6-18-2019

Comparison among technical and milled wood lignins through principal component analysis of FTIR spectra

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Co-hydrotreatment of Bio-oil Lignin-rich Fraction and Vegetable Oil

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Two-Step Hydrotreatment

To ensure economic competitiveness, bio-oil price needs to be a fraction of molasses ($ 300-400/ton) and petroleum ($ 200-700/ton). Bio-oil production cost needs to be below **$ 150/t**.

In our analysis we used the recommendations made by Lange (2016)

Product cost ~ (feed Price + conversion cost) / yield

Feed Price: $ 150/ ton_{feed}

Conversion Cost: $ 200/ton_{feed}

Yield: 0.33 ton fuel/ton_{feed}

Product Cost: $ 1060/ton_{feed}

Gasoline market: $ 700-800/ton_{feed}

Lange JP. Catalysis for biorefineries – performance criteria for industrial operation. Catal. Sci. Technol. 2016, 6, 4759

Bio-oil composition

High oxygen content ⇨

High carbon content ⇨

=

Water (19-30 wt. %)

C_2-C_4 light molecules (10-22 wt. %)

Acetol (5-9 wt. %)

Hydroxyacetaldehyde (1-14 wt. %)

Acetic Acid (2-6 wt. %)

Formic Acid (Less 1 wt. %)

Anhydrosugars (10-20 wt. %)

Levoglucosan

Cellobiosan

Mono- phenols (1-5 wt. %) and mono-furans (around 1 wt. %)

Phenol (0.1 wt. %)

Guaiacol (0.2-0.5 wt. %)

Cresol (0.1-0.4 wt. %)

Syringol (0.4 wt. %)

Eugenol (0.1-0.2 wt. %)

Furfural (0.1-0.2 wt. %)

2(5H)-Furanone (0.2-0.8 wt. %)

Pyrolytic lignin (15-27 wt. %)

C=O 5 %

$OH_{phen.}$ 7.5 %

$OH_{aliph.}$ 2.5 %

diphenyl

COOH

stilbene

OMe

phenyl coumaran

alkyl-arylether

resinol

free radicals 4/1000 C_9

Humins (3-7 wt. %)

Hybrid oligomers (11-18 wt. %)

DHH backbone (Patil et al. 2012)

Furanic unit

Coniferyl unit

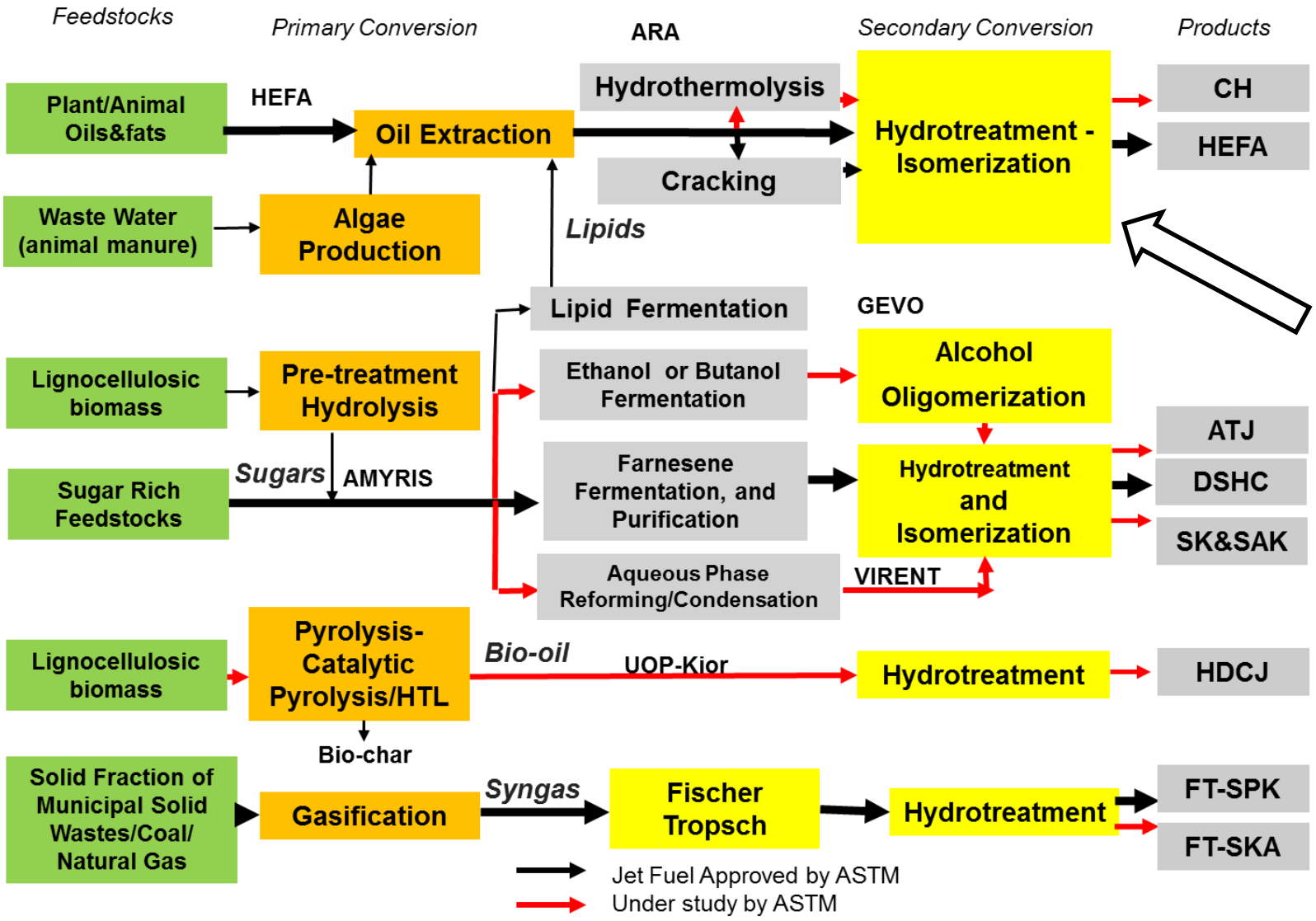
Carbonyl unit

Carbohydrate fraction

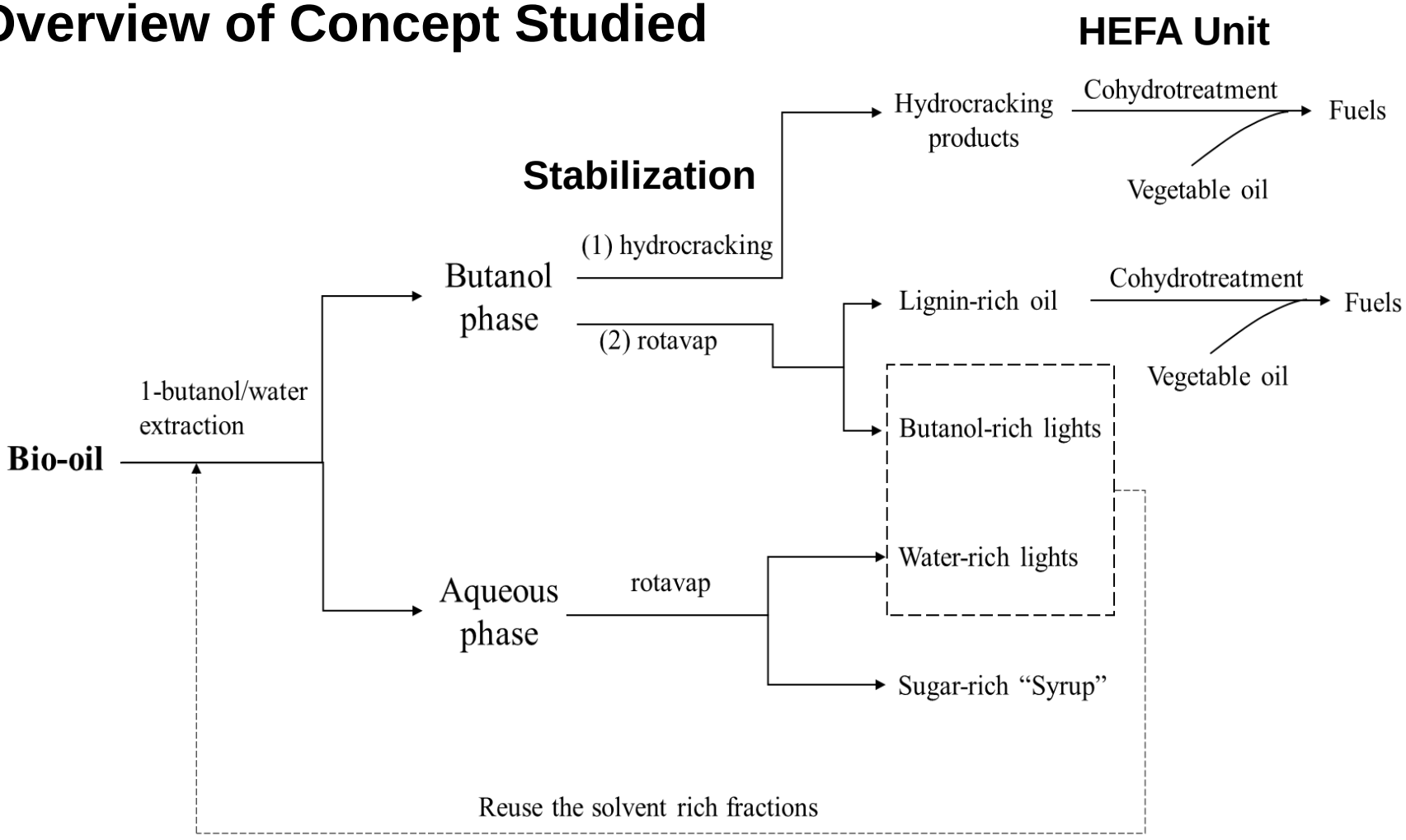
Carboxylic unit

Ester link aromatic to carbohydrate units (Fortin et al. 2015)

All biomass derived Jet Fuel Production Technologies end-up with a Hydro-deoxygenation step



Overview of Concept Studied



Can the cracking and stabilization step be avoided?

3. Experimental Scheme

Part 1: Bio-oil Fractionation

BTG oil (Netherland)

Liquid-liquid extraction → Lignin rich oil +lights → Rotavap → Lignin rich oil

LRO

Liquid-liquid extraction → Anhydrosugars + lights

Part 2: Cohydrotreatment of lignin rich oil (LRO) and Canola oil

LRO		Canola		LRO		Canola		1-BuOH
1	:	8		1	:	8	:	0.5
1	:	4		1	:	4	:	0.5
1	:	2	and	1	:	2	:	0.5
1	:	1		1	:	1	:	0.5

350˚C, 4h, 9.3MPa, 500rpm

$CoMo/Al_2O_3$ (C/F=1:50)

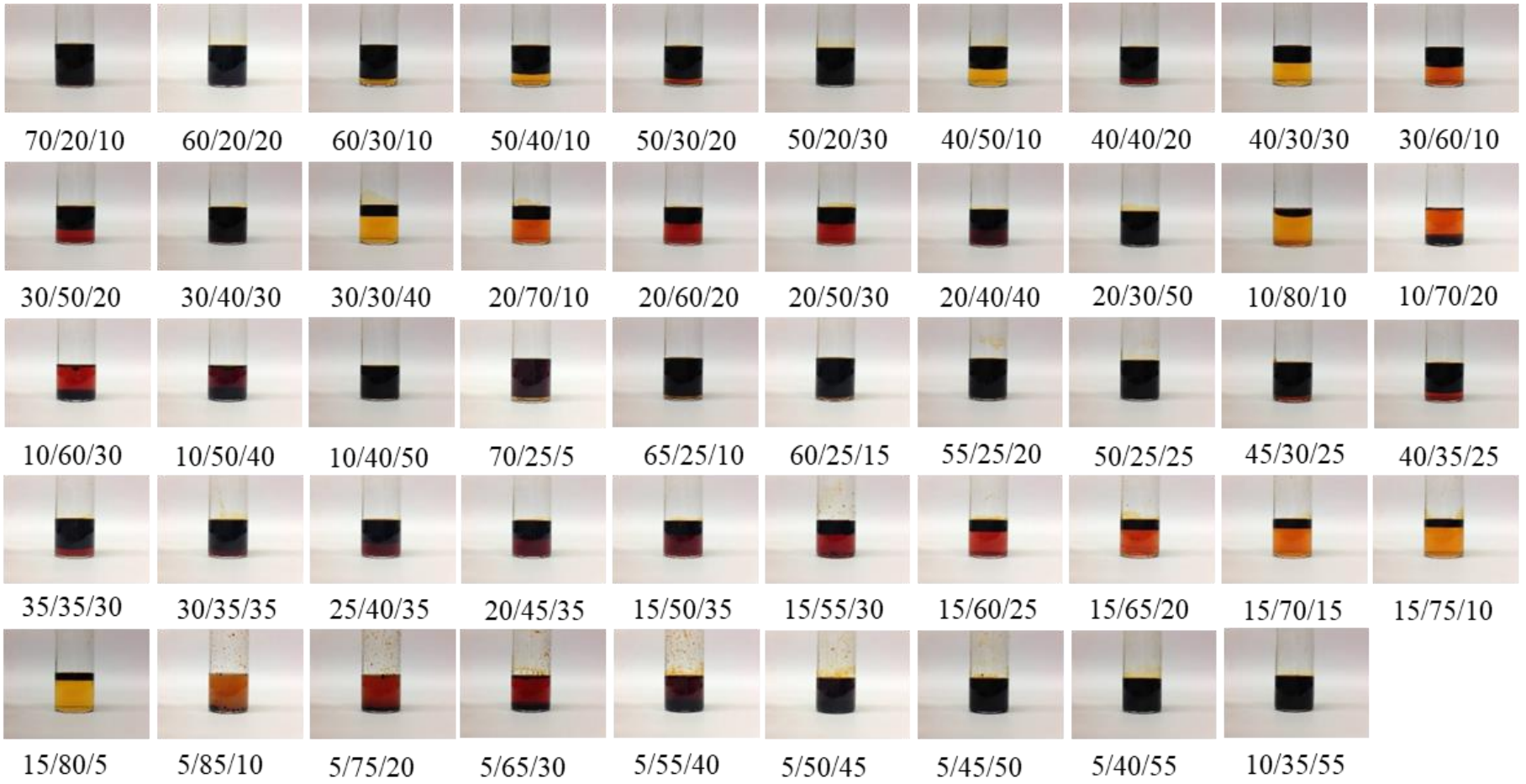
→ Hydrotreated oils → Distillation →

Naphtha
Kerosene
Diesel
Gas oil

*Each hydrotreatment was duplicated.

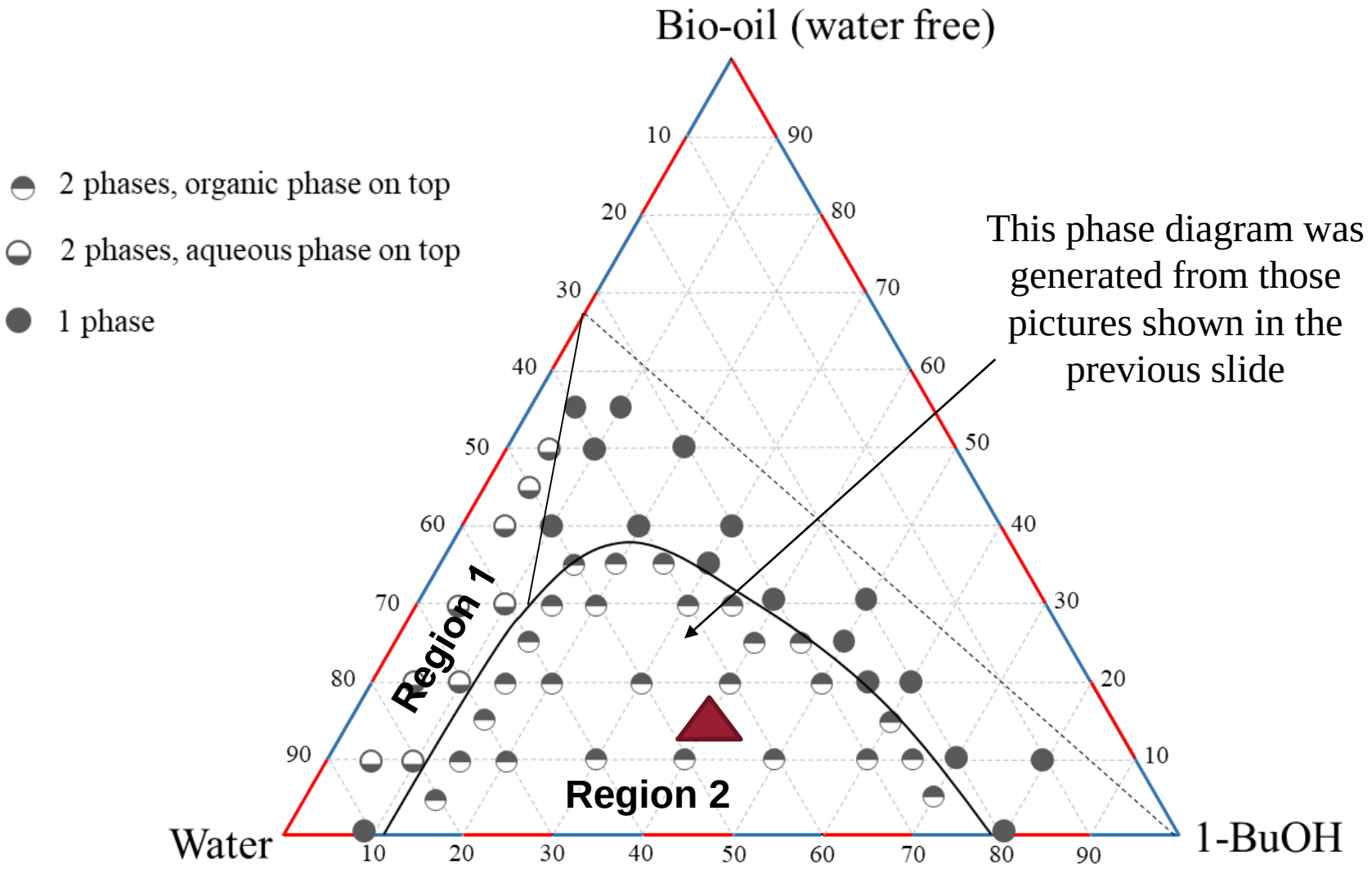
Bio-oil Pyrolytic Lignin Extraction

Butanol/Water/Bio-oil



Under each picture, the ratio of butanol/water/bio-oil is indicated, for example, Butanol/Water/Bio-oil: 70/20/10 for the first one on the top left.

Bio-oil Pyrolytic Lignin Extraction

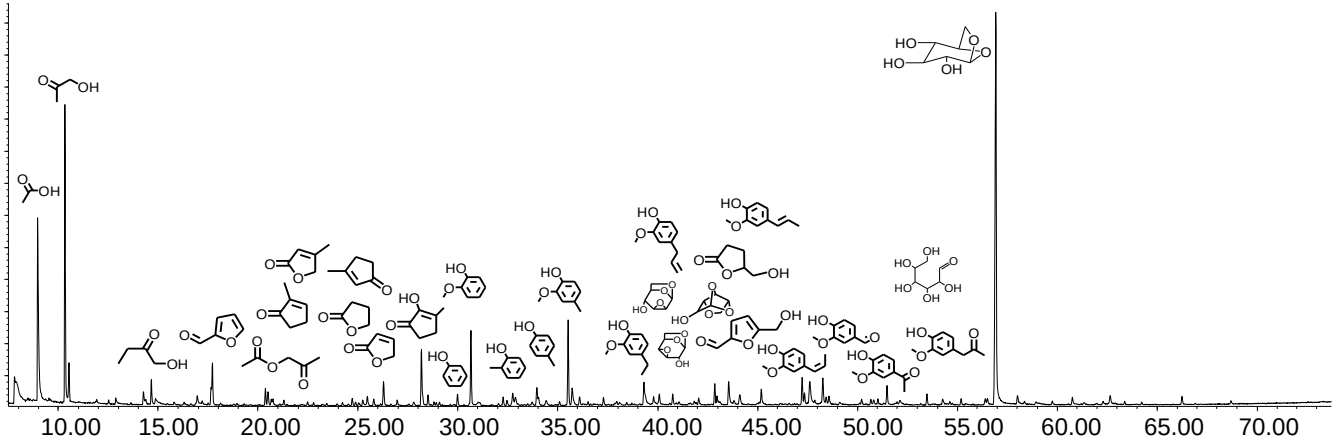


Water: 46.4 wt. %, BuOH: 40 wt. %, Bio-oil (water free): 13.8 wt. %

Bio-oil Pyrolytic Lignin Extraction

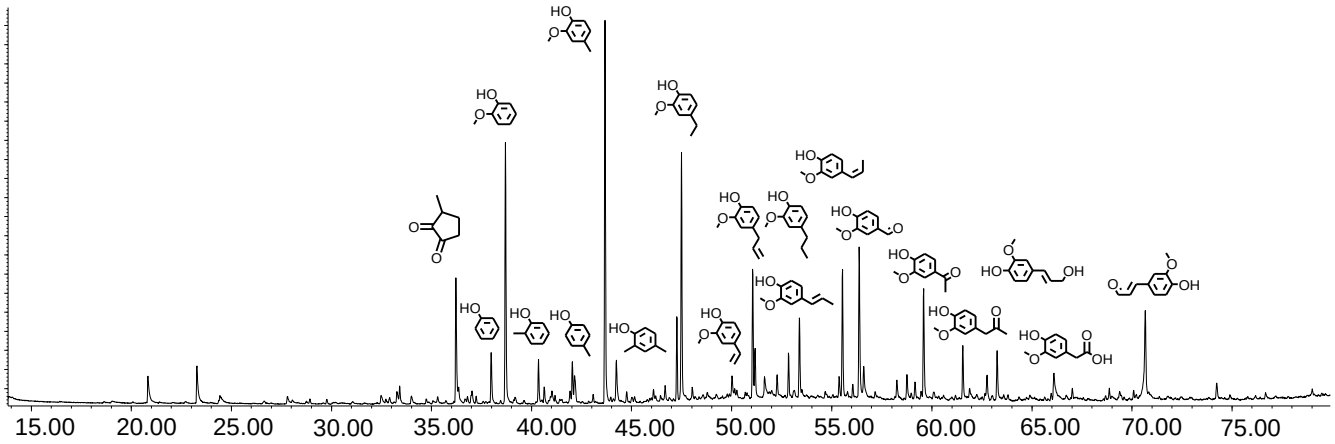
What is the difference between raw bio-oil and the lignin rich oil ?

BTG oil (raw):



Lignin-rich oil:

75 % Pyrolytic lignin + 20% phenolic (GC-detectable)



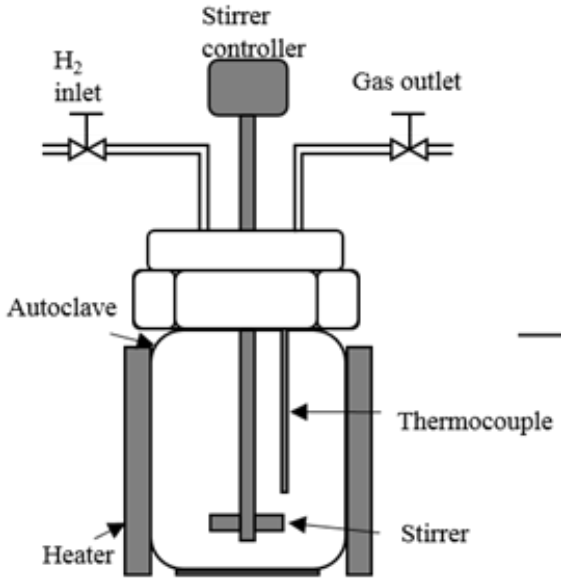
3. Experimental Scheme

No BuOH

LRO		Canola
1	:	8
1	:	4
1	:	2
1	:	1

With BuOH

LRO		Canola		1-BuOH
1	:	8	:	0.5
1	:	4	:	0.5
1	:	2	:	0.5
1	:	1	:	0.5



Batch reactor setup (Parr)

350˚C, 4h, 9.3MPa, 500rpm

$CoMo/Al_2O_3$ (C/F=1:50)

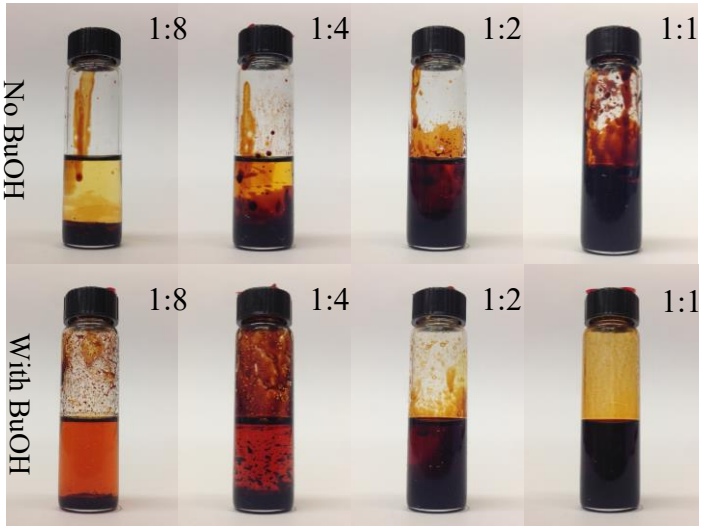
Hydrotreated oils

Distillation

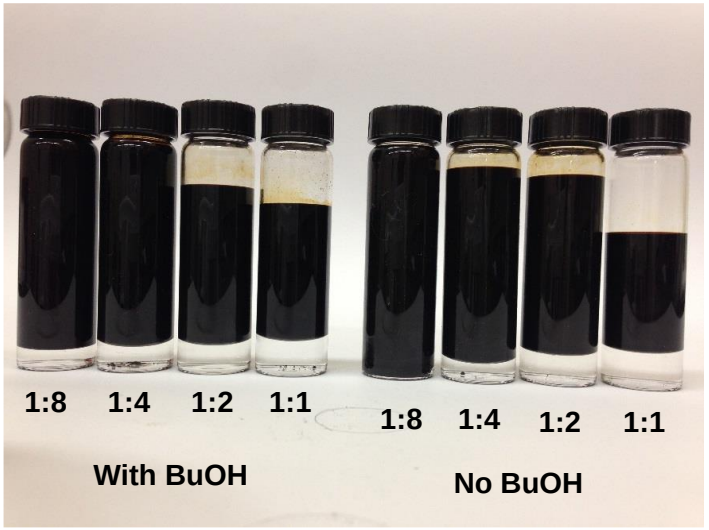
Naphtha
Kerosene
Diesel
Gas oil

The LRO/Canola blends with and without 1-butanol before and after hydrotreatement

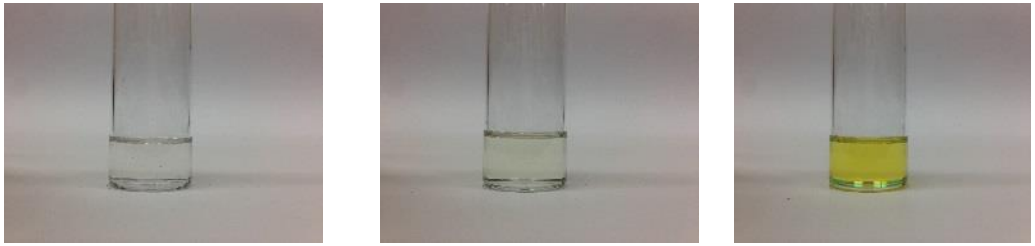
(a) Blends of LRO/Canola with and without 1-butanol



(b) The resulting liquid products from cohydrotreatment

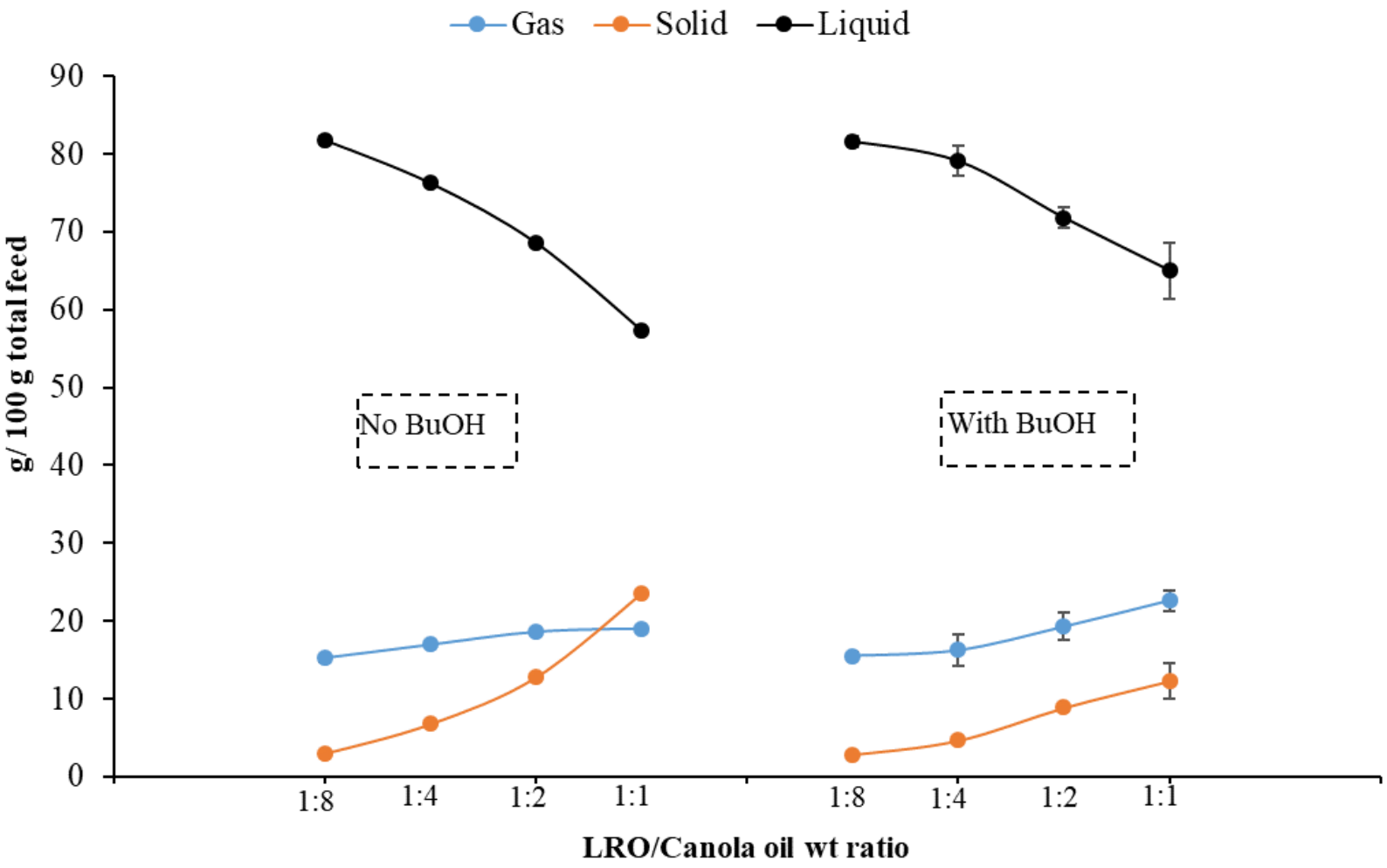


Focus here (top layer)

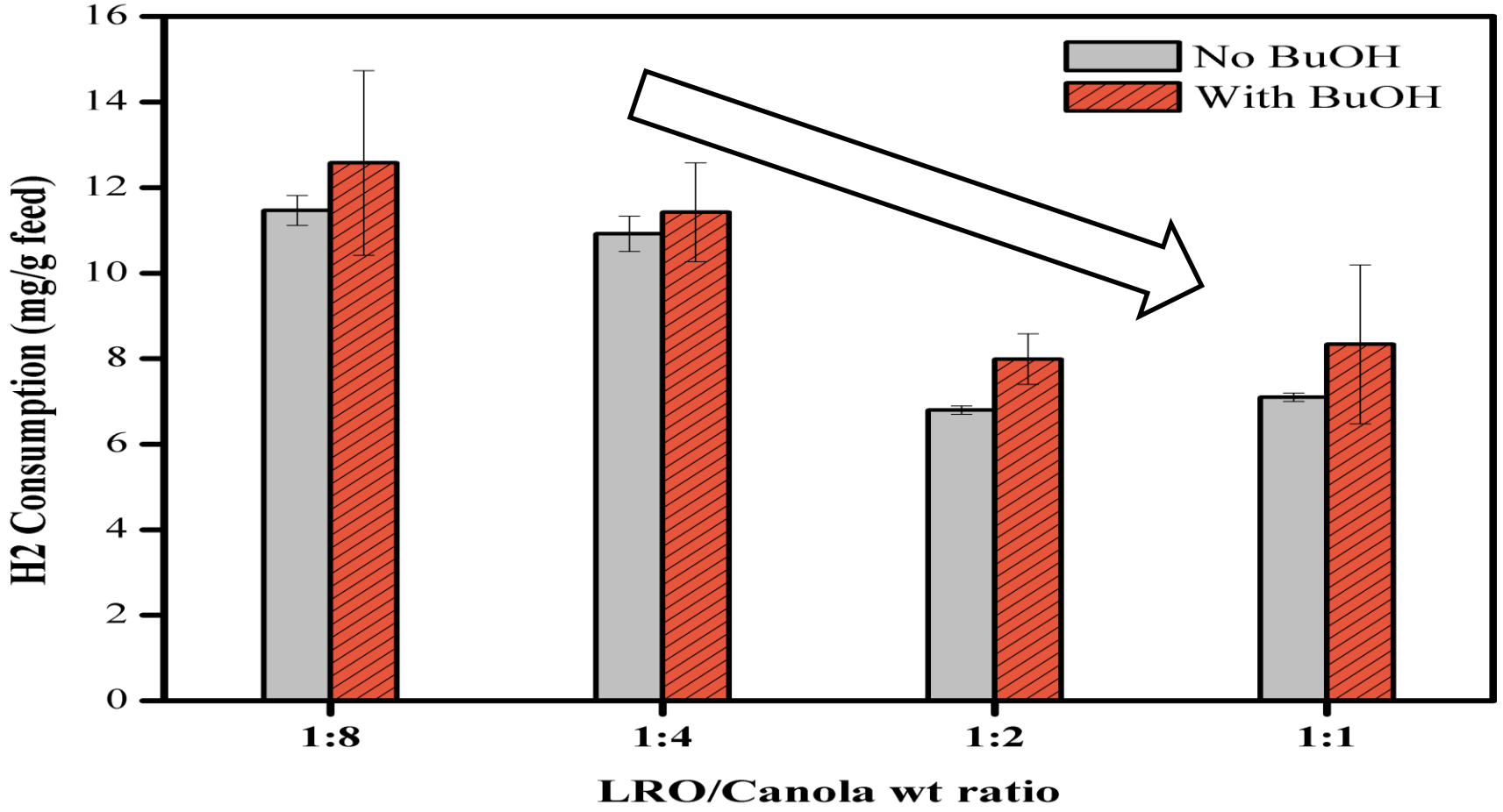


Naphtha cut (71-182˚C) | Kerosene cut (182-260˚C) | Diesel cut (260-330˚C)

Mass balance on co-hydrotreatment of different blends

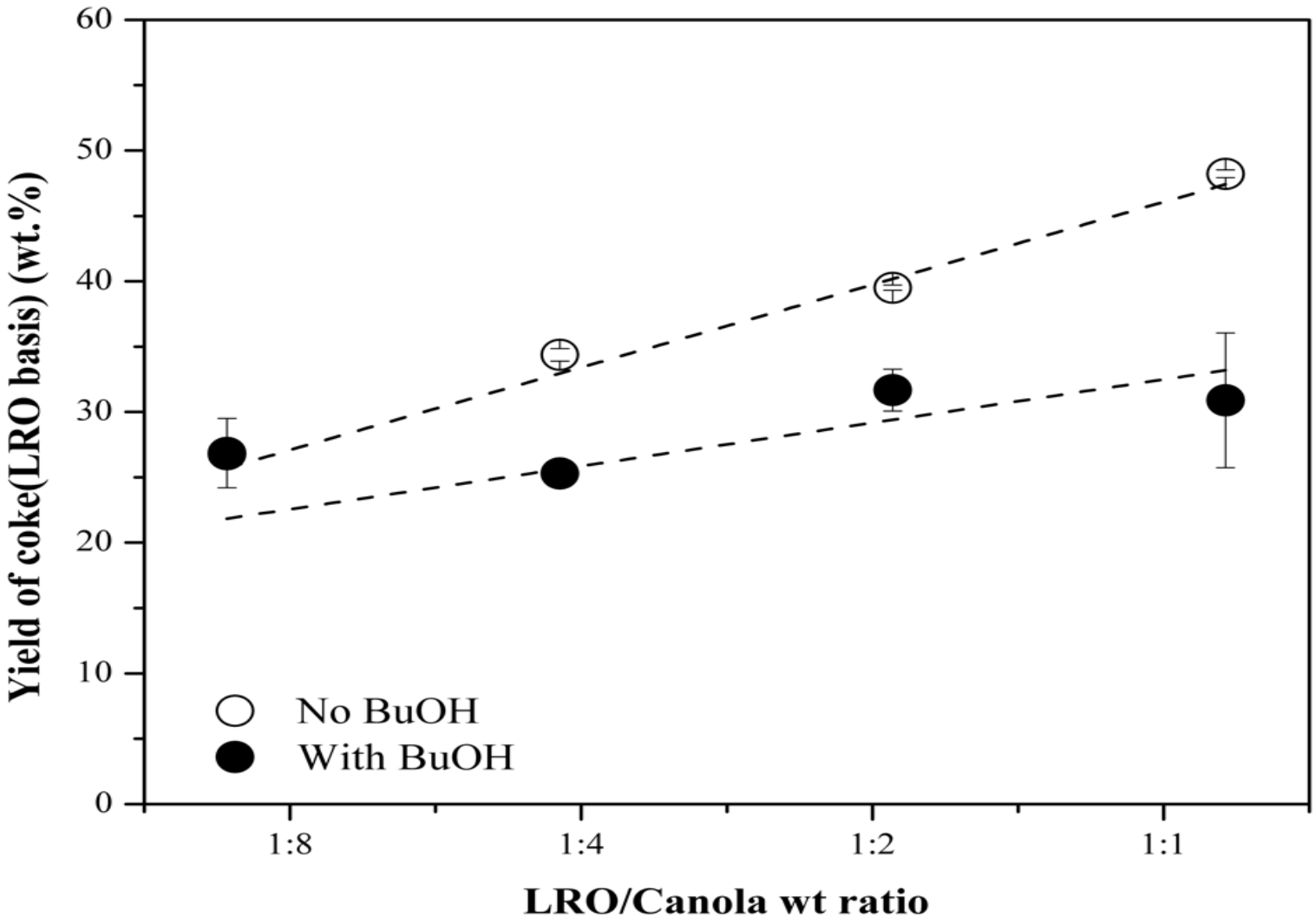


H_2 consumption of cohydrotreatment

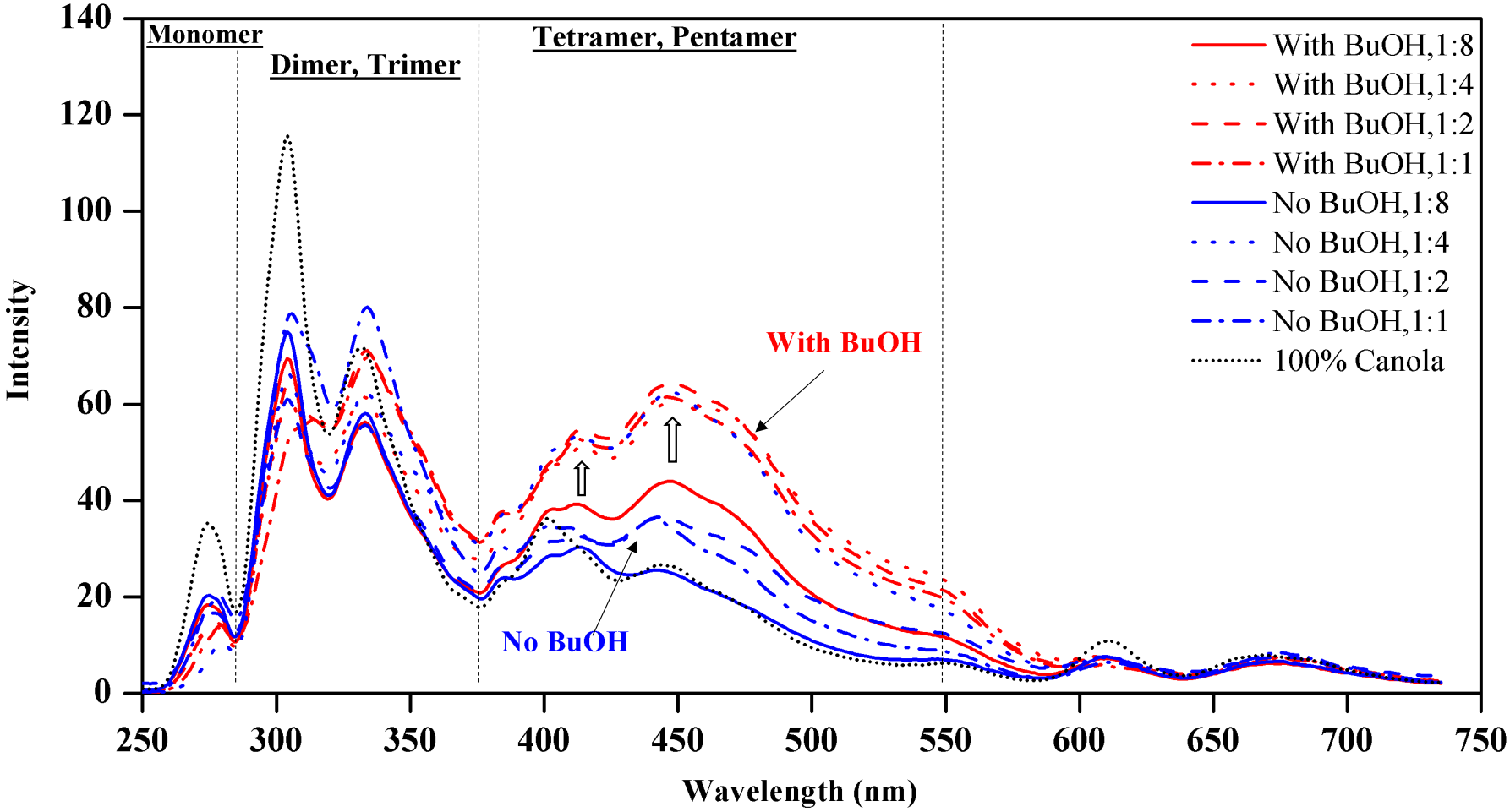


Hydrogen consumption decreased with the increase in pyrolytic lignin content

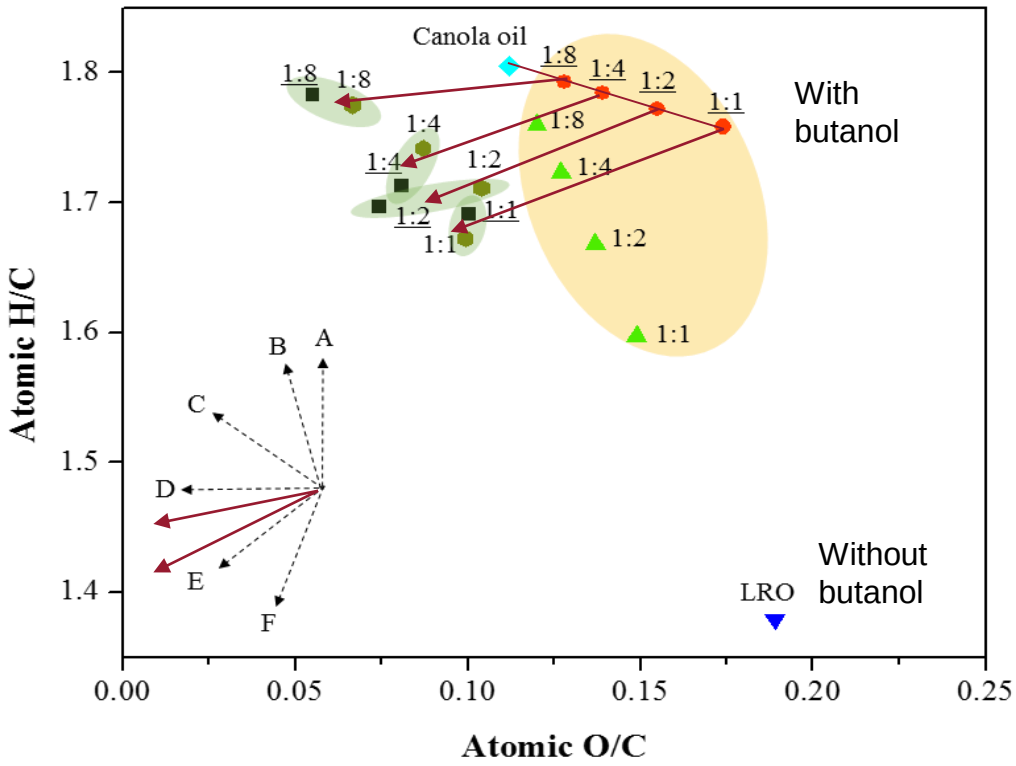
Mass balance on co-hydrotreatment of different blends



UV-Fluorescence on all the hydrotreated oils

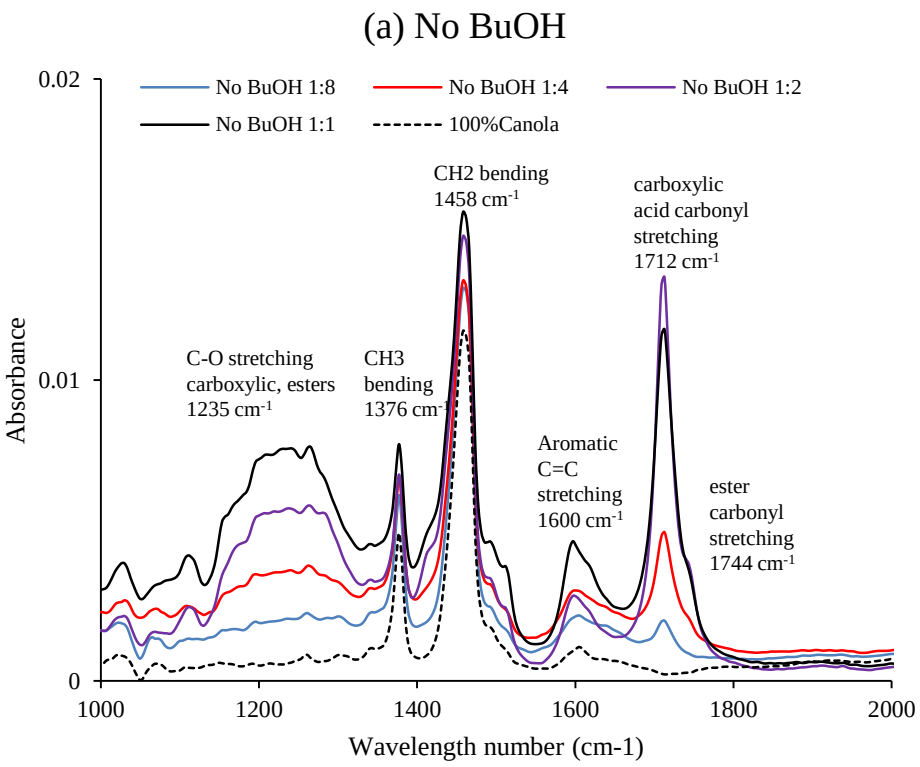


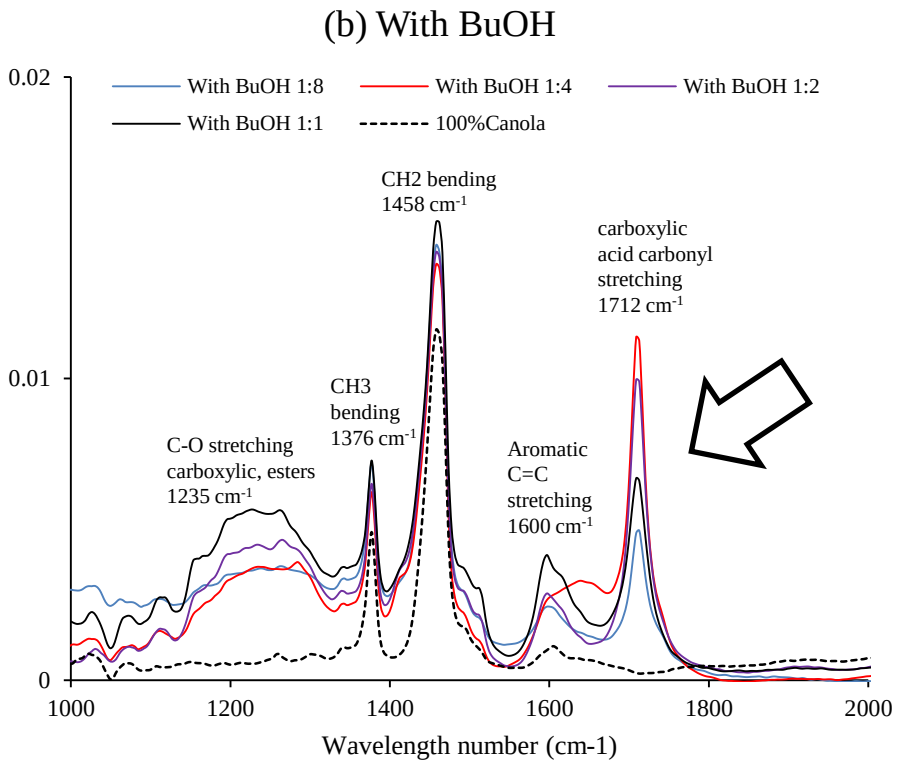
Van Krevelen plot for LRO, Canola oil, their blends



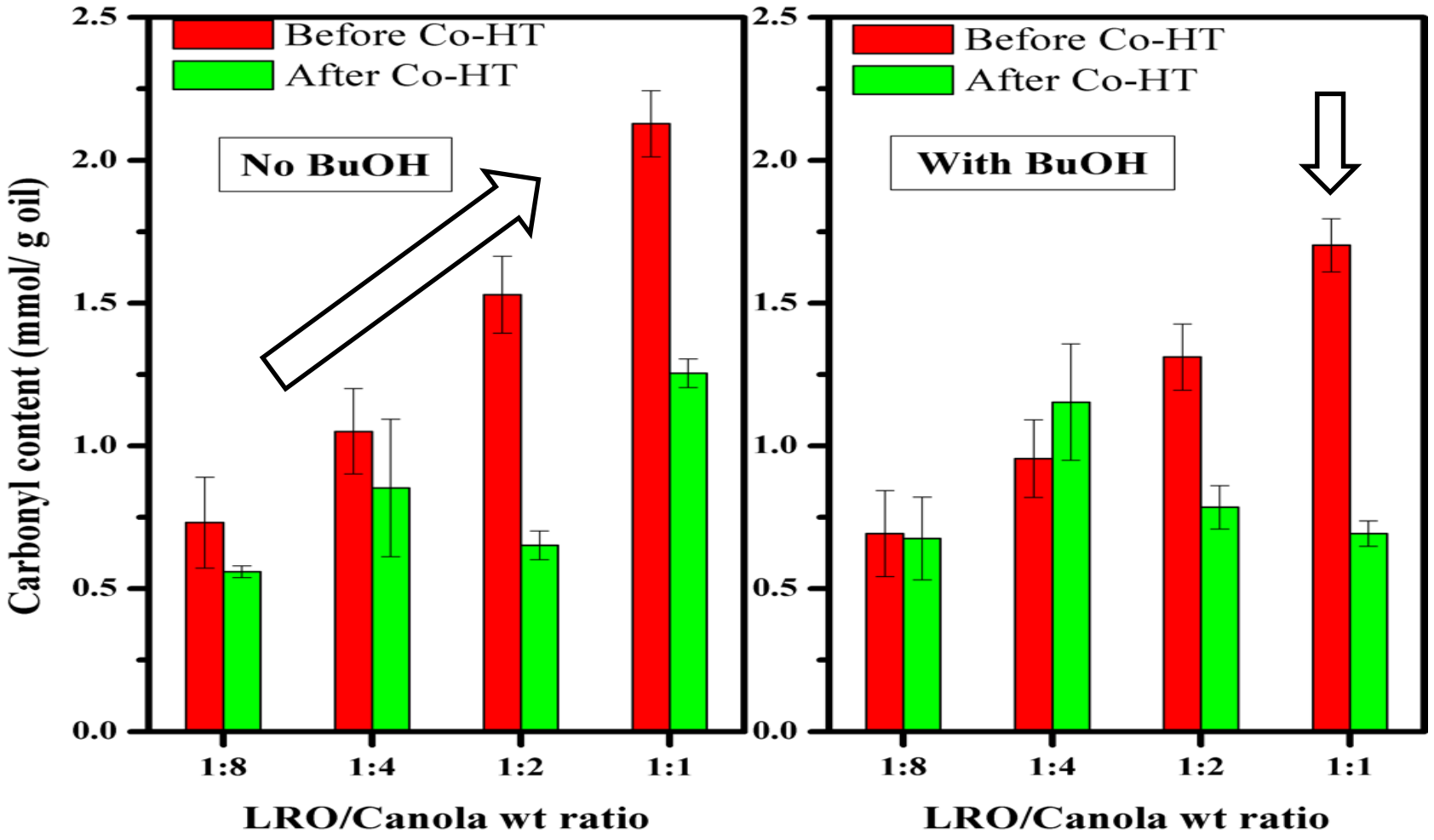
(yellow zone, ratios with underline, such as 1:8, represent the blends with 1-butanol) and the corresponding hydrotreated oils (green zones). Distinctive line patterns can be associated with specific reactions: (A) hydrogenation, (B) decarbonylation, (C) decarboxylation, (D) **direct deoxygenation**, (E) **dehydration**, (F) demethoxylation.

FTIR on the hydrotreated oils

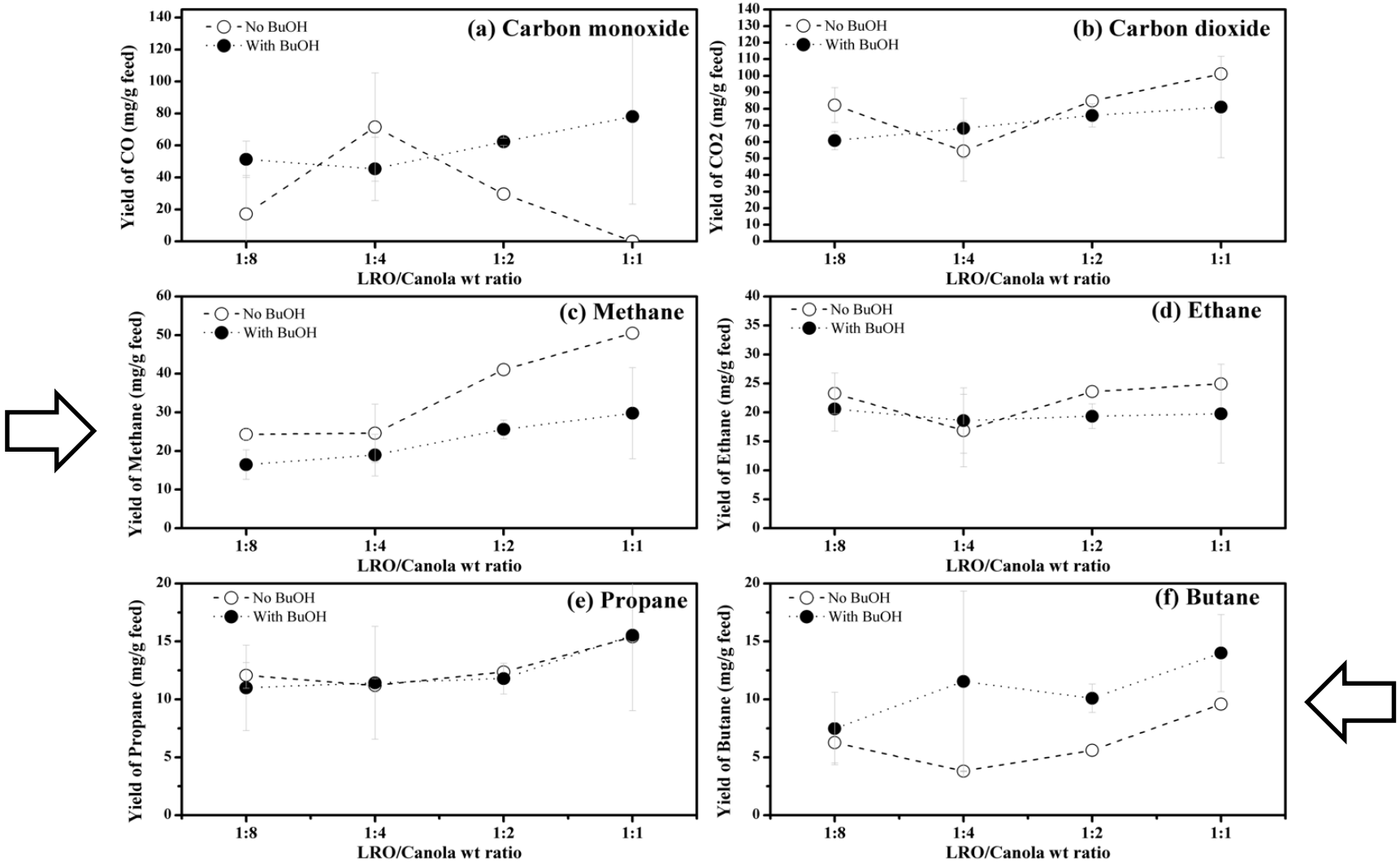




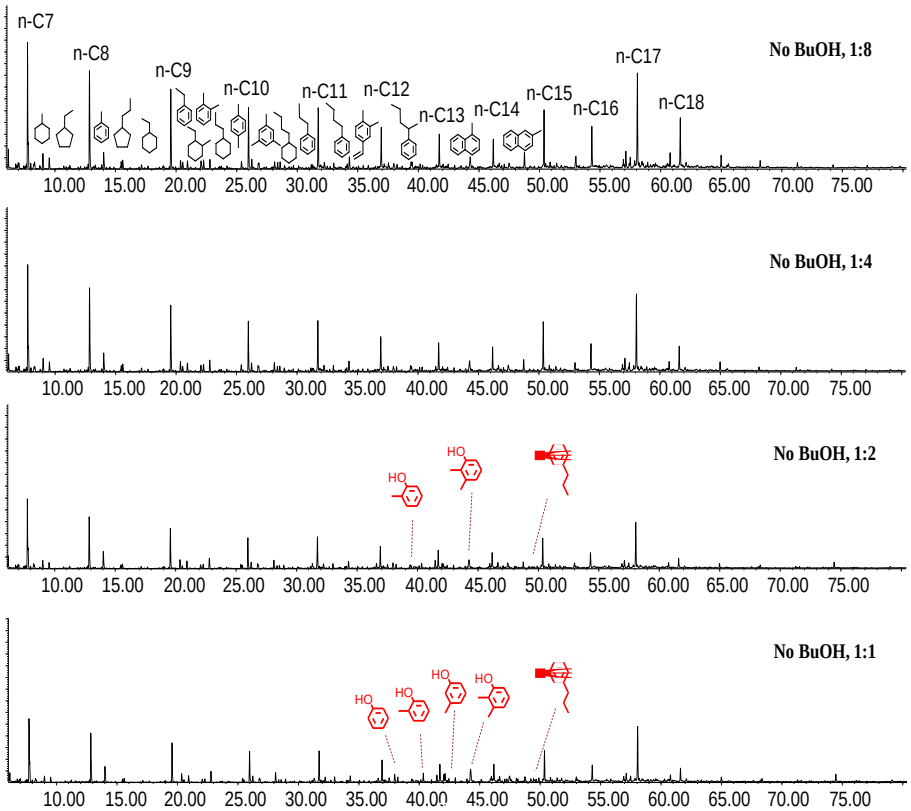
Carbonyl content of the LRO/Canola blends

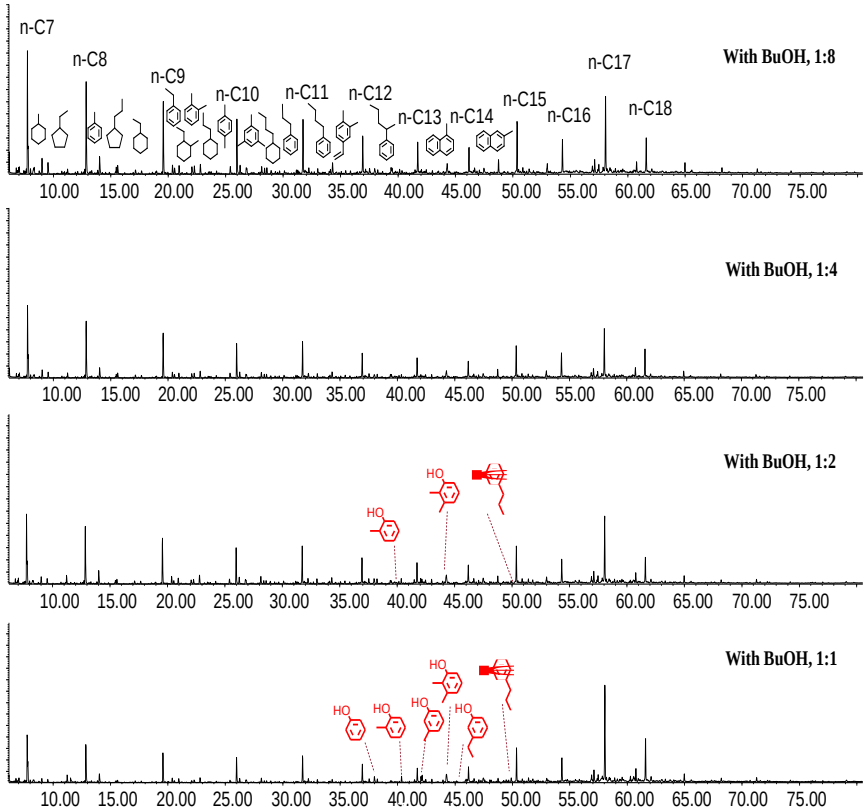


Gaseous products from cohydrotreatment of different blends

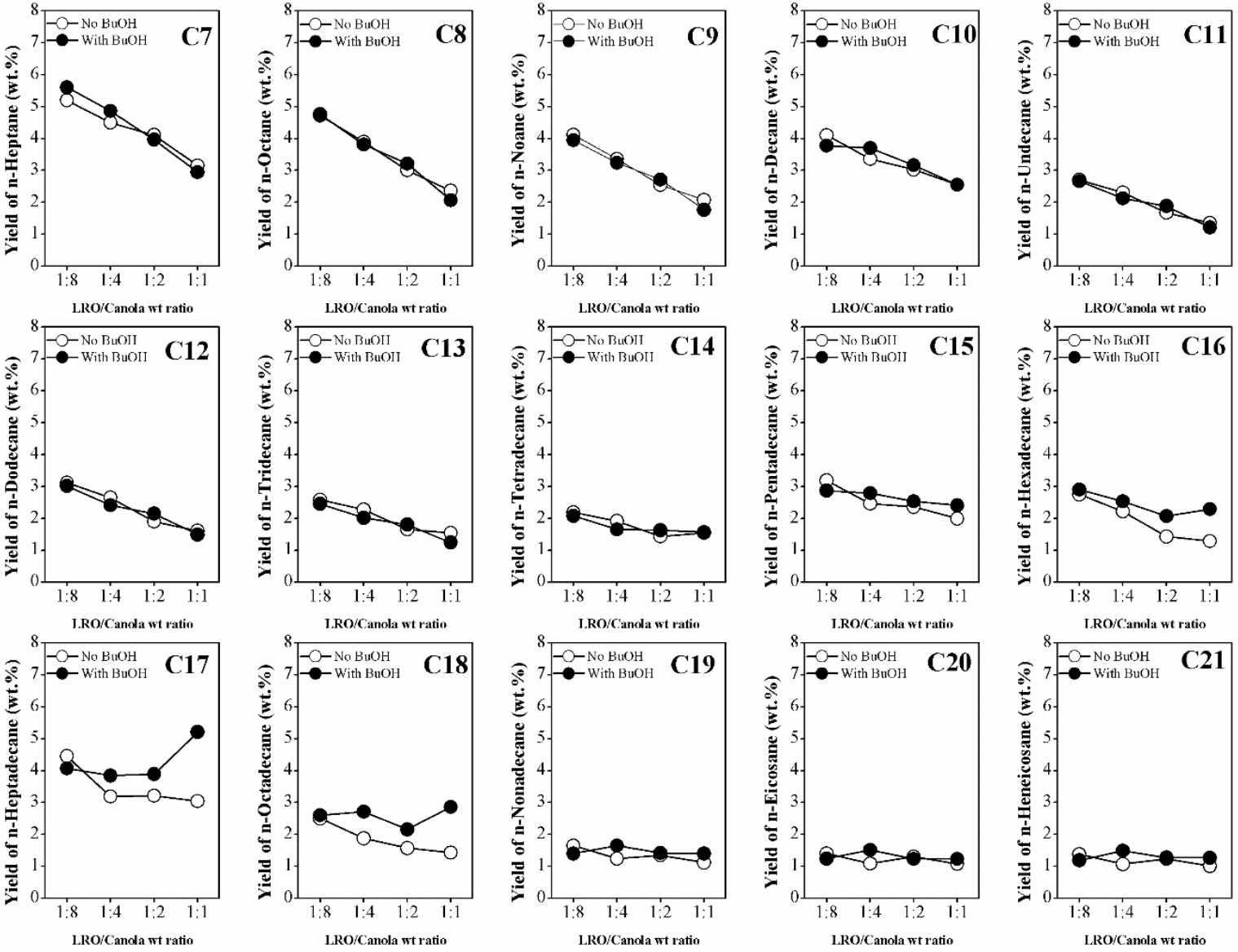


GC/MS on all the hydrotreated Oils

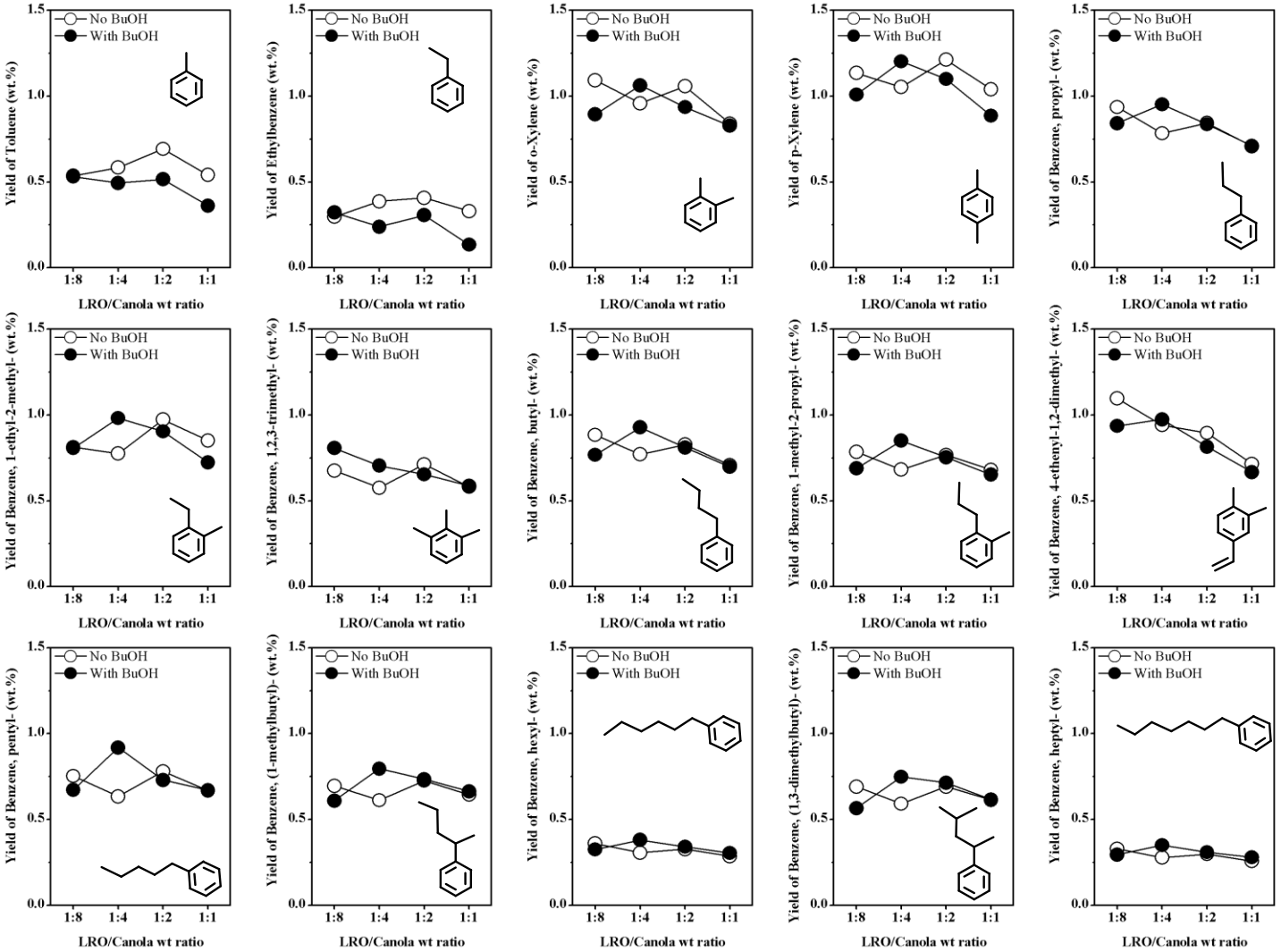




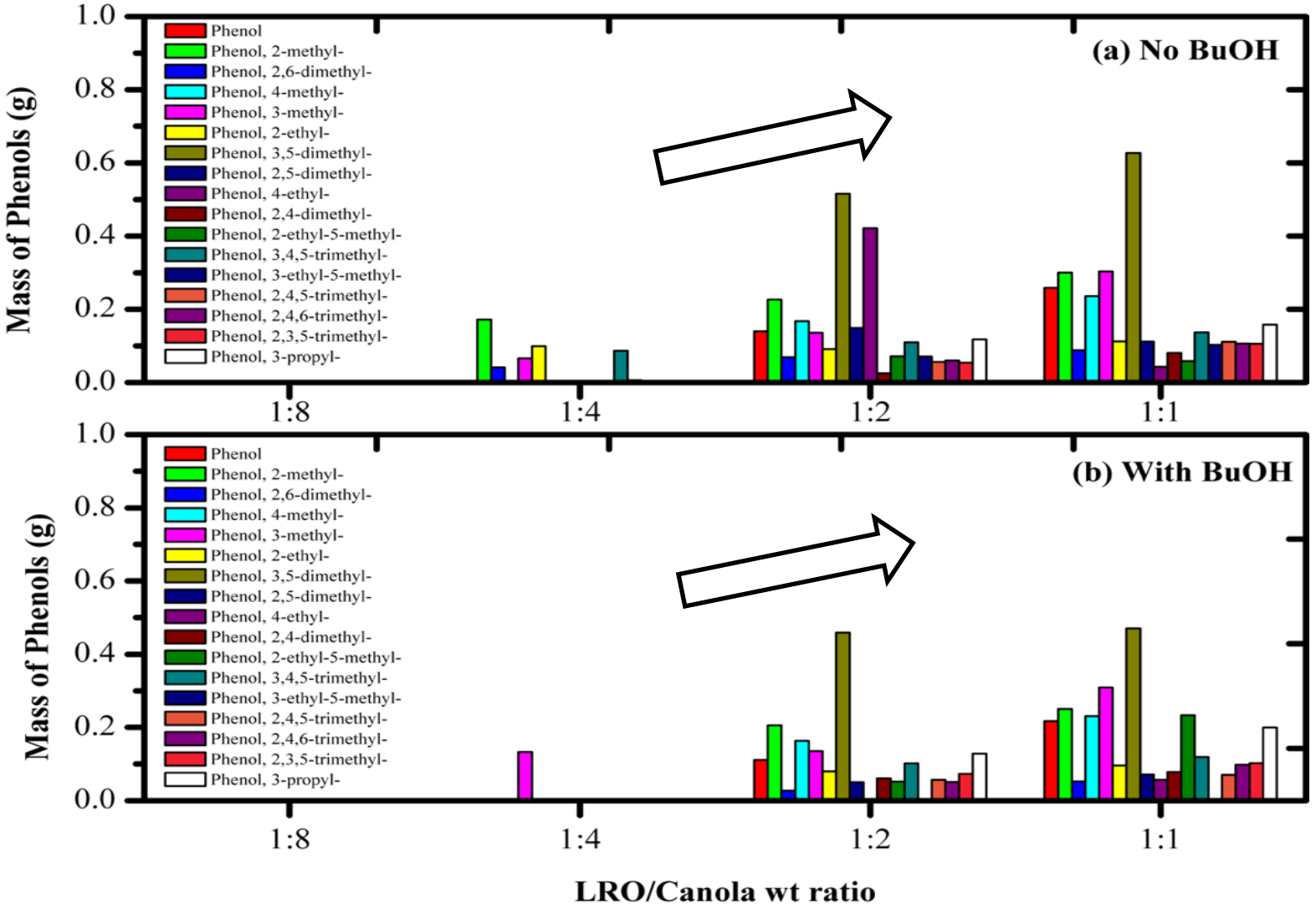
Yields of n-Paraffinic products



Yields of major Aromatic Products



Product distribution of phenolics after co-hydrotreating LRO/Canola blends



Hydrocracking and Stabilization

Cracking of LRO:

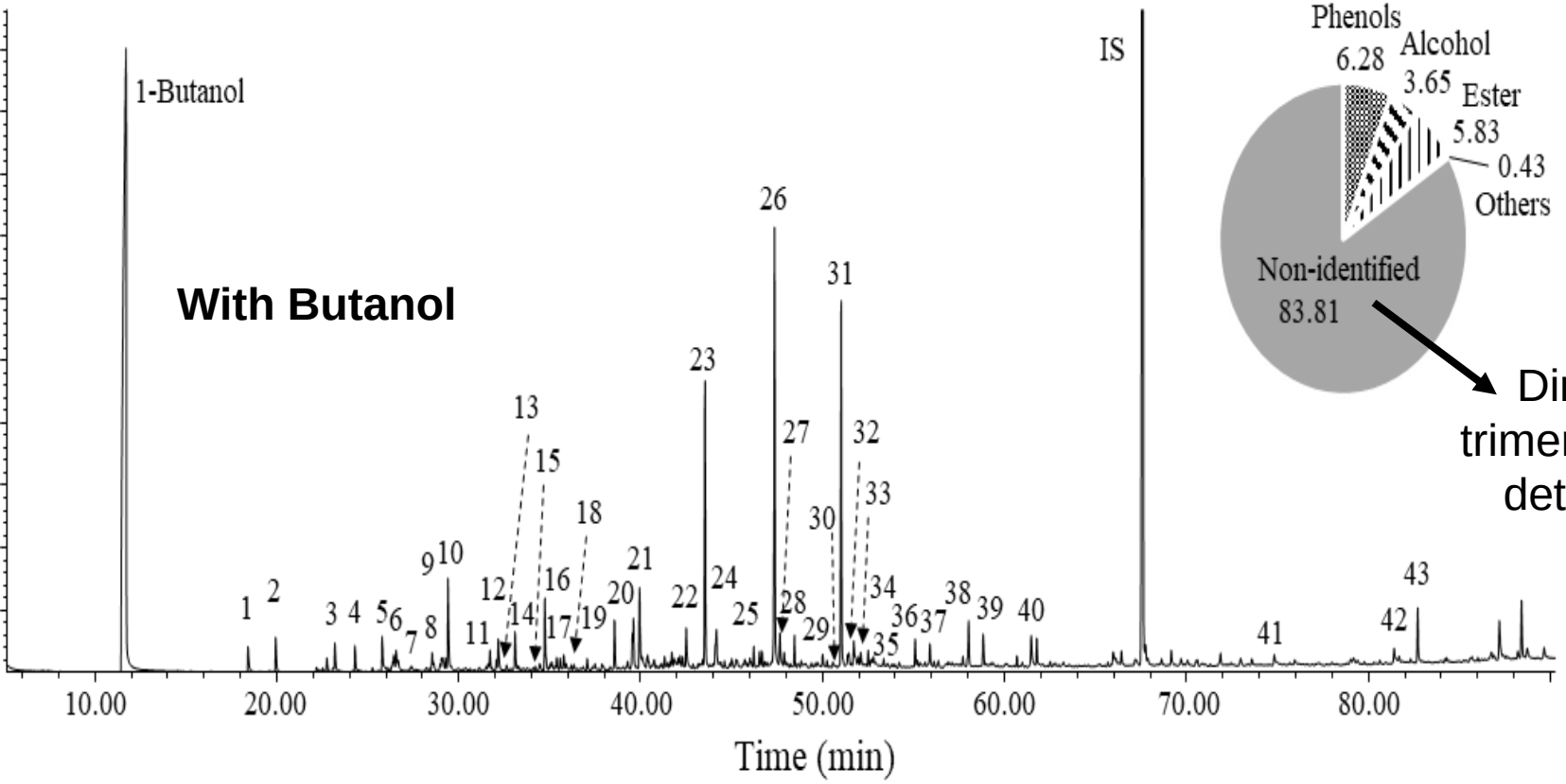
Catalyst: Ni/SiO_2-Al_2O_3

Solvent used: Methanol, Butanol

Temperature: 200 ^oC

Time: 24 hours

GC/MS (concentrated by rotavap)



Dimers or trimers (not GC detectable)

Product distribution of co-hydrotreatment (after hydrocracking)

	LRO/Canola=1:4	Cracked LRO* (in MeOH) /Canola=1:4	Cracked LRO* (in BuOH) /Canola=1:4	Canola
Overall product distribution				
Liquid	**76.43 %**	**80.69%**	**80.72%**	**84.31 %**
Gas	**16.72 %**	**16.14%**	**18.16%**	**15.65 %**
Solid	**6.85 %**	**3.18%**	**1.13%** ⟷	**0.04 %**
Distillation cuts of the resulting oils (wt.%)				
<71 ˚C	0	0	0	0
Naphtha 71-182˚C	20.80	21.69	23.08 ⟷	17.88
Kerosene 182-260 ˚C	14.59	18.26	**21.24** ⟷	**21.67**
Diesel 260-330 ˚C	13.16	18.00	**19.52** ⟷	**20.67**
330-566 ˚C	29.61	24.18	20.34	25.37
Residue	10.91	7.36	7.23	4.44
Weight loss	10.92	10.51	8.58	9.97
Coke formation (LRO basis)				
LRO basis coke	**34.73 %**	**16.08 %**	**6.65%**	**N/A**

Cracking and stabilization seems to help the hydro-deoxygenation of lignin rich fraction

Conclusions

1. An important HDO had been achieved for the blends of lignin-rich oil and vegetable oil, resulting in a two-phase liquid product formed with the oil stayed on the top and water at the bottom.
2. By varying the ratio between lignin rich oil and vegetable oil, some phenolics started to be detected when the weight percentage of lignin oil in the blend increased to 1/3 or above.
3. The major components of the hydrotreated oils were paraffinic and aromatic hydrocarbons, with less carbonyl groups than the pristine blends.
4. Adding BuOH into the lignin rich oil resulted in more tetramers and pentamers being produced in the oil which on the other hand mitigated the coke formation in cohydotreatments.
5. Hydrocracking/stabilization is an efficient step to depolymerize the lignin-rich oil which then effectively reduces the coke formation in the HDO step.

Thank you!

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- *Federal Aviation Administration*
- *USDA/NIFA*
- *WSU-BSE colleagues*

QUESTIONS?