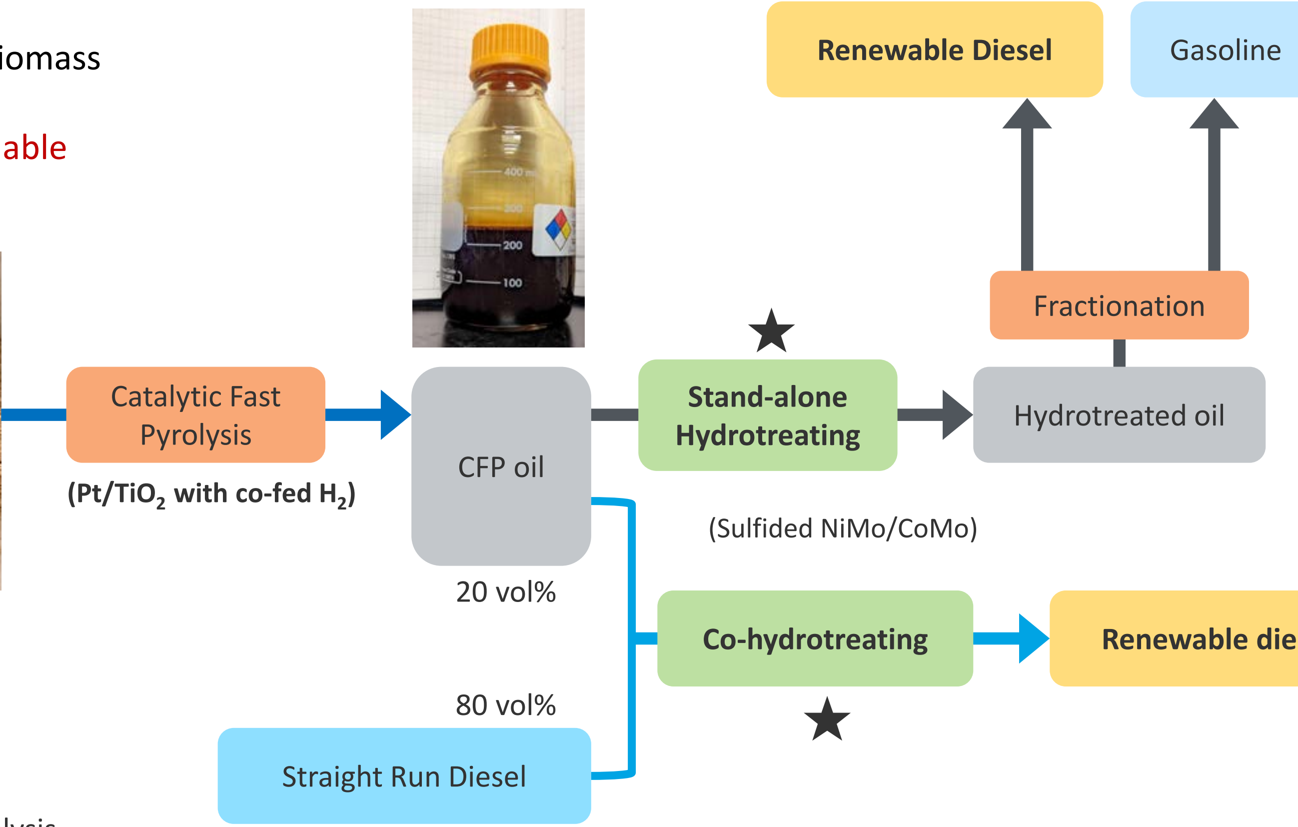
- ASTM D6751
- Produced through transesterification
- Must be blended with petroleum diesel (5-20%)
- High levels of NOx emissions
- Risk of damage to existing diesel engines

Our objective is to produce high-quality renewable diesel from non-food biomass with a large abundance.

Strategy

Feedstock: woody biomass
- Abundant
- Domestically available
- Inedible

50% Clean pine &
50% forest residues



Catalytic Fast Pyrolysis

(Pt/TiO_2 with co-fed H_2)

CFP oil

20 vol%

80 vol%

Straight Run Diesel

★

Stand-alone Hydrotreating

(Sulfided NiMo/CoMo)

Hydrotreated oil

Fractionation

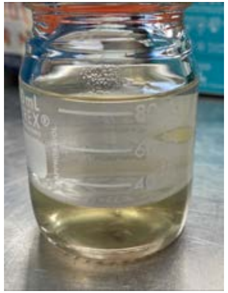
Renewable Diesel

Gasoline

Co-hydrotreating

★

Renewable diesel

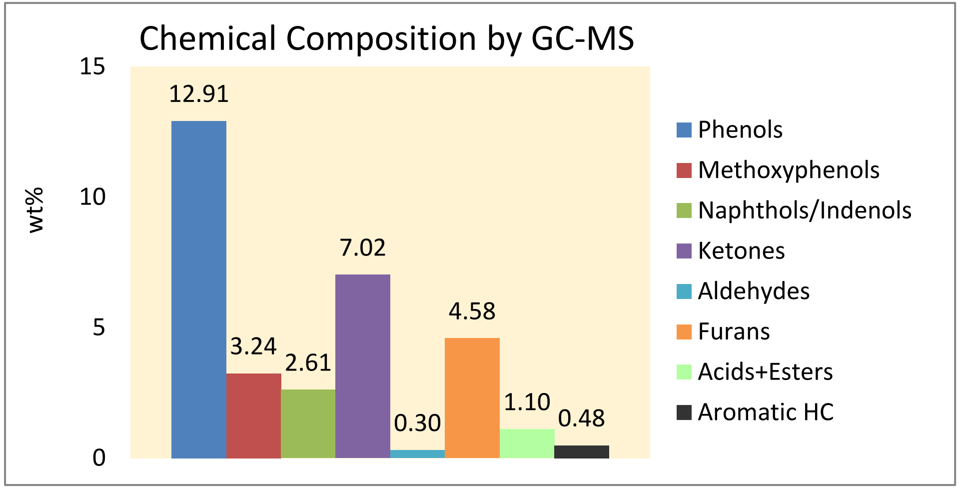


CFP = catalytic fast pyrolysis

Catalytic Fast Pyrolysis Oil

CFP oil produced from woody biomass over a bifunctional metal-acid catalyst (Pt/TiO_2) with co-fed H_2

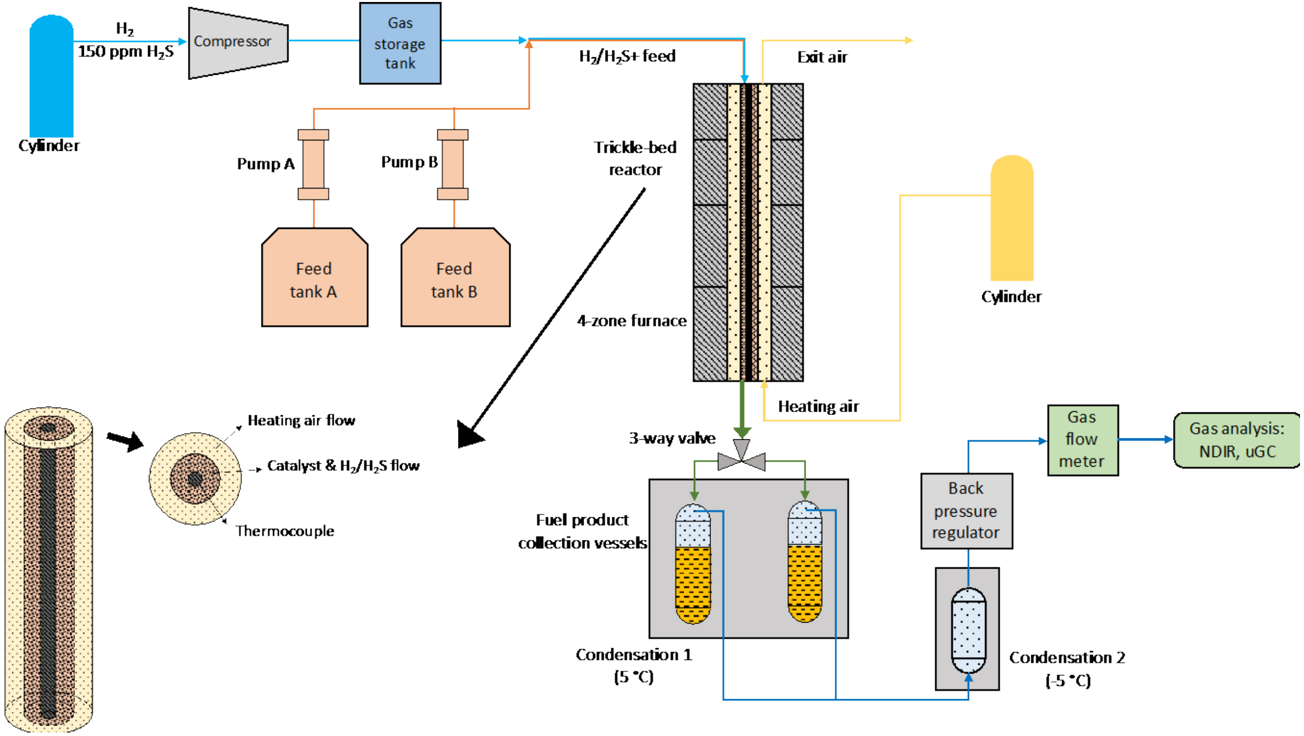
CFP Oil Elemental Analysis	
C, wt% db	76.4%
H, wt% db	7.8%
O, wt% db	15.6%
N, wt% db	0.2%
H_2O, wt%	2.8%



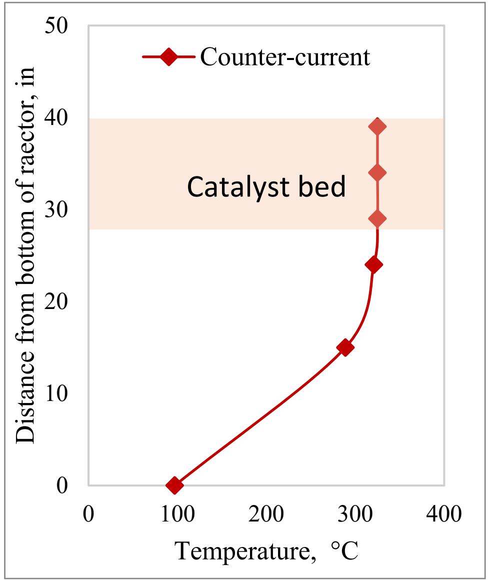
- CFP step produced stable bio-oil with low oxygen content.
- Bifunctional CFP catalyst enables hydrogenation of coke precursors
- Compared to zeolite catalyst, metal-acid catalyst resulted in a higher oil carbon yield, more phenols, and less aromatic hydrocarbons.

Co-hydrotreating

Continuous Hydrotreater System

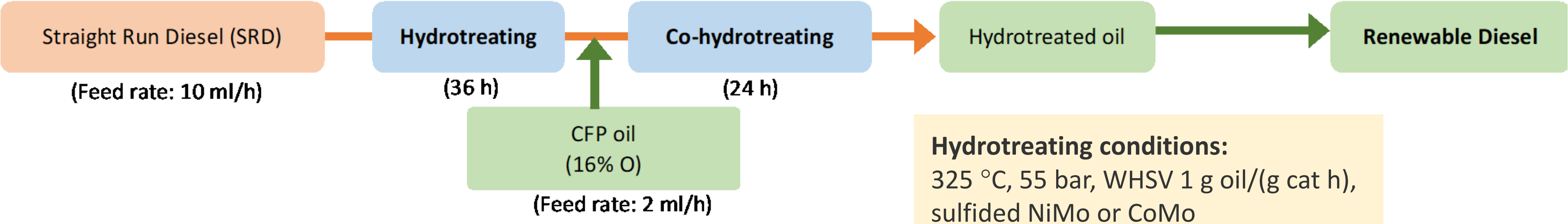


Reactor Temperature Profile



- Isothermal zone
- Ideal for co-hydrotreating

Co-hydrotreating



Straight Run Diesel (SRD)

(Feed rate: 10 ml/h)

Hydrotreating

(36 h)

Co-hydrotreating

(24 h)

CFP oil
(16% O)

(Feed rate: 2 ml/h)

Hydrotreated oil

Renewable Diesel

Hydrotreating conditions:
325 °C, 55 bar, WHSV 1 g oil/(g cat h),
sulfided NiMo or CoMo

Feed	SRD	SRD+CFP	SRD	SRD+CFP
Catalyst	NiMo	NiMo	CoMo	CoMo
H_2 consumption, g/g CFP oil	0.1	1.4	0.0	1.1
Oil mass yield, wt%	100	94	100	91
Oxygen content, wt%	< 0.1	0.1	< 0.1	0.1

Co-hydrotreating with CFP oil increased H_2 consumption due to deoxygenation of CFP oil.

Compared to CoMo, NiMo resulted in a higher H_2 consumption indicating enhanced hydrogenation reactions.

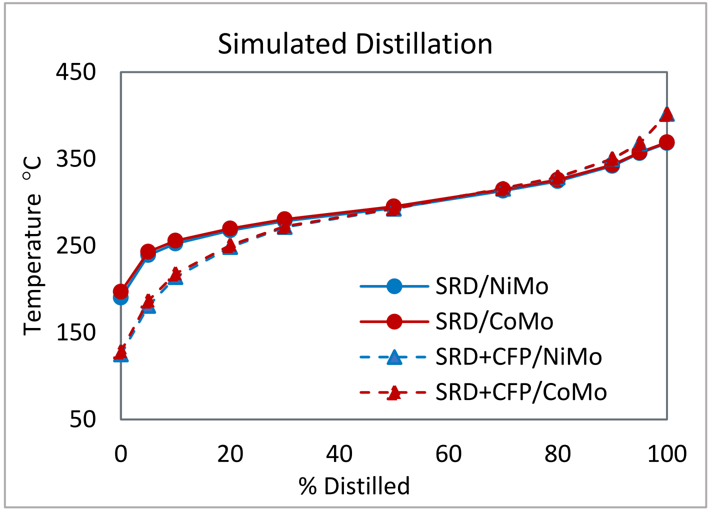
Co-hydrotreating

Feed	SRD	SRD+CFP	SRD	SRD+CFP
Catalyst	NiMo	NiMo	CoMo	CoMo
O, wt%	$\leq$0.3	$\leq$0.3	$\leq$0.3	$\leq$0.3
N, wt%	0.03	0.04	0.02	0.04
S, wt%	0.01	0.03	0.02	0.04
H:C, mol/mol	1.86	1.82	1.86	1.79

Oxygen content was below detection limit **compared to 15.6 wt% of oxygen content in CFP oil**.

Compared to CoMo, NiMo resulted in a higher H:C ratio of 1.82 and a lower sulfur content of 0.03%

Co-hydrotreating

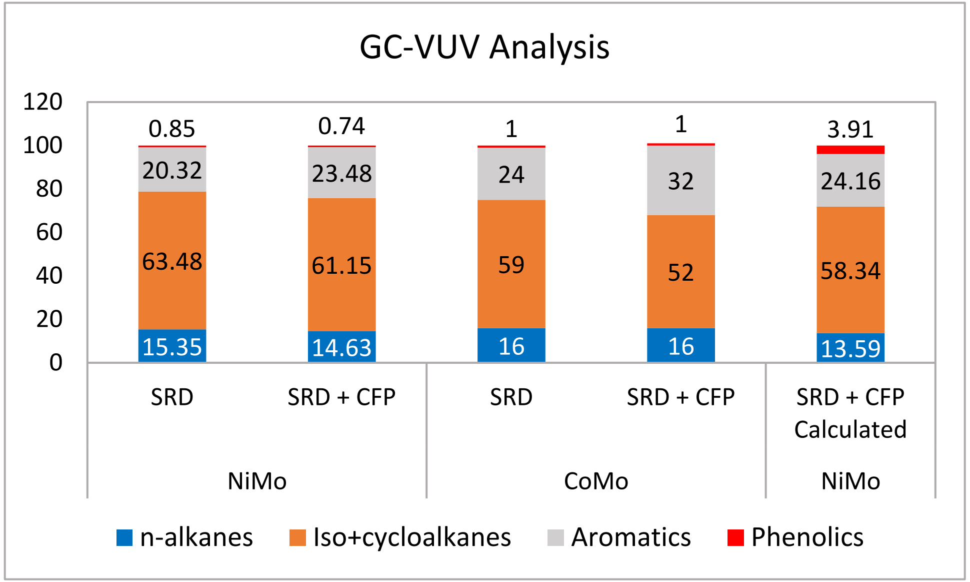


Feed	SRD	SRD+CFP	SRD	SRD+CFP
Catalyst	NiMo	NiMo	CoMo	CoMo
ICN	50	45	48	42
Density, g/ml	0.83	0.83	0.83	0.83

ICN = Indicated Cetane Number

- Co-hydrotreating with CFP oil increased volatile compounds.
- ICN of hydrotreated oil was within US on-road specifications.
- Density within 0.82-0.86 g/ml is considered ideal.

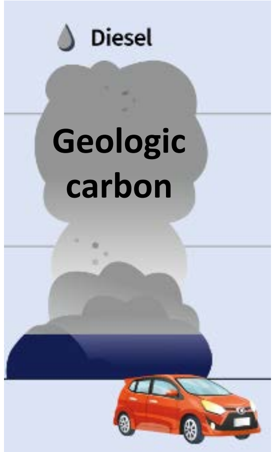
Co-hydrotreating



- Co-hydrotreating increased aromatics due to the aromatic nature of CFP oil.
- Compared to CoMo, NiMo promoted the conversion of aromatics into cycloalkanes.
- Calculated results indicated synergy during co-hydrotreating (e.g., hydrogen transfer).

Co-hydrotreating

- 91-97% of **biogenic carbon** was incorporated from CFP oil to hydrotreated oil (C-14 analysis).



vs.

Consumes CO_2 from atmosphere

Biogenic carbon

\+

SRD

91-97%

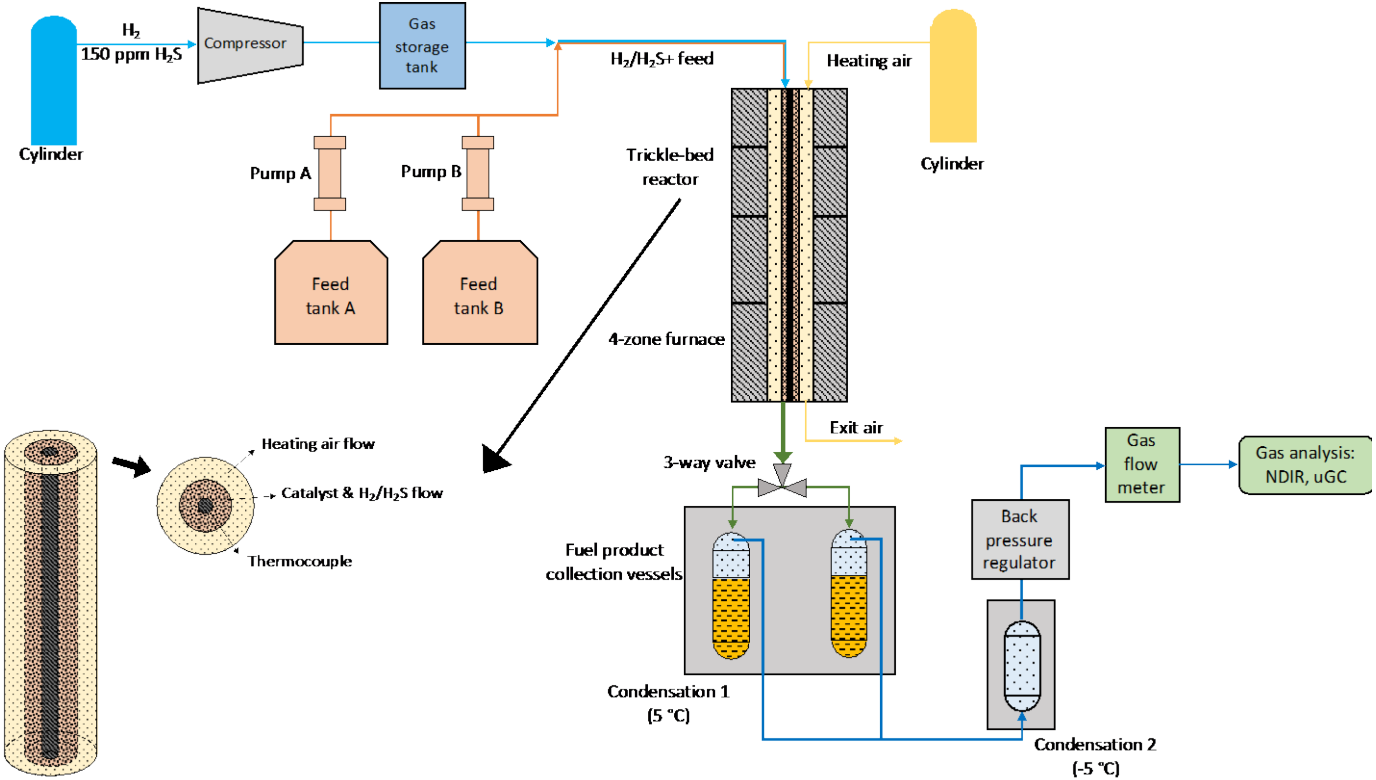
20% of biogenic carbon

Conclusion from Co-hydrotreating

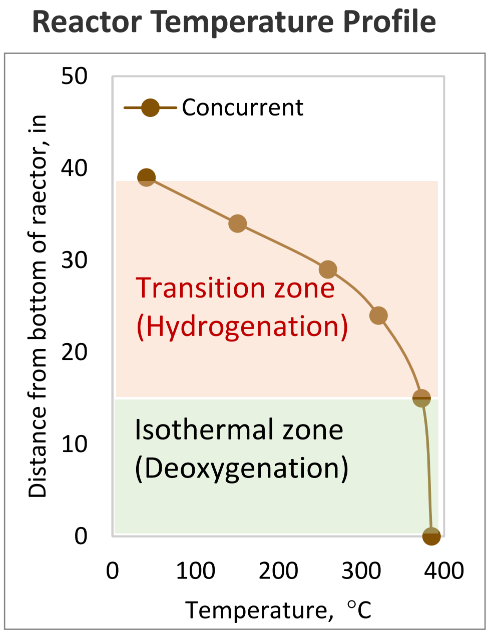
- The whole co-hydrotreated oil product has great potential to be used as renewable diesel.
- Sulfied NiMo was a preferable hydrotreating catalyst compared to sulfided CoMo.
- NiMo was chosen for the following stand-alone CFP oil hydrotreating study.

Stand-alone Hydrotreating

Continuous Hydrotreater System



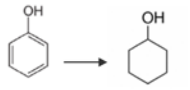
Stand-alone Hydrotreating



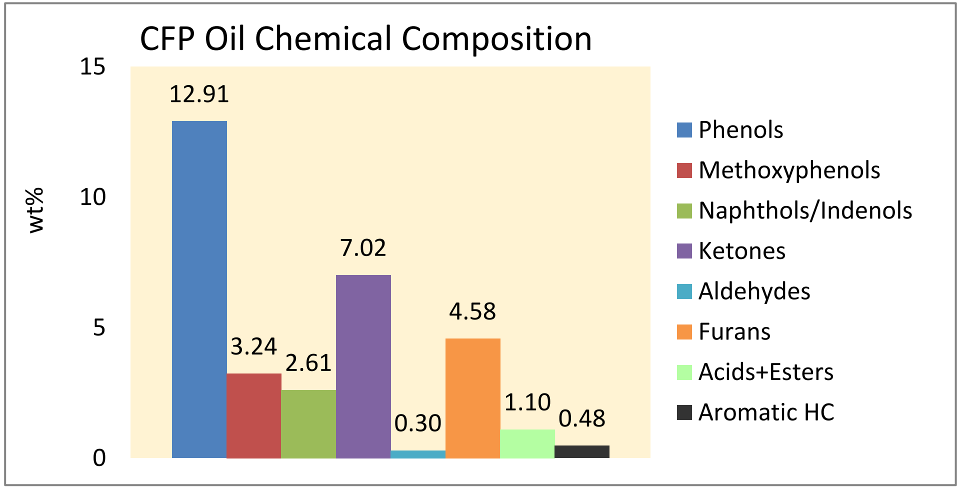
- Two-stage process
- Prolonged transition zone
- More complete hydrogenation
- Reducing the risk of plugging

- Low-temperature hydrogenation:

  C=O → C-OH



- High-temperature deoxygenation:



Stand-alone Hydrotreating

CFP oil

Stand-Alone Hydrotreating

Hydrotreated oil

Fractionation

Renewable Diesel & Gasoline

(Feed rate: 2 ml/h)

Condition	385 °C, 125 bar
Oil, g/g CFP oil	75%
Aqueous, g/g CFP oil	25%
Gas, g/g CFP oil	9%
H_2 consumption, g/g CFP oil	0.13
Mass balance, g/g (CFP oil+H_2 consumption)	97%
Oil carbon yield	89%
Gas carbon yield	10%
Carbon balance	99%
Product O content, wt%	<0.1%
H:C, mol: mol	2.01
Calculated HHV, MJ/kg	49.25
Density, g/ml	0.739

Hydrotreating conditions:

385 °C, 125 bar, WHSV 0.16 h^{-1}, over sulfided NiMo.

Compared to previous study (400 ℃, 130 bar)

H2 consumption of 0.04 g/g CFP oil

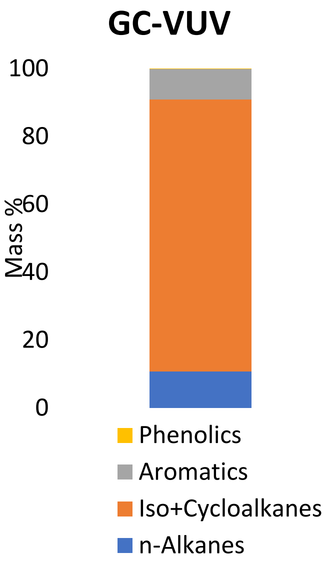
Oil carbon yield of 89%

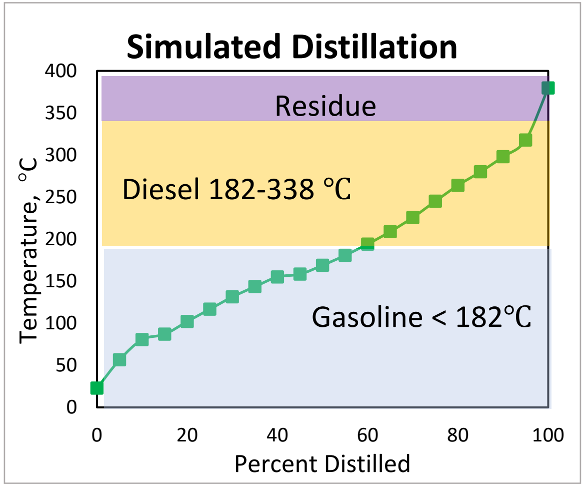
Oxygen content of 0.4 wt%

H:C ratio of 1.71

- The two-stage process achieved more complete hydrogenation reactions of CFP oil.
- Better results compared to previous study under more severe conditions.

Stand-alone Hydrotreating





Distillation fractions	
Gasoline	49 wt%
Diesel	45 wt%
Residue	4 wt%
Losses	2 wt%

Diesel Fraction GCxGC	
n-Alkane	5.7 wt%
Isoalkane	4.5 wt%
Cycloalkane	88.8 wt%
Unidentified	1%

Compared to previous study (400 °C, 130 bar):

45% of gasoline

39% of diesel

16% of residue

- Hydrotreated oil consisted of compounds of a broad range of volatilities.
- An improvement compared to the previous study.
- The ICN of diesel fraction was 45, which was vastly improved compared to 24 in the previous study.

Conclusion

Co-hydrotreating of SRD (80 vol%) and CFP oil (20 vol%) was studied in an isothermal configuration.

- Up to 100% of carbon yield of hydrotreated oil was produced with an oxygen content of 0.1 wt%.
- Up to 97% of biogenic carbon was incorporated from CFP oil to hydrotreated oil.
- The whole hydrotreated oil product could be used as renewable diesel with ICN up to 45.
- NiMo was a preferable hydrotreating catalyst due to a better ability to enhance hydrogenation.

Stand-alone hydrotreating of CFP oil was studied in a two-stage process.

- Up to 89% carbon yield of hydrotreated oil was produced with an oxygen content < 0.1 wt%.
- 45 wt% of diesel and 49 wt% of gasoline were obtained through fractionation of hydrotreated oil product.
- The distilled diesel fraction included 88.8% of cycloalkane.
- The ICN (45) of diesel fraction was vastly improved compared to previous study.

Both stand-alone and co-hydrotreating of CFP oil produced high-quality renewable diesel products.

Acknowledgements

- U.S. DOE BETO for funding
- NREL
  - Kristiina Iisa, Kellene Orton, Sean West, Andy Young, Alex Rein, Tyler Cary
  - Calvin Mukarakate, Scott Palmer, Carson Pierce, Rick French, Guy Winters, Cody Wrasman
  - Earl Christensen, Jon Luecke, Lisa Fouts, Cheyenne Paeper, Nick Katsiotis
  - Stephen Tifft, Nolan Wilson
  - Mike Griffin, Josh Schaidle
- Johnson Matthey Technology Center
  - Luke Tuxworth
  - Mike Watson

Thank you very much!

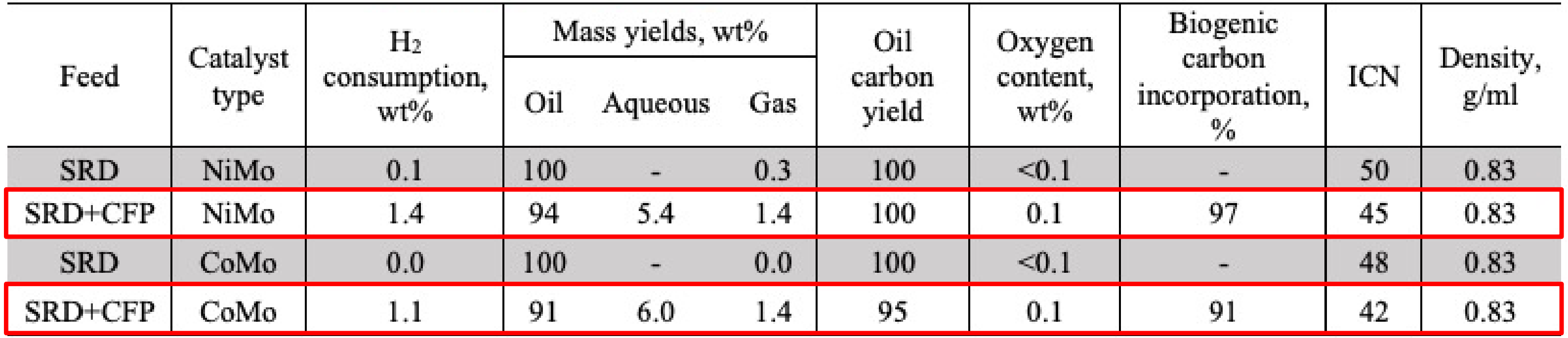
www.nrel.gov

NREL/PR-5100-85590

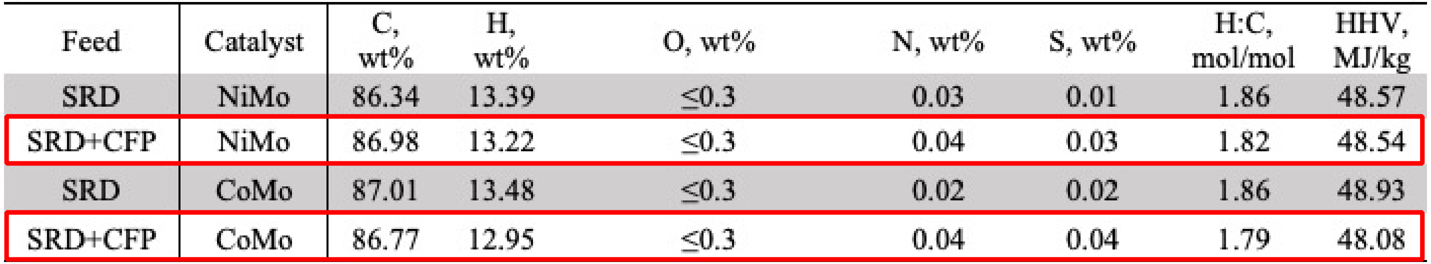
This work was authored by the National Renewable Energy Laboratory, operated by Alliance for Sustainable Energy, LLC, for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. Funding provided by the U.S. Department of Energy Office of Energy Efficiency and Renewable Energy Bioenergy Technologies Office. The views expressed in the article do not necessarily represent the views of the DOE or the U.S. Government. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes.

NREL
Transforming ENERGY

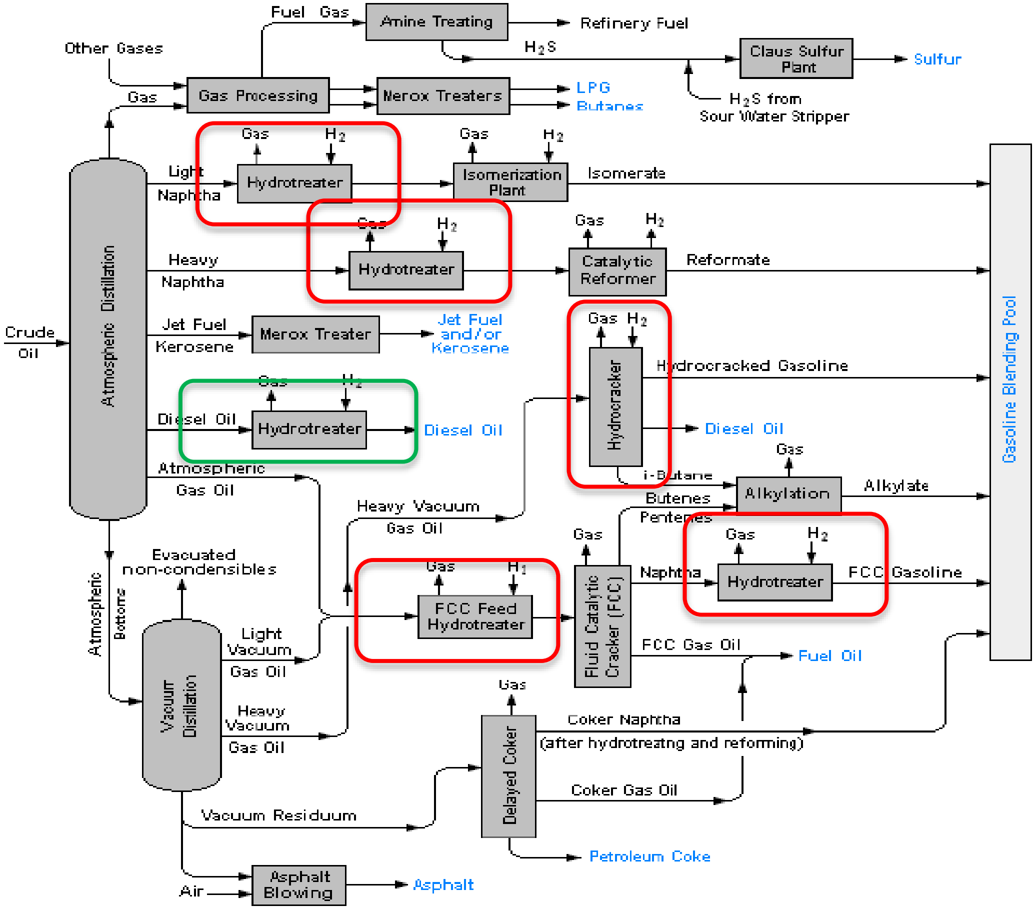
Supplement



Feed	Catalyst type	H_2 consumption, wt%	Mass yields, wt%			Oil carbon yield	Oxygen content, wt%	Biogenic carbon incorporation, %	ICN	Density, g/ml
			Oil	Aqueous	Gas					
SRD	NiMo	0.1	100	-	0.3	100	<0.1	-	50	0.83
SRD+CFP	NiMo	1.4	94	5.4	1.4	100	0.1	97	45	0.83
SRD	CoMo	0.0	100	-	0.0	100	<0.1	-	48	0.83
SRD+CFP	CoMo	1.1	91	6.0	1.4	95	0.1	91	42	0.83



Feed	Catalyst	C, wt%	H, wt%	O, wt%	N, wt%	S, wt%	H:C, mol/mol	HHV, MJ/kg
SRD	NiMo	86.34	13.39	$\leq$0.3	0.03	0.01	1.86	48.57
SRD+CFP	NiMo	86.98	13.22	$\leq$0.3	0.04	0.03	1.82	48.54
SRD	CoMo	87.01	13.48	$\leq$0.3	0.02	0.02	1.86	48.93
SRD+CFP	CoMo	86.77	12.95	$\leq$0.3	0.04	0.04	1.79	48.08



Fuel Gas
Amine Treating
Refinery Fuel
Other Gases
H_2S
Claus Sulfur Plant
Sulfur
Gas
Gas Processing
Merox Treaters
LPG
Butanes
H_2S from Sour Water Stripper
Gas
H_2
Gas
H_2
Light Naphtha
Hydrotreater
Isomerization Plant
Isomerate
Gas
H_2
Gas
H_2
Heavy Naphtha
Hydrotreater
Catalytic Reformer
Reformate
Crude Oil
Atmospheric Distillation
Jet Fuel Kerosene
Merox Treater
Jet Fuel and/or Kerosene
Gas
H_2
Hydrocracker
Hydrocracked Gasoline
Gasoline Blending Pool
Gas
H_2
Diesel Oil
Hydrotreater
Diesel Oil
Diesel Oil
Gas
Atmospheric Gas Oil
i-Butane
Alkylation
Alkylate
Heavy Vacuum Gas Oil
Butenes
Pentenes
Atmospheric Bottoms
Evacuated non-condensibles
Gas
Gas
H_2
Gas
H_1
Naphtha
Hydrotreater
FCC Gasoline
FCC Feed Hydrotreater
Fluid Catalytic Cracker (FCC)
Light Vacuum Gas Oil
FCC Gas Oil
Fuel Oil
Vacuum Distillation
Gas
Heavy Vacuum Gas Oil
Coker Naphtha
(after hydrotreatng and reforming)
Delayed Coker
Coker Gas Oil
Vacuum Residuum
Petroleum Coke
Asphalt Blowing
Air
Asphalt

CFP Catalyst

Zeolite (Ex-situ)

- Favors the formation of **aromatic hydrocarbons and phenols**
- Coke formation-**deactivate catalyst**
- Highest gasoline fraction due to the high aromatic content

Pt/TiO_2 (Ex-situ)

- Favor the formation of **phenols and cyclopentenone**
- Enables hydrogenation of coke precursors
- Requires co-fed H2
- High carbon efficiency

Red mud (In-situ)

- Low deoxygenation
- High carbon efficiency