Pyroliq 2019: Pyrolysis and Liquefaction of Biomass and Wastes

Proceedings

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Characterization of hydroprocessed fast pyrolysis oil fractions

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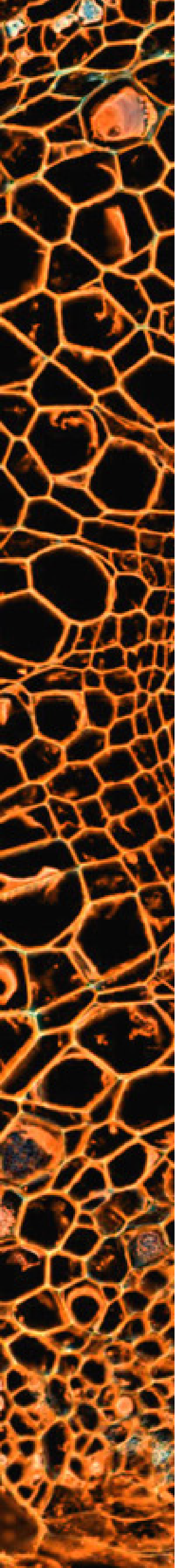
Asanga B. Padmaperuma



Characterization of Hydroprocessed Fast Pyrolysis Fractions

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Pacific Northwest National Laboratory

Pyroliq2019
Products characterization, Separation and Upgrading
June 19, 2019

PNNL is operated by Battelle for the U.S. Department of Energy

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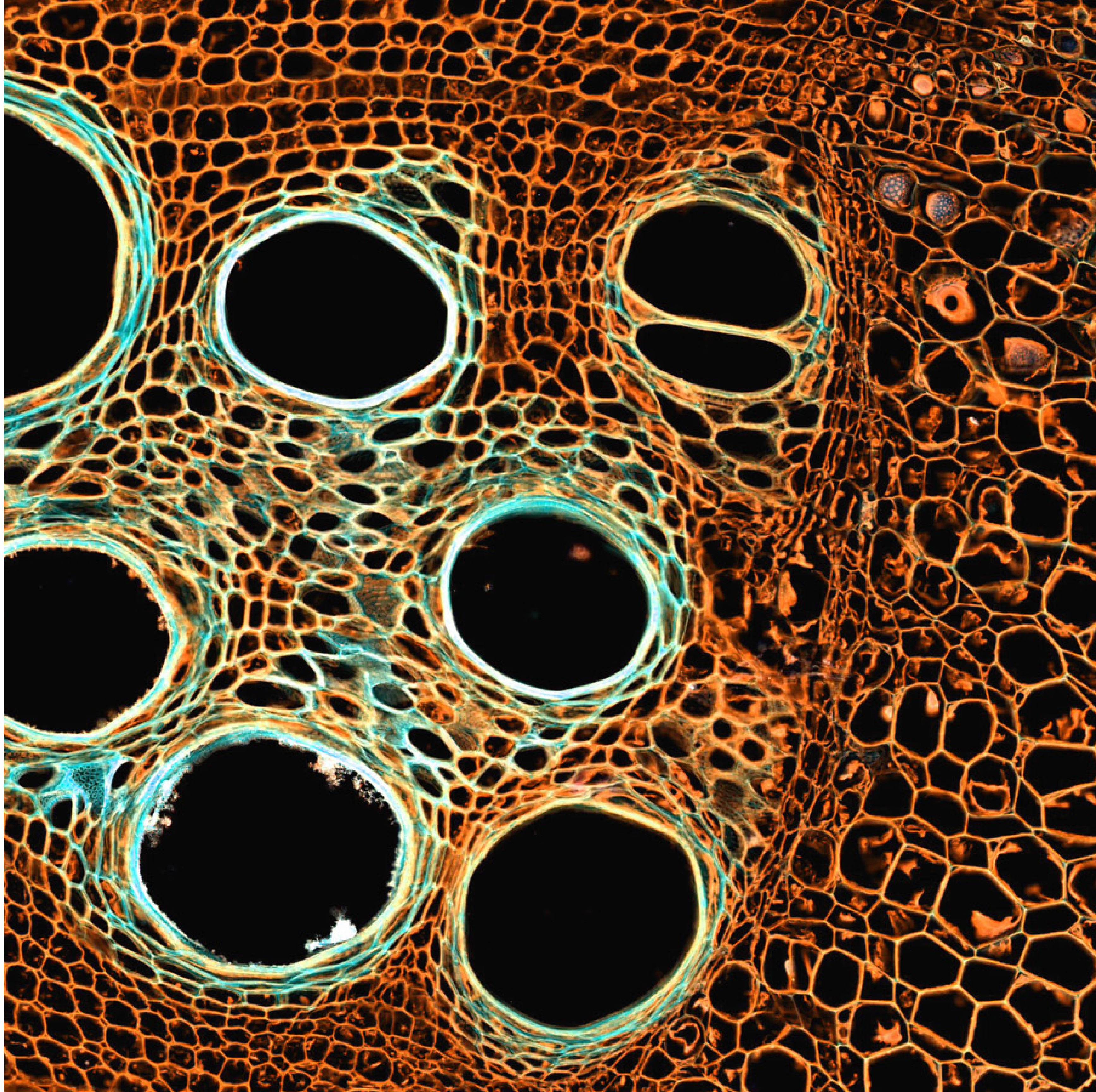
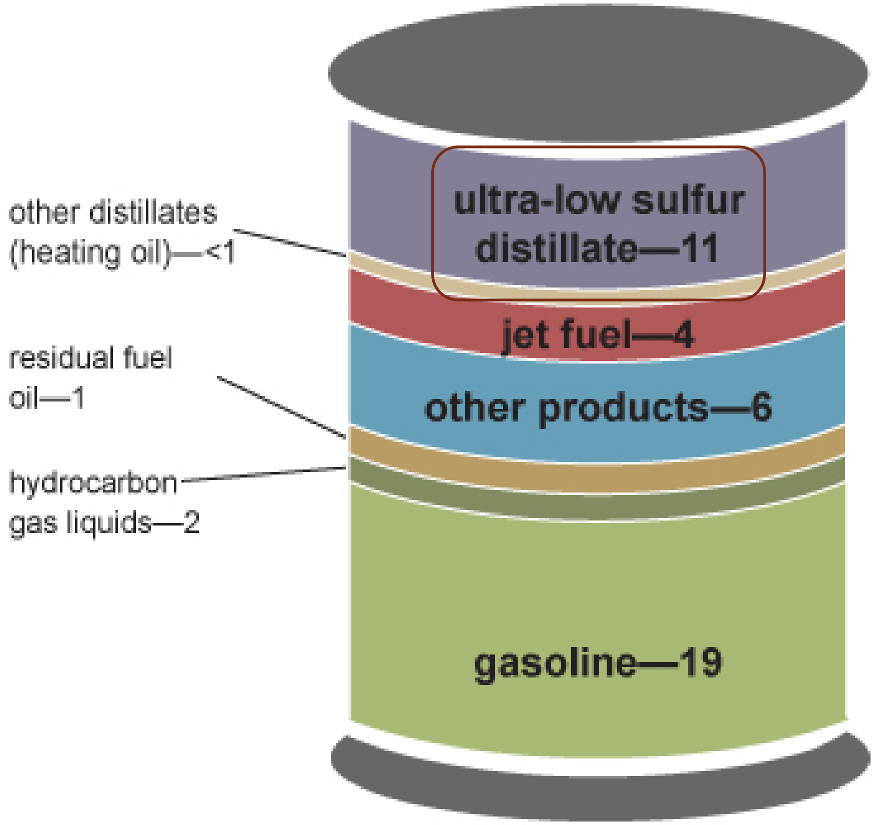


Future needs for transportation fuels change, e.g. due to electrification.

Petroleum products made from a barrel of crude oil, 2018
gallons

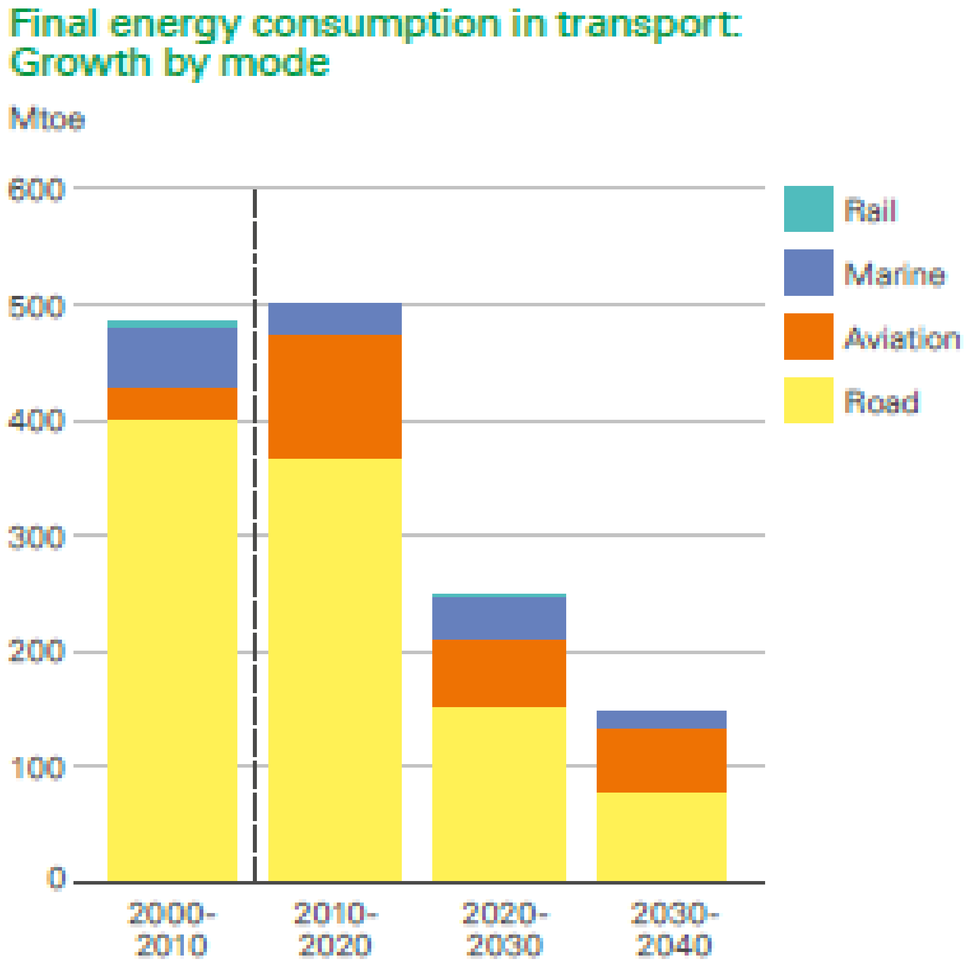


Note: A 42-gallon (U.S.) barrel of crude oil yields about 45 gallons of petroleum products because of refinery processing gain. The sum of the product amounts in the image may not equal 45 because of independent rounding.

Source: U.S. Energy Information Administration, *Petroleum Supply Monthly*, April 2019, preliminary data

Source: www.wikipedia.com

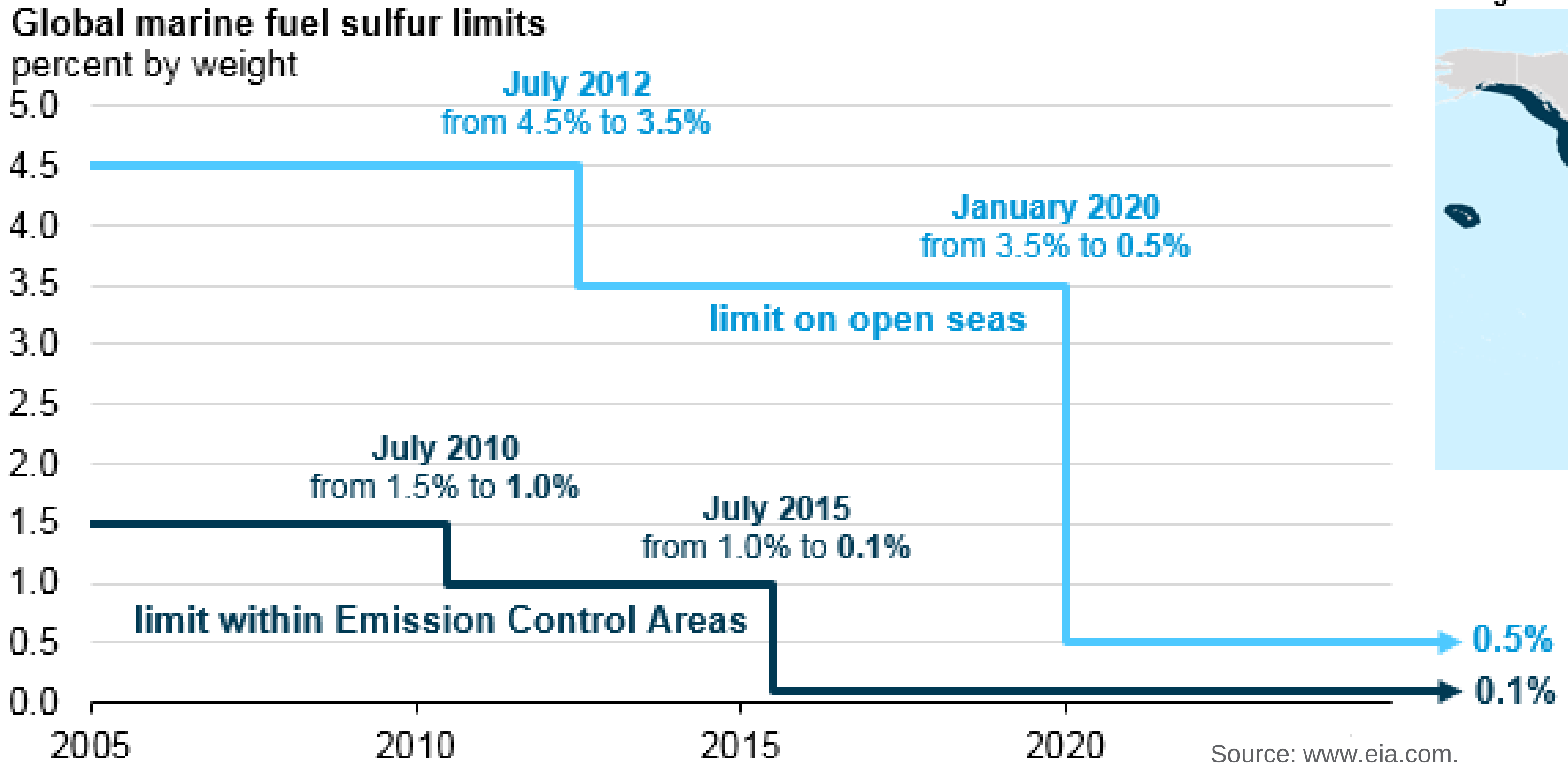
Road transportation may gain electrification improvements but heavy-duty road applications and aviation fuels will still require liquid fuels.



Source: BP Energy Outlook 2019.

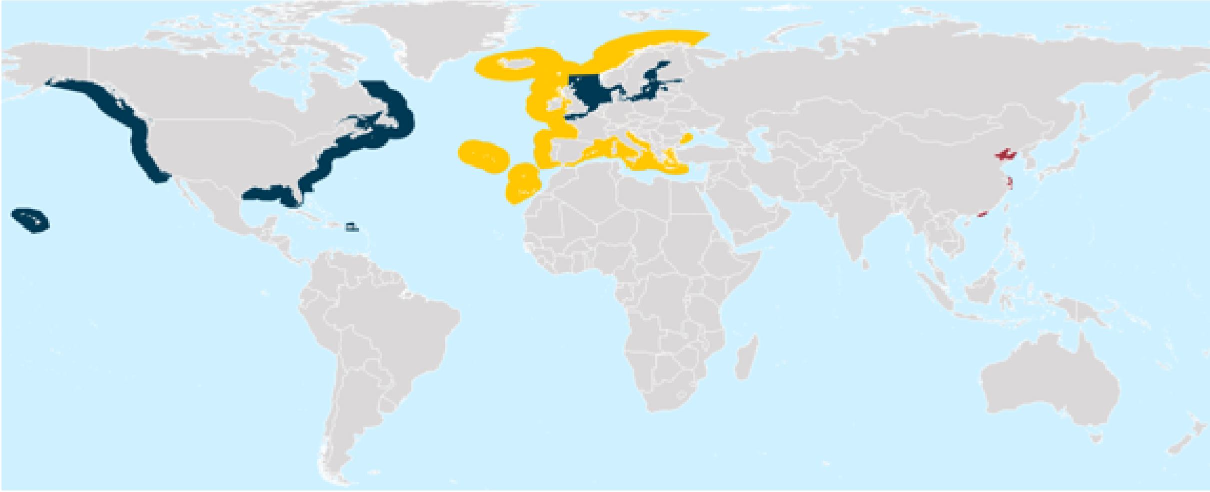
Percentage of aviation and marine fuels in the total expected market consumption becomes higher.

Policies for transportation fuels are also changing.



Source: www.eia.com.

Designated marine sulfur limitation areas

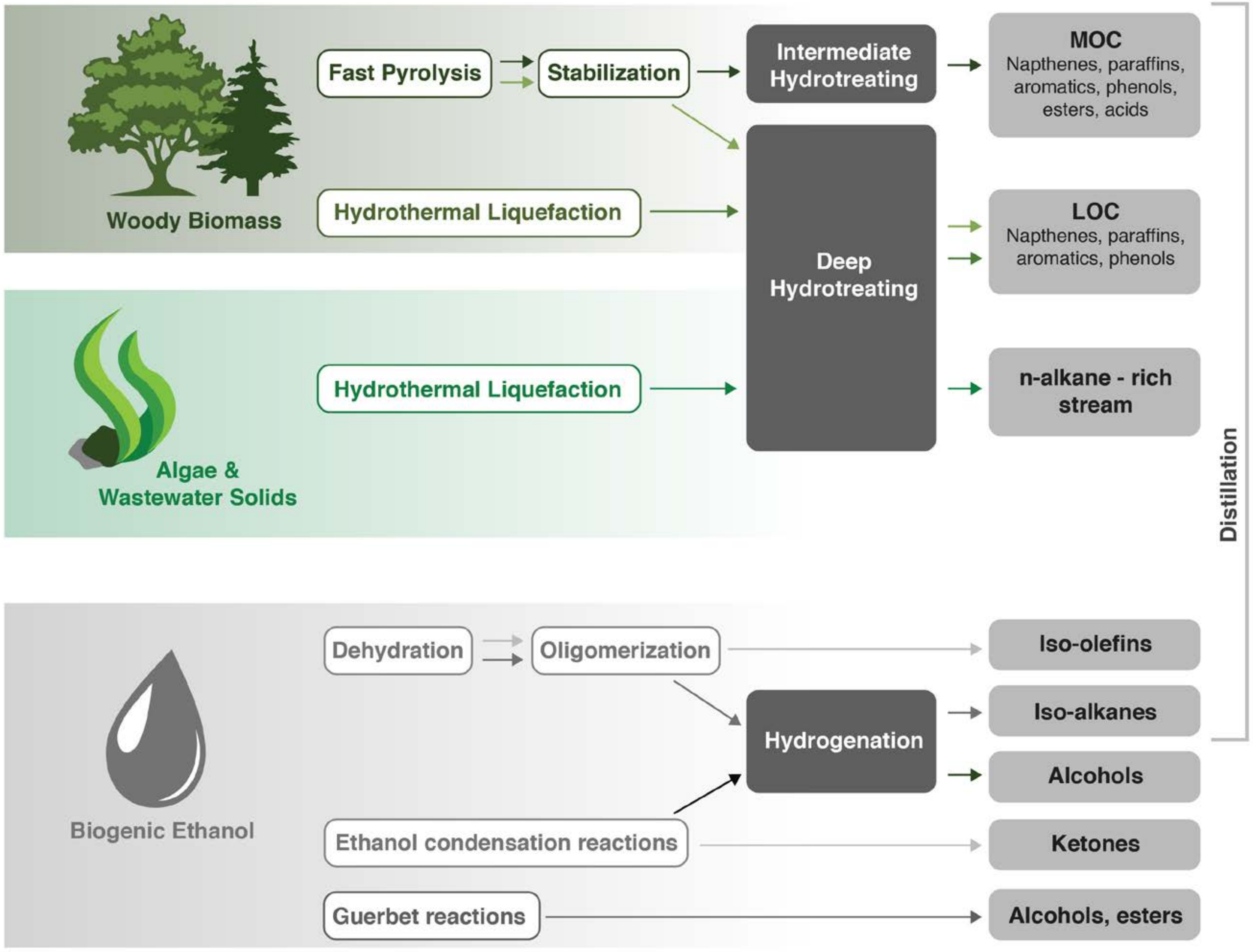


Implementation of new sulfur and ethanol policies will likely cause changes in fuel production and affect the supply chain.

Trump signs executive order on E15 at ethanol plant in Council Bluffs

By 6 News | Posted: Tue 2:34 PM, Jun 11, 2019 | Updated: Tue 7:54 PM, Jun 11, 2019

Biomass is still considered as a renewable source of transportation fuels.



- Biomass captures CO_2 from the atmosphere.
- Woody biomass can have lower sulfur content than some crude oil sources.
- Several routes are available for biomass conversion:
  - *Fast pyrolysis
  - *Catalytic Fast Pyrolysis
  - *Hydrothermal Liquefaction
  - Gasification → FT hydrocarbons, ethanol

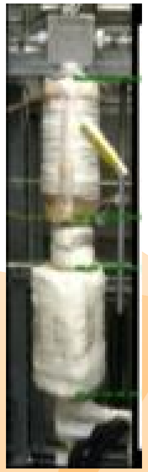
* Still require catalytic upgrading

Olarte, et al. (2019). Fuel. 238, 493-506.

Flow reactors at PNNL for catalytic hydroprocessing.

Nominal temperature: Up to 450C
Nominal pressure: Up to 2000psi

8 x 1.4ml beds



40ml bed (3 systems)

400/800ml bed

1 liter fixed and moving bed

20 liter bed + distillation

Catalyst Discovery

Process Development

Product Accrual

PNNL-SA-133096

The advantage of woody biomass is its low sulfur and yet a report showed otherwise.

Energy & Fuels ARTICLE

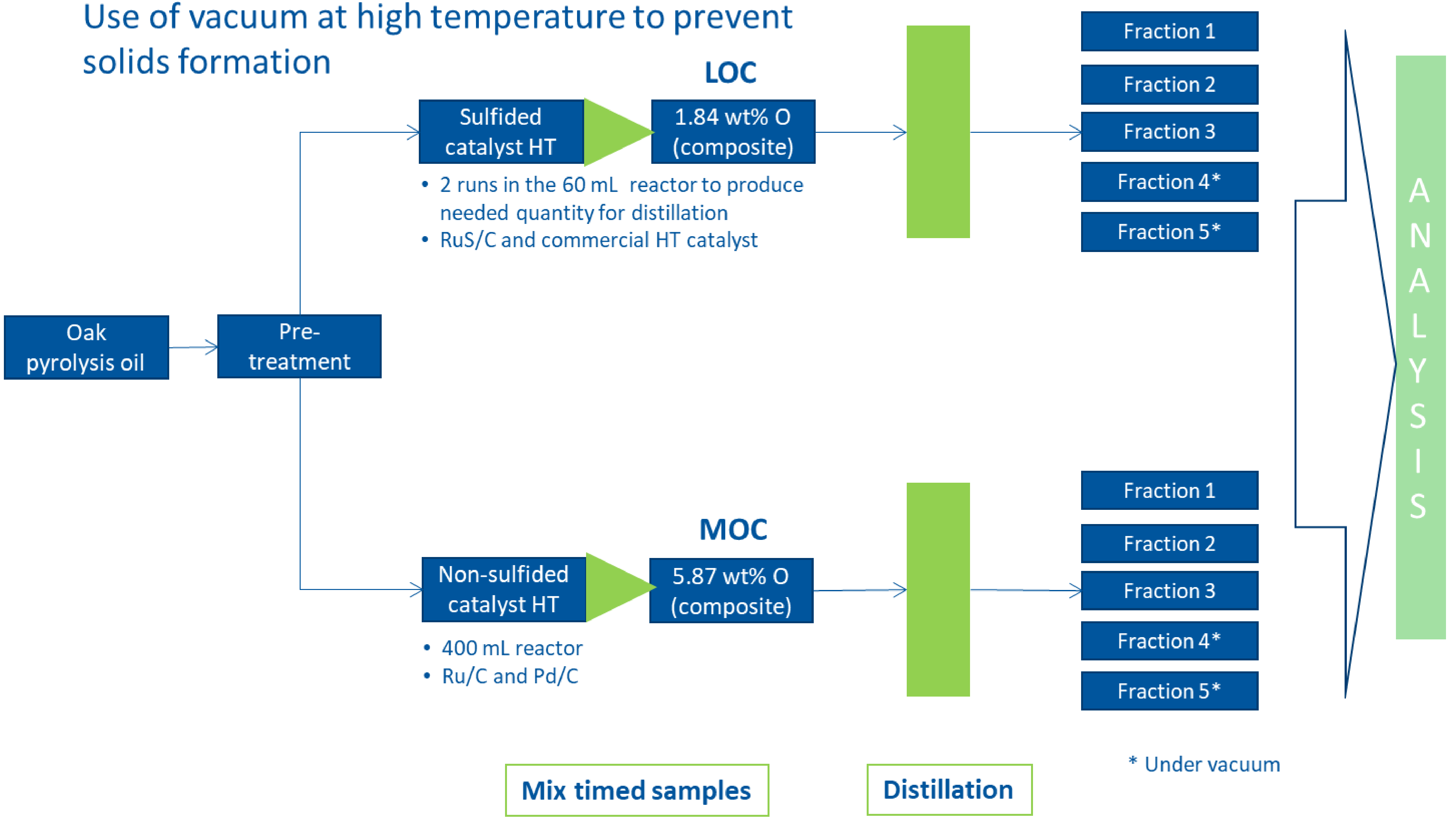
Table 1. Elemental Analysis Results

oil samp.	frac.	distillate frac., % w/w	C, % w/w	H, % w/w	N, % w/w	S, ppm	O, % w/w	H/C	O/C
HOC	lights	5.3	72.8	11.9	0.01	25	14.2	1.96	0.146
	naphtha	19.7	73.7	11.5	0.01	19	14.4	1.88	0.147
	jet	18.7	77.8	11.0	0.03	23	11.9	1.69	0.114
	diesel	17.2	82.4	10.7	0.09	101	7.5	1.56	0.068
	gas oil	30.3	84.6	10.4	0.14	354	5.3	1.47	0.003
MOC	lights	4.6	85.6	13.6	0.02	8	0.5	1.91	0.005
	naphtha	17.7	84.5	11.9	0.05	8	3.9	1.68	0.035
	jet	23.1	83.9	10.1	0.14	12	6.6	1.44	0.059
	diesel	18.3	85.7	10.2	0.32	21	4.4	1.43	0.039
	gas oil	32.6	87.8	9.9	0.40	116	2.5	1.35	0.022
LOC	lights	13.9	85.9	14.6	0.01	2	0.3	2.04	0.003
	naphtha	30.2	86.3	13.3	0.02	2	0.3	1.85	0.003
	jet	22.0	87.0	12.3	0.02	12	0.7	1.70	0.006
	diesel	20.6	88.4	11.4	0.02	310	0.5	1.55	0.004
	gas oil	13.5	88.6	11.5	0.03	243	0.4	1.55	0.003

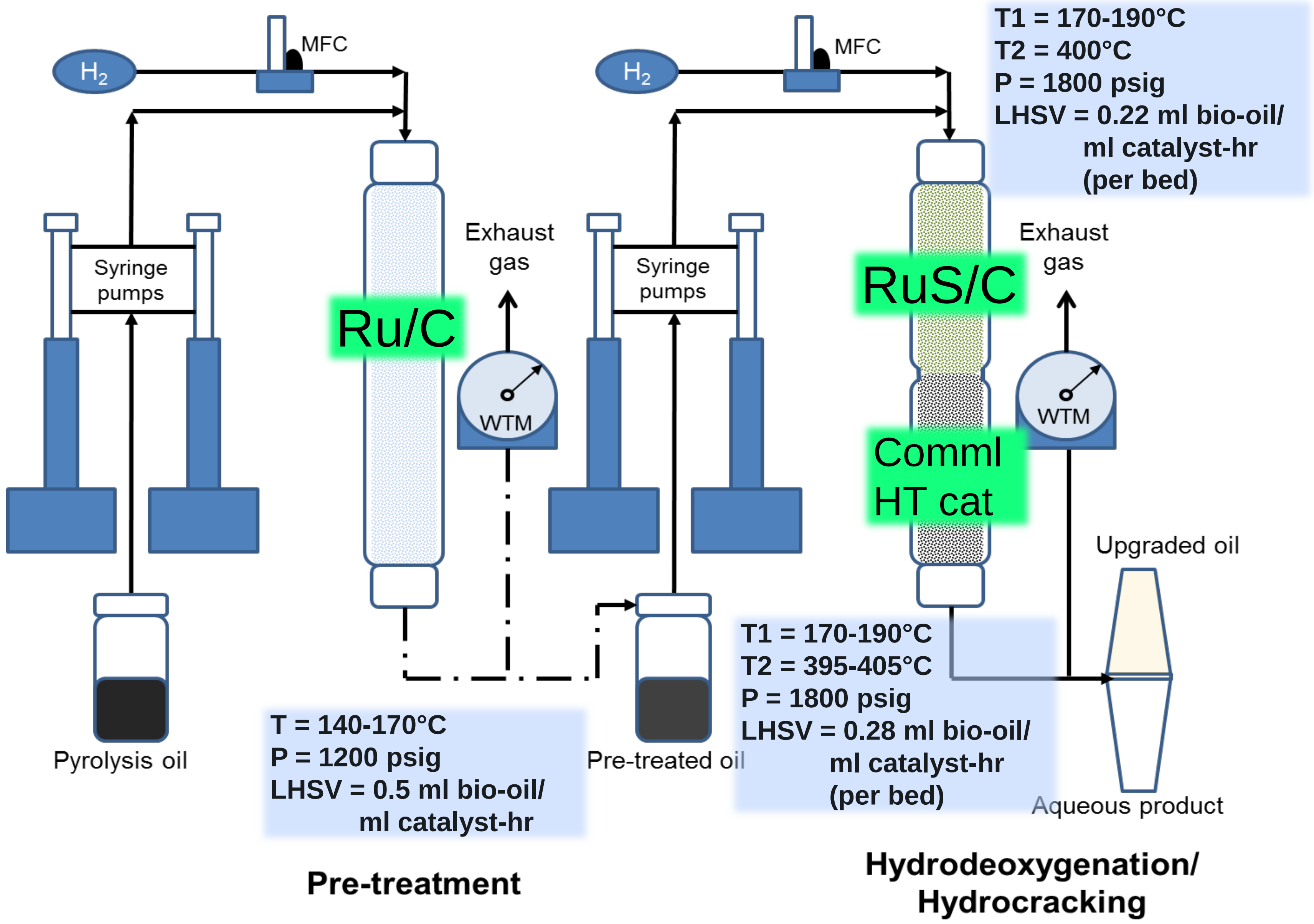
Christensen, et al. (2011). Energy and Fuels. 25, 5462-5471.

Strategy: Single type of fast pyrolysis oil, two target oxygen levels by adjusting catalysts

Use of vacuum at high temperature to prevent solids formation

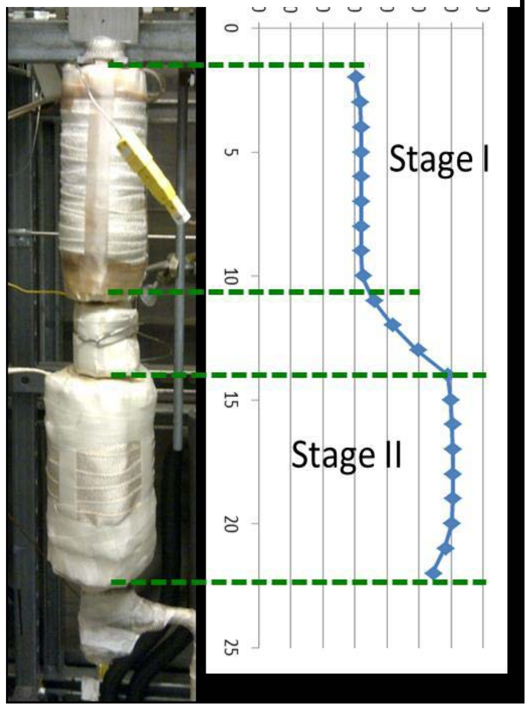


Hydroprocessing: LOC Production



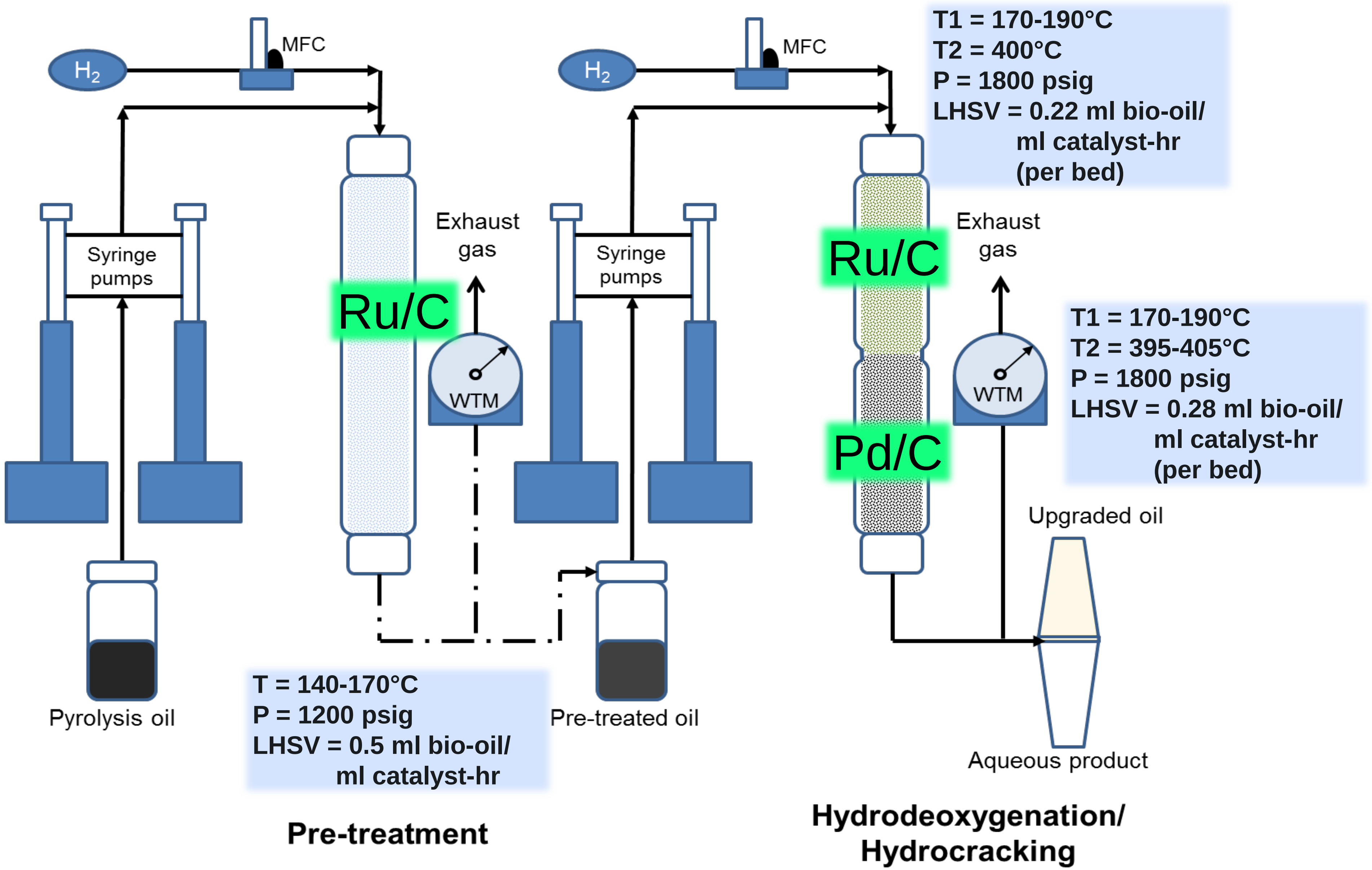
400 dual T zone packed bed reactors

30/60 ml dual T zone packed bed reactor



Olarte, et. al. (2017). Fuel, 202, 620-630.

Hydroprocessing: MOC production



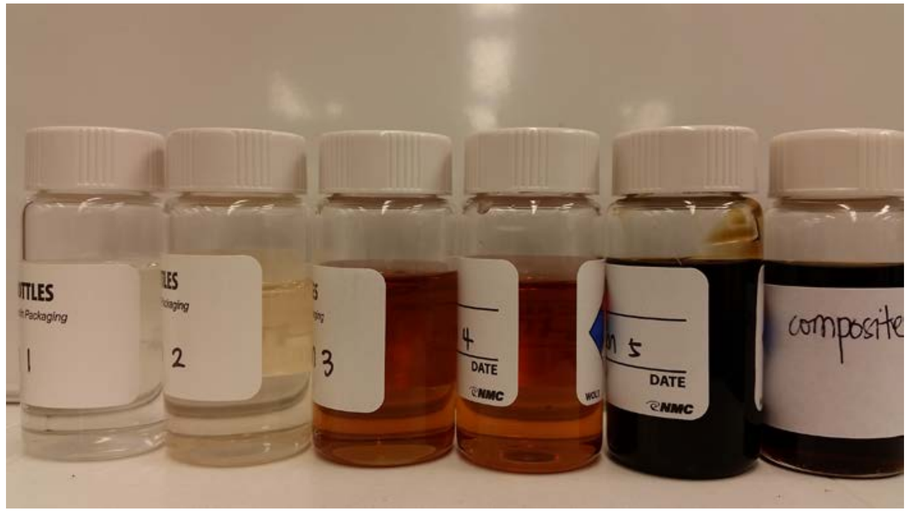
400 ml dual T zone packed bed reactors

Olarte, et. al. (2017). Fuel, 202 (3), 620-630.

Distillation cut-off points for LOC and MOC upgraded fractions.

Typical gasoline range

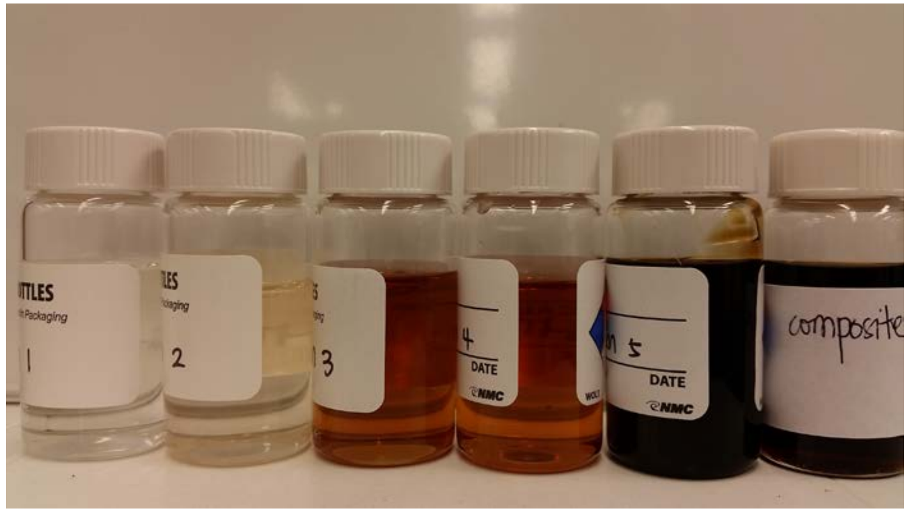
Fraction 1	20°C-150°C, atmospheric
Fraction 2	150°C-184°C, atmospheric



Distillation cut-off points for LOC and MOC upgraded fractions.

Typical jet fuel range

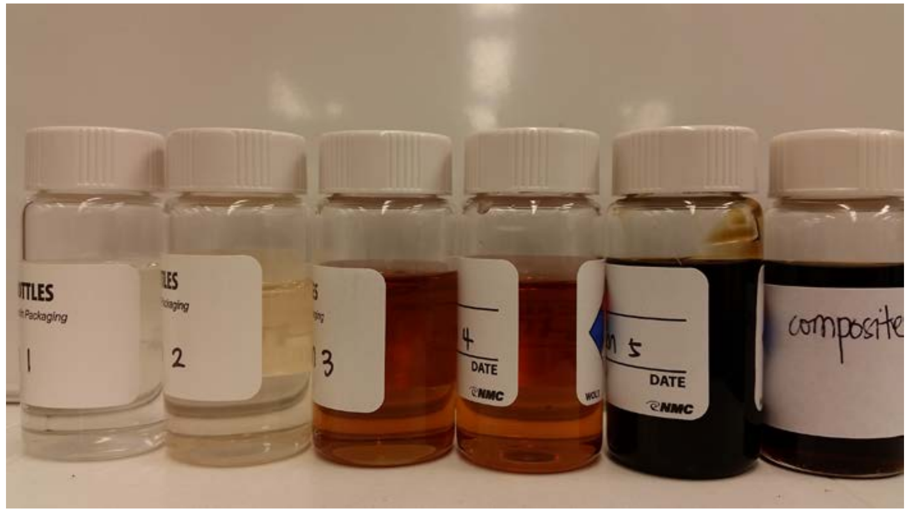
Fraction 2	150°C-184°C, atmospheric
Fraction 3	184°C-250°C, atmospheric



Distillation cut-off points for LOC and MOC upgraded fractions.

Typical diesel fuel range

Fraction 3	184°C-250°C, atmospheric
Fraction 4	250°C-338°C (atm.), vacuum applied (107°C-198°C @ 6 mmHg)



List of characterizations:

- Elemental Analysis
- Density
- Viscosity
- ASTM D2887 – boiling point ranges
- ASTM D6890 – derived cetane
- PIONA analysis – (Paraffins, Isoparaffins, Olefins, Naphthenes, Aromatics) functional groups present in the sample
- Total Acid Number
- GC-MS
- S Distribution

Liquid Stream Properties

	Oak Pyrolysis oil	Pre-treated oil	LOC composite oil	MOC composite oil
Carbon (D5373/D5291), dry wt%	45.2	56.92	84.91	81.88
Hydrogen (D5373/D5291), dry wt%	7.09	6.72	13.26	12.25
Nitrogen (D5373/D5291), dry wt%	0.07	0.07	<0.05	<0.05
Oxygen (D5373 mod), dry wt%	47.7	36.34	1.84	5.87
Sulfur (D4239/D1552), ppm	<0.02	<0.02	<0.02	<0.03
O/C molar ratio	0.79	0.48	0.02	0.05
H/C molar ratio	1.88	1.42	1.87	1.80
Water content (KF, ASTM D6869), %	19.1	20.35	<0.3	0.6
Total acid number (TAN, ASTM D3339), mg KOH/g oil	106.9	109.7	<0.01	39.29
Density, g/cc	1.24 (40°C)	1.23 (40°C)	0.83 (20°C)	0.87 (20°C)
Viscosity, mm^2/s	113.71(40°C)	160.77(40°C)	1.82 (20°C)	2.67 (20°C)

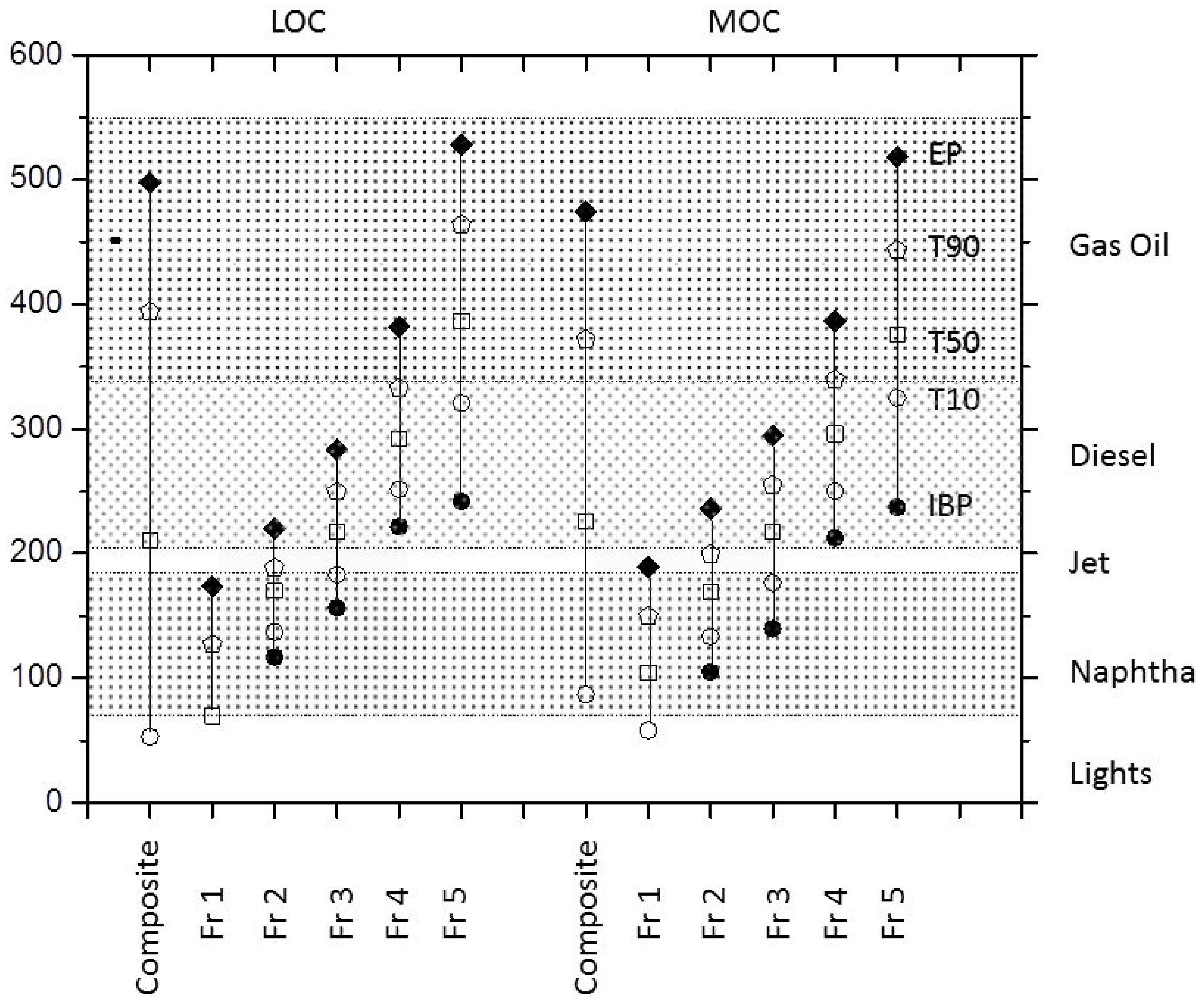
Olarte, et. al. (2017). Fuel, 202 (3), 620-630.

Batch distillation closely approximates simulated distillation data (ASTM D2887)

		LOC Weight percent, %		MOC Weight percent, %	
BP Range (°C)	Frxn #	SimDist	Batch Distillation	SimDist	Batch Distillation
0-150	1	34%	29%	28%	32%
150-184	2	9%	12%	11%	10%
184-250	3	16%	16%	18%	19%
250-338	4	20%	19%	27%	24%
>338	5	20%	22%	16%	15%

Olarte, et. al. (2017). Fuel, 202 (3), 620-630.

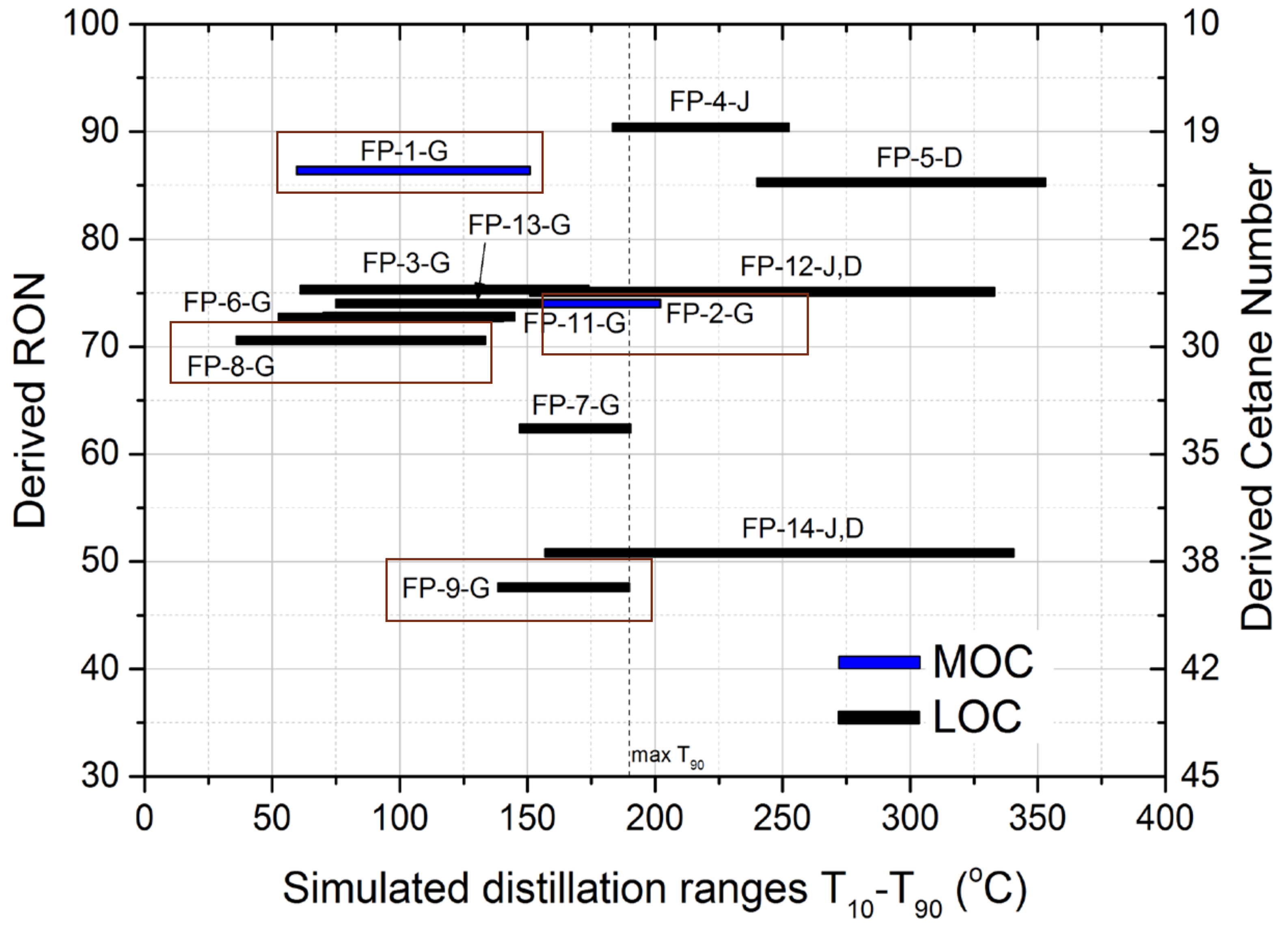
T_{10}-T_{90} ranges show boiling range quality of the cuts.



Olarte, et. al. (2017). Fuel, 202 (3), 620-630.

- **SimDist of fractions**
  - MOC fraction 1 falls within BP requirements for gasoline – however, other considerations exist
  - LOC and MOC Fraction 3 falls within jet BP range
  - MOC Fraction 4 falls within diesel BP range

Satisfying the distillation range does not necessarily guarantee good ignition properties.



Olarte, et al. (2019). Fuel. 238, 493-506.

- Key:
  - FP-1-G – MOC 1
  - FP-2-G – MOC 2
  - FP-8-G – LOC 1
  - FP-9-G – LOC 2
- Derived RON – derived Research Octane Number
  - Calculated measure based on derived cetane number (ASTM D6890)
  - For small amount of samples
- RON – measure of fuel behavior during combustion
  - Official ASTM sample size requires liter levels

Modified PIONA Analysis (GC method)

	LOC fraction 1 (vol %)	LOC fraction 2 (vol %)	MOC fraction 1 (vol %)
Paraffin	44.4	21.0	12.9
I-Paraffins	14.0	14.8	12.7
Aromatics	2.8	19.6	2.1
Naphthenes	36.7	30.6	43.9
Olefins	1.6	4.8	1.9
Unidentified	0.5	9.2	14.6
Benzene	0.5	0.0	0.1
RON*	65	38	78
MON*	60	41	59

* by GC correlation

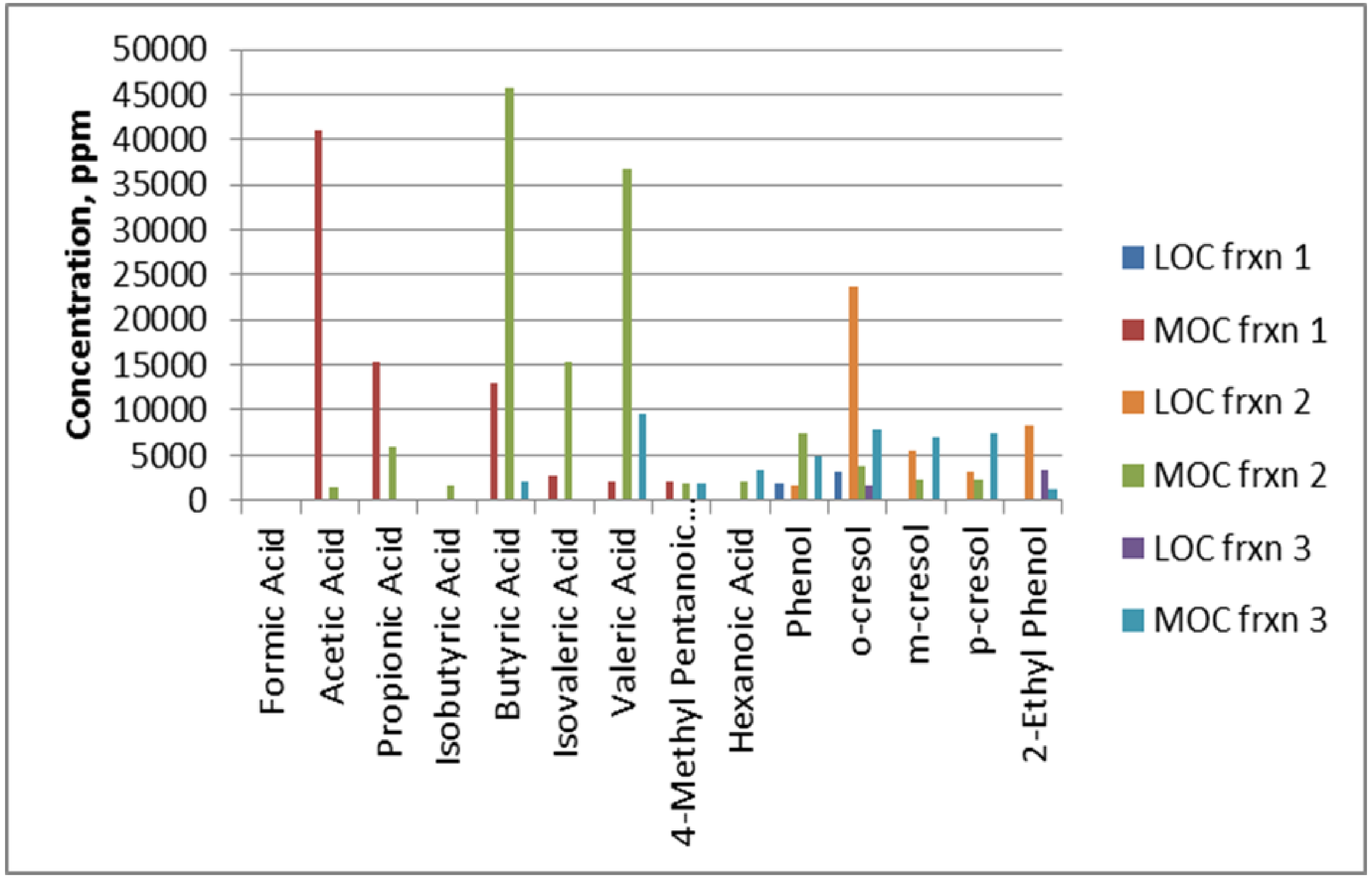
Olarte, et. al. (2017). Fuel, 202 (3), 620-630.

Total Acid Number (TAN) of MOC fractions can be quite high.

	TAN (vol %)
LOC frxn 1	<0.01
LOC frxn 2	<0.01
LOC frxn 3	<0.01
LOC frxn 4	<0.01
LOC frxn 5	<0.01
MOC frxn 1	55.31
MOC frxn 2	116.62
MOC frxn 3	39.44
MOC frxn 4	4.77
MOC frxn 5	0.3

Olarte, et. al. (2017). Fuel, 202 (3), 620-630.

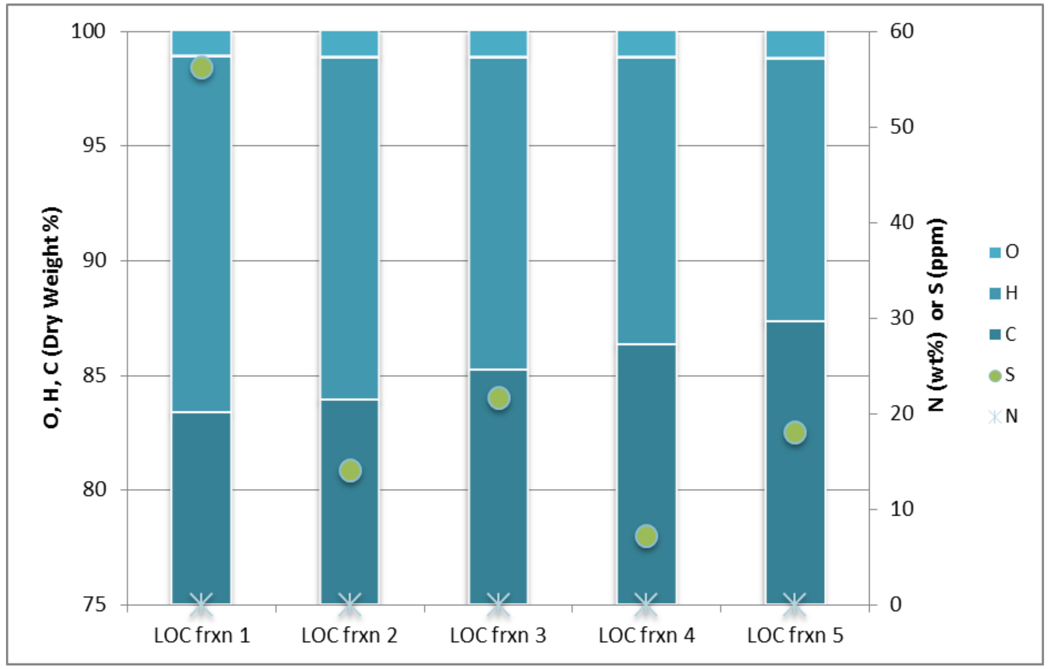
MOC has more acids and phenols

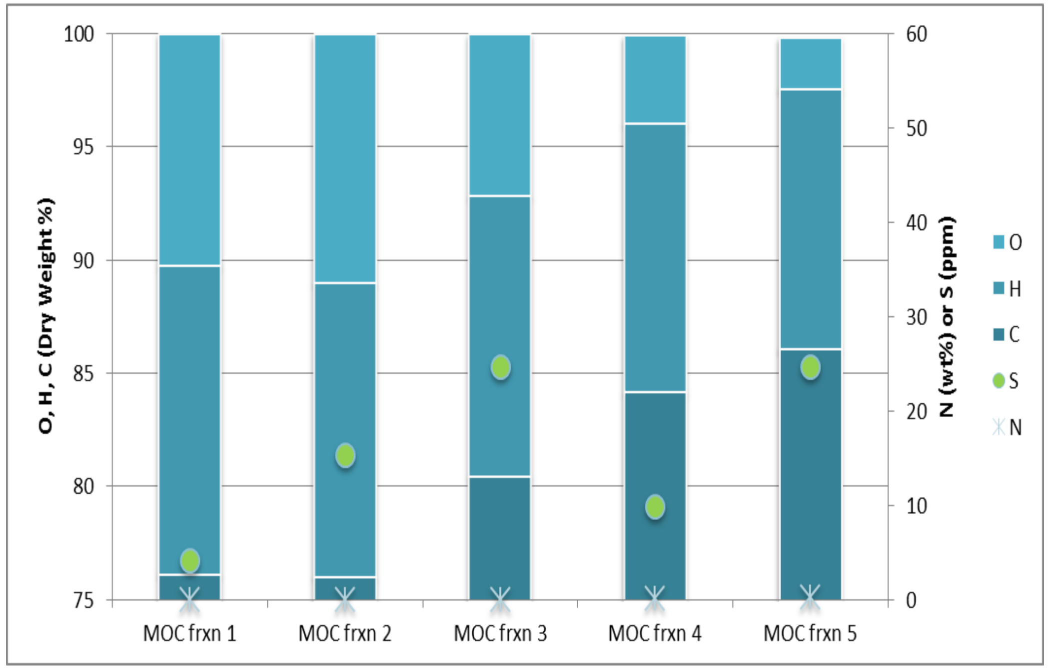


- Only found in fractions 1 to 3
- LOC has phenols
- MOC has acids and phenols
- Acid: valeric acids (*n* + *iso*) > butyric acid > acetic acid
- Phenol: o-cresol

Olarte, et. al. (2017). Fuel, 202 (3), 620-630.

Elemental distribution has some similarities…

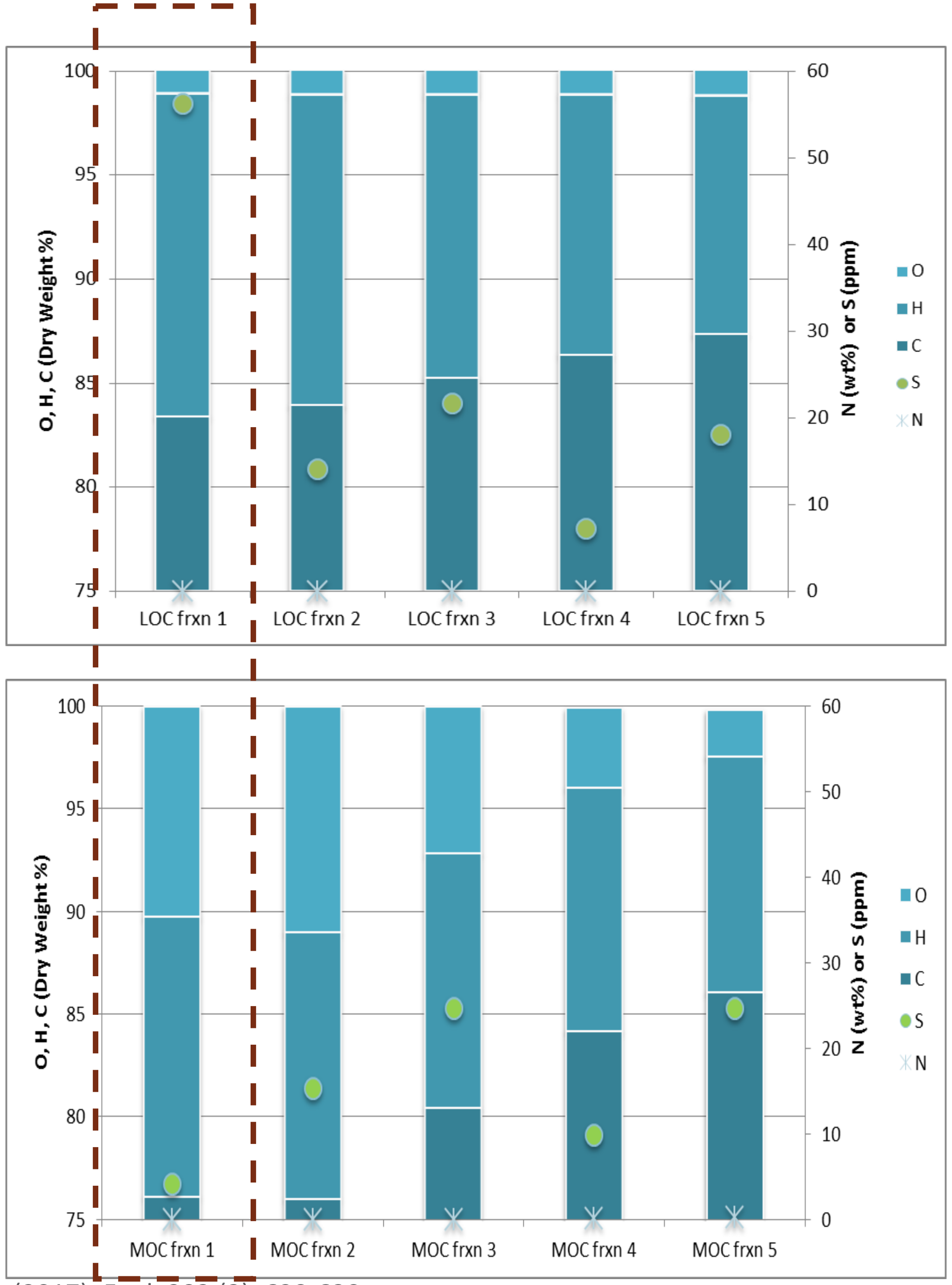




- **As the fraction becomes heavier:**
  - ↑ C, ↓ H as ↑ BP of fraction
  - ↓ H/C – more unsaturation ~ aromatics in ^{13}C NMR

Olarte, et. al. (2017). Fuel, 202 (3), 620-630.

… and differences…



Olarte, et. al. (2017). Fuel, 202 (3), 620-630.

- **For LOC:**
  - Almost same O content in all fractions
  - Highest S in Fraction 1 – due to sulfided catalyst
  - Negligible N
- **For MOC:**
  - ↓ O content
  - Lowest S in Fraction 1
  - Highest N in heaviest fraction
    - Lower degree of HDN

MOC used non-sulfided catalysts. S in LOC and MOC frxn 2-4 are likely from feed.

Conclusions

- Presented a comprehensive analysis of distillates with two composite O content from a single source.
- Incomplete deoxygenation may reduce cost for hydrotreating requirements but will have consequences on the quality of the final product.
- Difference in S distribution was found to be only at the lightest fraction and likely due to the use of sulfided and non-sulfided catalysts
  - S present in fractions 2 to 4 for both oils suggest S derived from the feedstock.
  - May impact sulfur management
- Determining the effect of oxygenate and upgraded compounds from biomass on fuel blend qualities is important
  - Fractions may be within SimDist boiling point range but not have expected fuel properties

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Thank you for listening!