Molecular Weight Distribution Analysis of Pyrolysis Oils by Gel Permeation Chromatography

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Background – Bio-oil

Light oil products

Aqueous layer

Heavy oil products, "CFP oil"

- **Fast pyrolysis (FP) bio-oil:** liquid produced from rapid thermal decomposition of biomass in the absence of oxygen
 - Highly complex – analytes come from different components in biomass (lignin, sugars, etc.)
 - Not stable, “ages”
- **Catalytic fast pyrolysis (CFP) bio-oil:** fast pyrolysis oil produced in the presence of a catalyst
 - “Upgrade” in composition and properties
 - Often reduction in oxygenation, still complex
- **All bio-oils are difficult to characterize!**

Background - GPC

Gel Permeation Chromatography (GPC): separation of analytes on the basis of hydrodynamic volume ($\sim$ size) using porous beads as stationary phase; used to determine molecular weight of polymers (weight average molecular weight, **Mw**; number average molecular weight, **Mn**, etc.)

- Often **calibrated against standard polymers** that should be representative of samples
- **Uses different types of detectors:** UV-DAD, refractive index, light scattering, viscosity

Bio-oil molecular weight metrics (distribution, Mw, Mn, etc.) provides insight to properties of oil and conversion conditions necessary to produce oils of optimal properties for use as fuel or chemical feedstocks

Harman-Ware, A. E.; Ferrell, J. R., Methods and Challenges in the Determination of Molecular Weight Metrics of Bio-oils. *Energy & Fuels* **2018**, 32 (9), 8905-8920

An Introduction to Gel Permeation Chromatography and Size Exclusion Chromatography 5990-6969EN, Agilent Technologies 2015

Harman-Ware, A. E.; Orton, K.; Deng, C.; Kenrick, S.; Carpenter, D.; Ferrell, J. R., Molecular weight distribution of raw and catalytic fast pyrolysis oils: comparison of analytical methodologies. *RSC Advances* **2020**, 10 (7), 3789-3795.

Background - MALS

- Multi-angle laser light scattering detector
- Intensity of light scattered is proportional to molar mass
- Doesn't require external calibrants for elution volume to molar mass conversion
- Still requires concentration-dependent detector and has limitations

GPC-MALS/RI/visc may provide new or different insights related to bio-oil molecular weight analyses

Methodology

Biomass

Consisting of
lignin, cellulose
and
hemicelluloses

Bio-oil Production

$T = 500^{\circ}\text{C}$;
upgrading over
H-ZSM5 catalyst

Sample Preparation

Bio-oil is collected
and solubilized in
solvent

GPC separation and detection

Optimize
chromatography,
detection

Molecular weight metrics

Mw, Mn, MWD,
etc.

Bio-oil Properties – functional groups, compound classes, viscosity, water content, CHO content amongst most important

CFP – less oxygen, less water, less viscous, more components detectable by GC/MS in comparison to FP

Bio-oil	C=O (%)	Aromatic C-O (%)	Aromatic C-C (%)	Aromatic C-H (%)	Aliphatic C-O (%)	Methoxyl (%)	Aliphatic C-C (%)	C (%)	H (%)	O (%)	KF water (%)	Intrinsic viscosity (mL/g)
FP oil	13.8	13.3	11.8	20.5	20.6	2.6	17.4	58.6	6.7	34.6	17.3	2.99 (±0.04)
CFP oil	6.7	14.8	13.5	42.1	4.1	1.9	17.1	75.4	7.0	17.3	4.8	2.42 (±0.05)

Properties of FP and CFP oils obtained from ¹³C NMR and CHO analyses (% values reported on moisture free basis) as well as intrinsic viscosity, [η] determined by viscometry with standard deviation of triplicate analyses.

FP oil has higher MW than CFP oil based on UV/DAD detection

Comparison of intensity on consistent concentration basis indicates differences in abundance and detection of species over range of elution volumes (g/mol relative to polystyrene)

MALS consistently gives higher Mw, Mn followed by RI and UV/DAD

Difference between FP and CFP oils MWD is significant based on UV/DAD (which depends on functionality!) as well as RI relative to polystyrene standards, MALS shows similar Mw, Mn for CFP and FP oils

**MALS/RI/Visc implies
components eluting are
larger in comparison to
polystyrene calibration**

Concentration-dependent RI coupled with universal detection MALS shows higher abundance of larger components in FP oil and higher abundance of smaller components in CFP oil (similar to UV/DAD)

**Minor changes in
intrinsic viscosity over
course of elution**

Consistent intrinsic viscosity means more reliable MALS data – provides comparison insights (especially related to Mark-Houwink parameters and universal calibration!) and other information about polymers

Weight fraction distribution differences from MALS/RI/Visc

Remaining high MW fraction from FP: 39.61%

Remaining high MW fraction from CFP: 44.75%

Low MW not detected by MALS, complicated in RI based on signal

Summary and Conclusions

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- More detectors better for method development...
 - UV/DAD – only chromophores
 - RI – sensitivity and baseline issues
 - MALS – low MW issues
- FP vs CFP – property differences impact ability to compare and analyze accurately (differences in intrinsic viscosity and functionality make traditional GPC with elution standards and the common use of UV/DAD only not very accurate)
- FP vs CFP – lower molecular weight expected and apparent for CFP

Future Directions

- Improvement in chromatography/resolution
- Expansion of oil composition and property analysis – FTICR-MS, GPC-MS
- Physical separation of oil components and subsequent analysis
- Pipe dream: standardization of robust, adaptable methodology

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GPC Methodology

Detailed Information

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Pyrolysis oil production

“Bio-oil samples were solubilized at 1 mg/mL in tetrahydro- furan (THF). GPC analysis using RI and UV-DAD (or referred to as simply UV) was performed using an Agilent 1200 HPLC with 3 GPC columns (Agilent, 300 x 7.5 mm) packed with 10 mm polystyrene-divinyl benzene copolymer gel beads with nominal pore diameters of 10^4 , 10^3 and $50 \text{ \AA}$. The UV-DAD measured absorbance at 270 nm (80 nm bandwidth). An injection volume of 20 mL was used with an eluent (THF) flow rate of 1.0 mL min⁻¹ for a total run time of 45 min. Polystyrene standards (Agilent Technologies) were used to calibrate for relative Mw and Mn, with assumptions of Mark–Houwink parameters for relative comparison only. GPC analysis using MALS coupled with differential RI and viscometry analysis was performed using the same chromatographic method and columns described for UV detection. A Wyatt DAWN HELEOS II detector with a 785 nm MALS was used with a Wyatt ViscoStar III viscometer and Wyatt Optilab T-REX differential refractometer (RI) with 785 nm LED. Data were collected and processed using ASTRA 7 for molecular weight analysis.”

“Ex situ catalytic pyrolysis was conducted in a dual fluidized bed reactor system²³ using a ZSM-5 catalyst from Zeolyst (CBV 3024E), silica-to-alumina ratio of 30, sized 300–1000 mm after the original extrudates were ground and sieved. Biomass was fed into the pyrolysis reactor (5.2 cm inner diameter x 43 cm height) at a rate of 420 g/h over a 200 mL bed of silica sand. A cyclone separator was used to remove char from the stream allowing the pyrolysis vapors to enter the upgrading reactor (5.2 cm inner diameter x 15 cm tall lower section and a 7.8 cm diameter x 35.6 cm disengagement section). The ZSM-5 catalyst was metered into the upgrading reactor at a rate of 300 g/h and removed continuously via an overflow tube. A stainless- steel mesh hot gas filter was used to filter gases and upgraded vapors and then the vapors were condensed using various collectors including an air-cooled condenser, an electrostatic precipitator, dry-ice traps, and a coalescing filter. Nitrogen was used as the carrier gas during experiments at a flow of 17.4 L/min and total flow through the system was measured using a dry test meter. The pyrolysis temperature was 500 C, while the upgrading temperature was 550C. “

Additional data

GC/MS calibration Compound	Concentration (mg/mL)
Acetaldehyde	0.05 - 1.0
Benzene	0.05 - 1.0
n-octane	0.10 - 2.0
1-octene	0.05 - 1.0
cis-1,4-dimethyl-cyclohexane	0.10 - 2.0
Toluene	0.05 - 1.0
p-Xylene	0.10 - 2.0
n-decane	0.10 - 2.0
2-Cyclopentenone	0.05 - 1.0
Benzene, propyl-	0.05 - 1.0
Phenol	0.05 - 1.0
2,3- Benzofuran	0.05 - 1.0
Indene	0.05 - 1.0
o-Cresol	0.05 - 1.0
o-Methoxyphenol	0.05 - 1.0
Tetralin	0.10 - 2.0
Naphthalene	0.05 - 1.0
Phenanthrene	0.05 - 1.0