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Ternary System of Pyrolytic Lignin, Mixed Solvent, and Water: Phase Diagram and Implications

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Introduction

Biomass pyrolysis → Bio-oil

Fuel
- Hydrogen
- Upgrading

Chemical
- Flavours
- Resins
- Acids

Heat
- Co-firing

Power
- Diesel engine
- Turbine

One key consideration: Bio-oil phase separation during processing and handling that cause significant operational challenges.

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Research Gaps

- How to understand and control the phase stability of fast pyrolysis bio-oil
- Complete phase diagrams of water-insoluble fraction of bio-oil/water-soluble fraction of bio-oil/water system are not available

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Compositions of Fast Pyrolysis Bio-oils

fraction/main compounds	Content (wt %) dry basis	Content (wt %) water- and PL-free basis	average content (wt %, on a water and PL free basis)	average content in five major chemical families
pyrolytic lignin	16.0–35.0	N.A.[b]	N.A.[b]	N.A.[b]
acids	12.5–25	18.5–36.5	27.5	35.0
acetic acid	3.0–15.0			
formic acid	0.9–7.6			
propionic acid	0.2–1.3			
butanoic acid	0.2–0.5			
pentanoic acid	0.1–0.8			
isocrotonic acid	0.1–1.2			
butanoic acid, 2-hydroxy-	0.1–1.0			
phenol and phenol derivates	5.0–10.0	7.5–14.5	11.0	14.0
phenol	0.1–5.0			
cresol (*o*-cresol, *m*-cresol, and *p*-cresol)	0.3–1.5			
catechol	0.6–3.0			
guaiacol	0.8–2.5			
aldehydes and ketones	8.5–25	12.5–36.5	24.5	31.5
hydroxyacetone	1.2–9.5			
glycolaldehyde (unstable, exist as dimers)	0.5–8.0			
acetaldehyde	0.1–2.0			
acetone	0.1–3.0			
linear ketones (pentanone, octanal etc.)	0.1–2.0			
cyclic ketones (C5 and C6 cyclic ketones)	0.5–5			
furan and furan derivates	5.0–10.0	7.5–14.5	11.0	14.0
furfural	1.0–5.0			
2(5H)-furanone	0.1–1.5			
furfural alcohol	0.1–1.0			
methylfurfural	0.1–0.8			
alcohols	1.0–5.0	1.5–7.5	4.5	6.0
methanol	0.5–3.5			
ethanol	0.2–1.5			
ethylene glycol	0.2–1.0			
sugars	3.0–7.0	4.5–10.0	7.3	N.A.[b]
levoglucosan	0.5–3.0			
cellobiosan	0.2–3.0			
glucose	0.4–1.3			
esters and ethers	1.0–2.0	1.5–3.0	2.3	N.A.[b]
methyl butanoate	0.1–1.3			
acetic anhydride	0.1–1.3			
methyl pyruvate	0.1–0.5			
propane, 1-ethoxy-2-methyl-	0.3–1.0			
alkene and alkane	1.0–2.0	1.5–3.5	2.5	N.A.[b]
decane	0.1–0.2			
octadecane	0.1			
2-hexene	0.1			
cyclic alkanes and alkenes	<1.0			
nitrogen compounds	<1.0	<1.0	<1.0	N.A.[b]
aniline	0.1			
pyridine	0.1			
2-hydroxypyridine	trace			
aromatics	<1.0	<1.0	<1.0	N.A.[b]
benzene	trace			
tolune	trace			
naphthalene	trace			

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Theoretical Considerations for Formulating the MS

selected compound for the solvent	content (wt %)	solubility parameter,[a] δ (cal$^{1/2}$ cm$^{-3/2}$)
acetic acid	33.3	10.45
hydroxyacetone	33.3	13.08
phenol	13.3	11.78
furfual	13.3	12.14
methanol	6.8	14.48

- The closer the solubility parameters of the solute and the solvent are, the more likely the solubility of the solute are high in the given solvent [1]
- The solubility parameters of the solvent and solute must be <2 cal$^{1/2}$ cm$^{-3/2}$ [2]
- The δ value of the formulated MS (δ_{MS} = 11.99 cal$^{1/2}$ cm$^{-3/2}$)

[1] *Hansen, C. M. Hansen Solubility Parameters: A User's Handbook*

[2] *Ye, Y.; Liu, Y.; Chang, J. Bio Resources 2014, 9 (2), 3417.*

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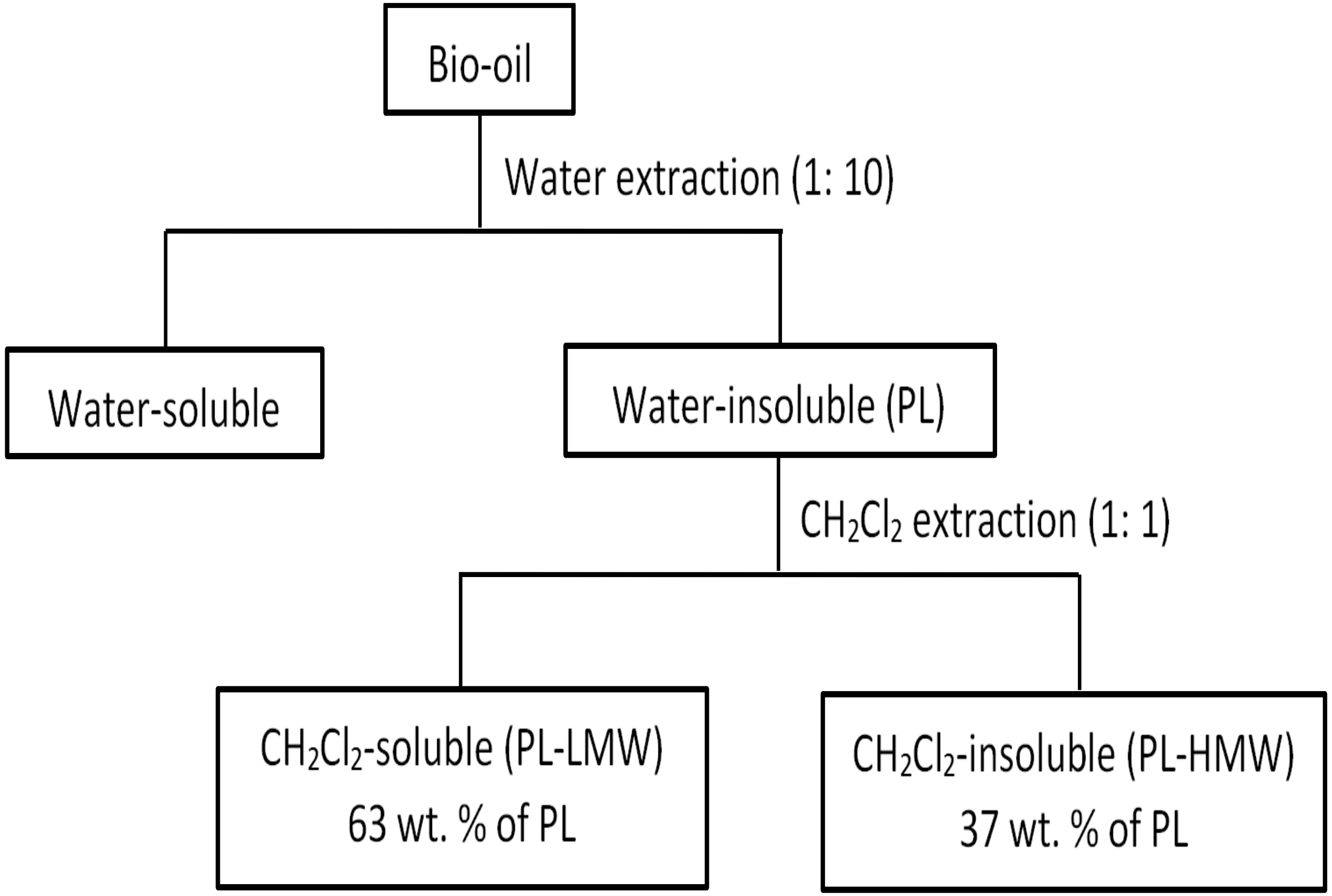
Preparation of pyrolytic lignin and its fractions from bio-oil



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Characterisation of PL samples

	PL-LMW[e]	PL[f]	PL-HMW[g]
moisture (wt %, ar[a])	1.1	1.8	1.8
ash (wt %, db[b])	0.6	1.5	0.9
volatile (wt %, db[b])	81.8	75.8	68.9
fixed carbon (wt %, db[b])	17.6	22.7	30.2
C (wt %, daf[c])	68.09	66.26	62.79
H (wt %, daf[c])	6.81	6.37	5.92
N (wt %, daf[c])	0.06	0.11	0.19
O (wt %, daf[c])[d]	25.04	27.26	31.1
atomic H/C	1.20	1.15	1.13
atomic O/C	0.28	0.31	0.37

[a]As received. [b]Dry basis. [c]Dry-ash-free basis. [d]By difference. [e]PL-LMW: CH_2Cl_2-soluble fraction of pyrolytic lignin. [f]PL: pyrolytic lignin. [g]PL-HMW: CH_2Cl_2-insoluble fraction of pyrolytic lignin.

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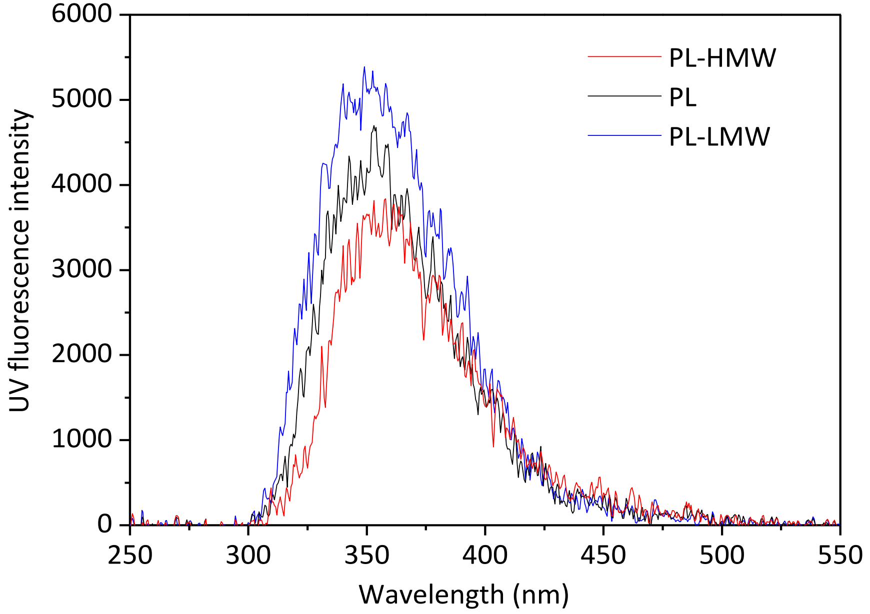
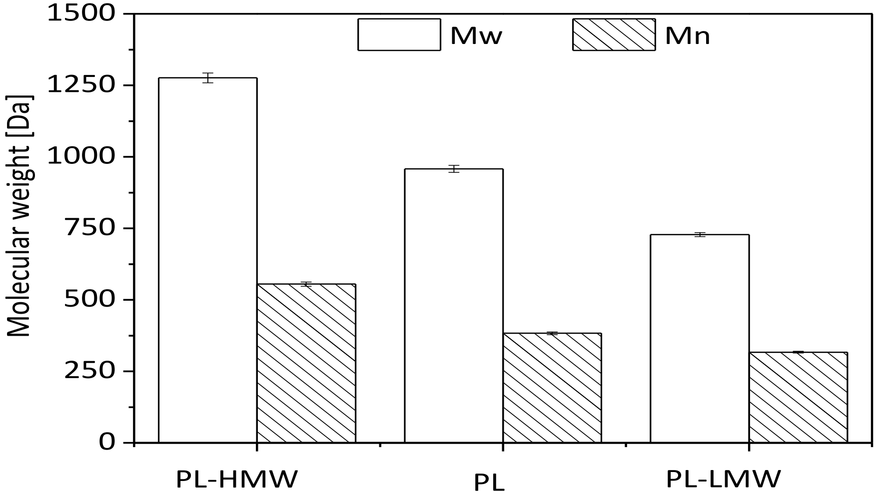
UV-fluorescence spectra and molecular weight of PL samples





UV-fluorescence spectra

- Mainly centred at ~350 nm
- PL-HMW slightly shifts toward higher wavelength

Molecular weight

- Previous reports indicated that the Mw value of PL sample are between 649 and 1317 g/mol [1]

[1] *Meier, D et.al. J Anal Appl Pyrolysis 2001, 58-59, 387-400.*

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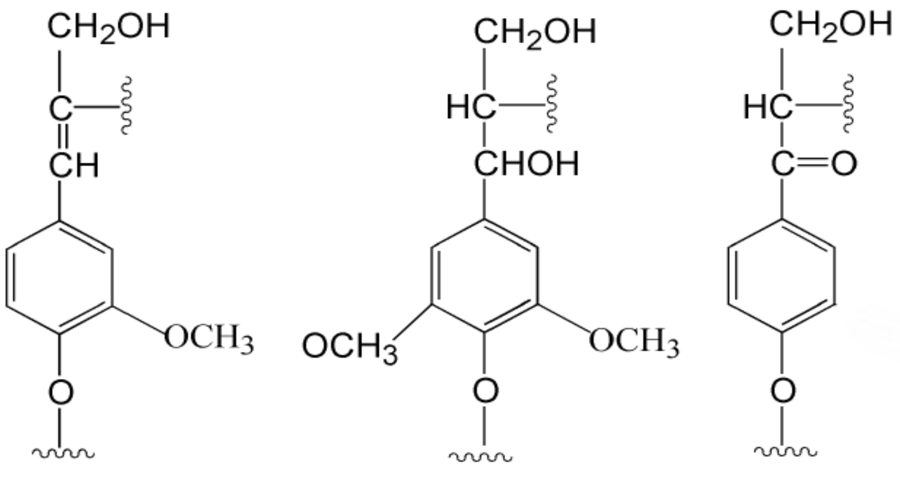
Solubility parameter of PL samples



	G/H/S ratio	Solubility parameter (cal$^{1/2}$ cm$^{-3/2}$)
G unit	N/A	13.52
H unit	N/A	14.12
S unit	N/A	14.23
PL-LMW	1.84/0.63/1.0	13.83
PL	1.49/0.29/1.0	13.84
PL-HMW	0.81/0.1/1.0	13.92

- Lignin has three different units[1]
- Differences in the solubility parameters for G, H, and S are very small
- The G/H/S ratios of PL samples are determined by ^{13}C NMR.

[1] *Wang, Q et.al. BioResources 2011, 6 (3), 3034−3043.*

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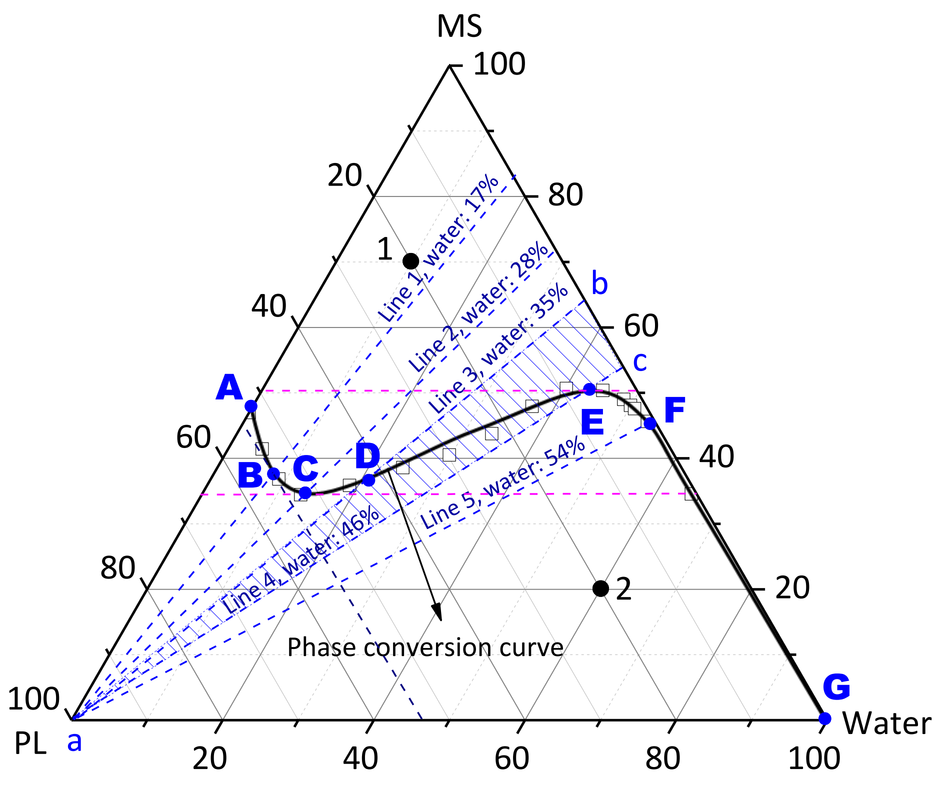
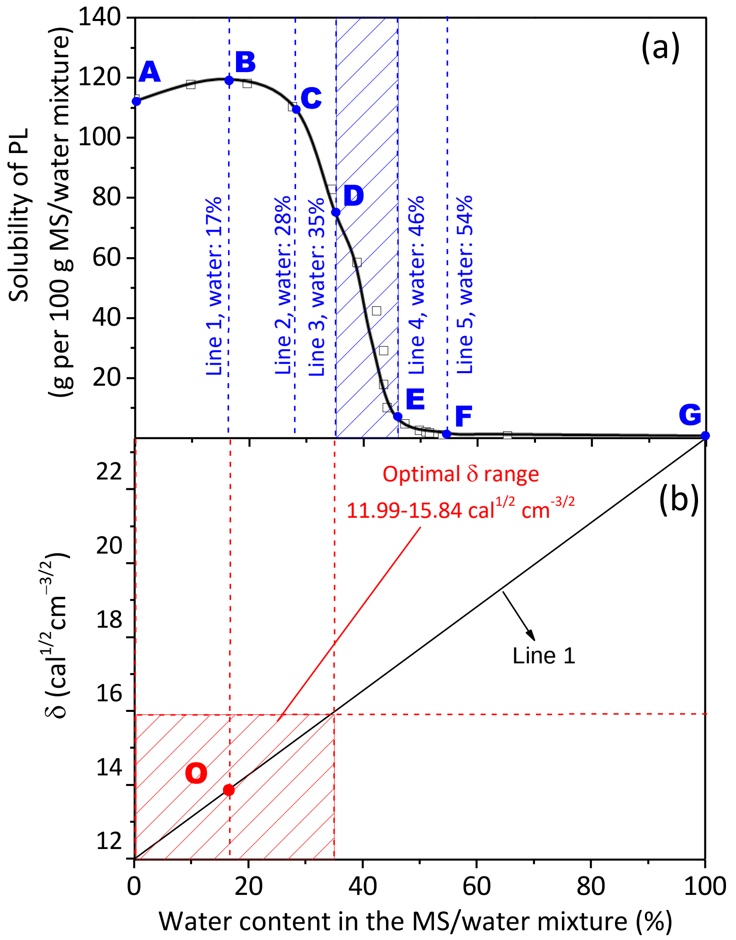
Ternary phase diagram of the PL/MS/water system and solubilities of PL in various MS/water mixtures.





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Ternary phase diagram of the PL/MS/water system and solubilities of PL in various MS/water mixtures.

- PL has a maximal concentration of ~53 wt % in the PL/MS binary (point A)
- Increasing the water content from point A to point B enhances the solubility of PL in the MS/ water mixture to ~118 g PL per 100 g of MS/water mixture.
- Point C represents the minimal solvent (~35 wt % in the PL/MS/water system) required to possibly form a homogeneous PL/MS/water solution
- A drastic reduction in the solubility of PL in the MS/water mixture is evident as the content of water increases from point D to point E.
- Point E represents the minimal solvent at which a homogeneous solution is always formed for the ternary system

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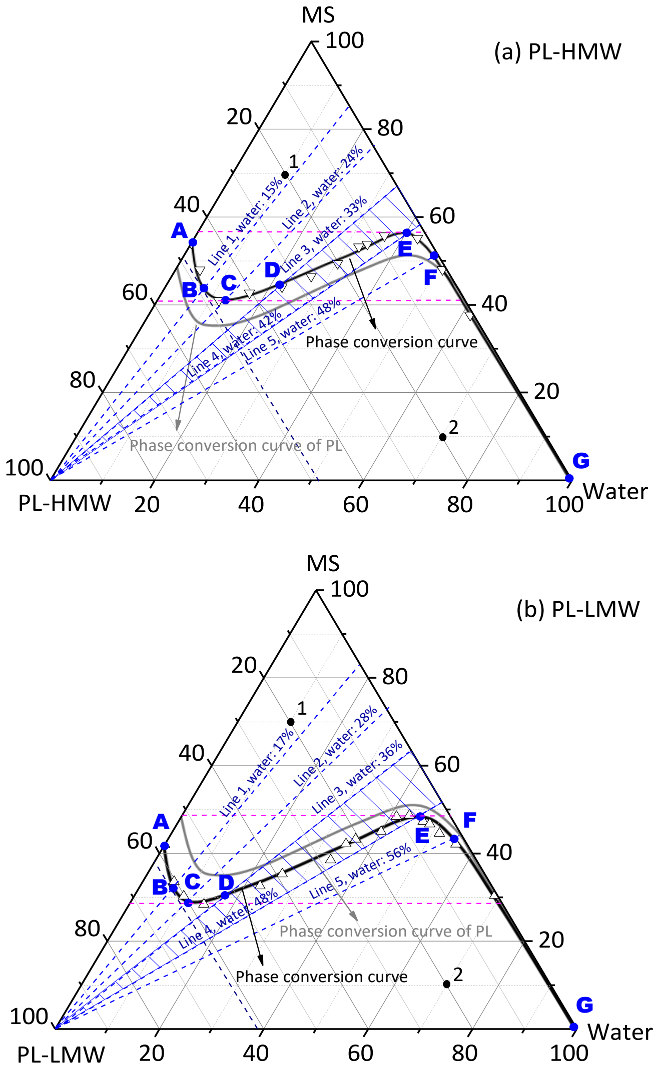
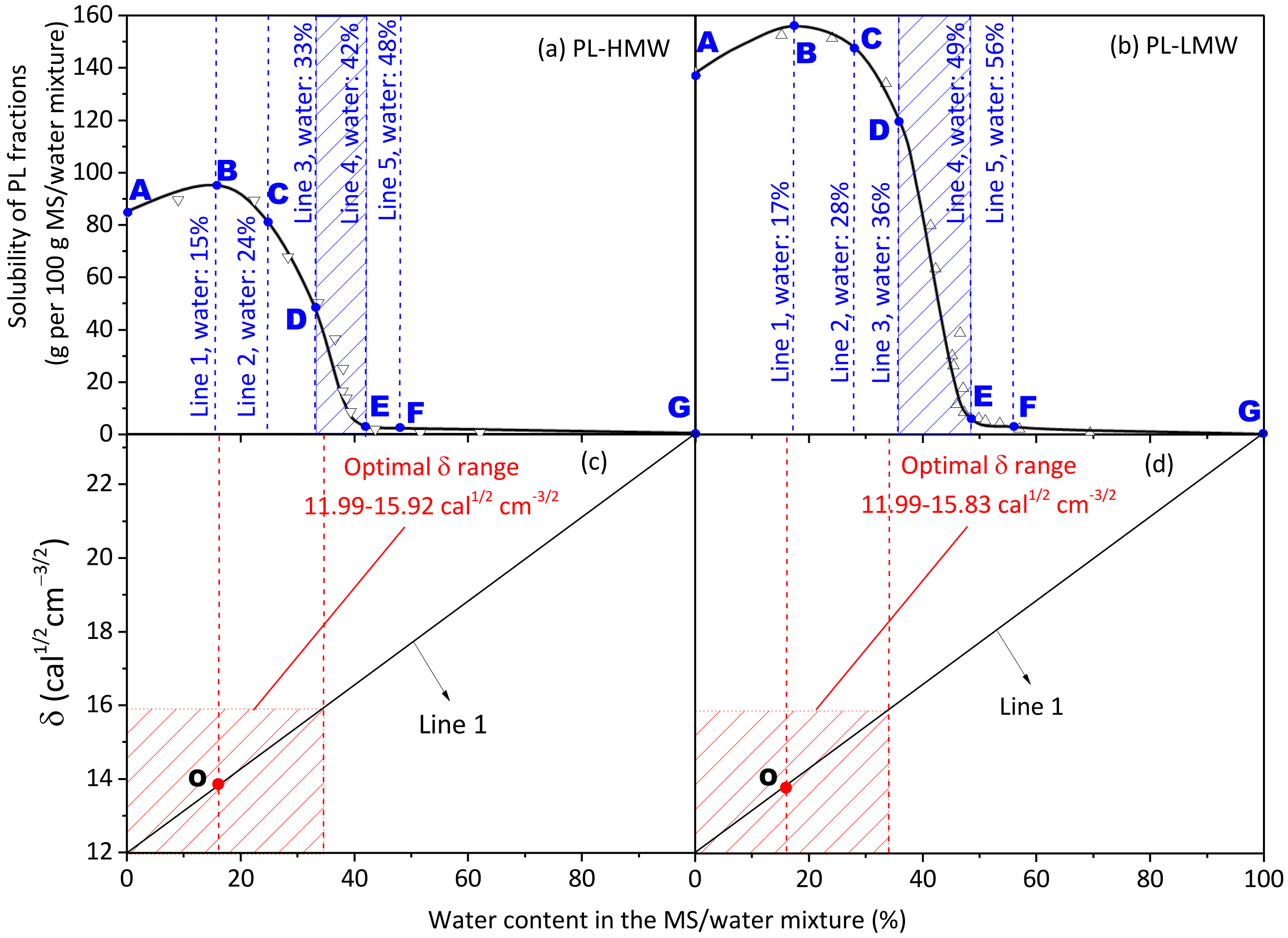
Ternary phase diagrams of PL-HMW/MS/water and PL-LMW/MS/water





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Ternary phase diagrams of PL-HMW/MS/water and PL-LMW/MS/water

- The solubilities of different PL fractions in the same MS/water mixture follow an order of PL-LMW > PL > PL-HMW.
- The trends of the phase conversion curves for PL fractions follow a similar pattern to that for the PL
- The maximal solubilities of PL-HMW and PL-LMW are ~96 and ~156 g per 100 g of MS/water mixture respectively

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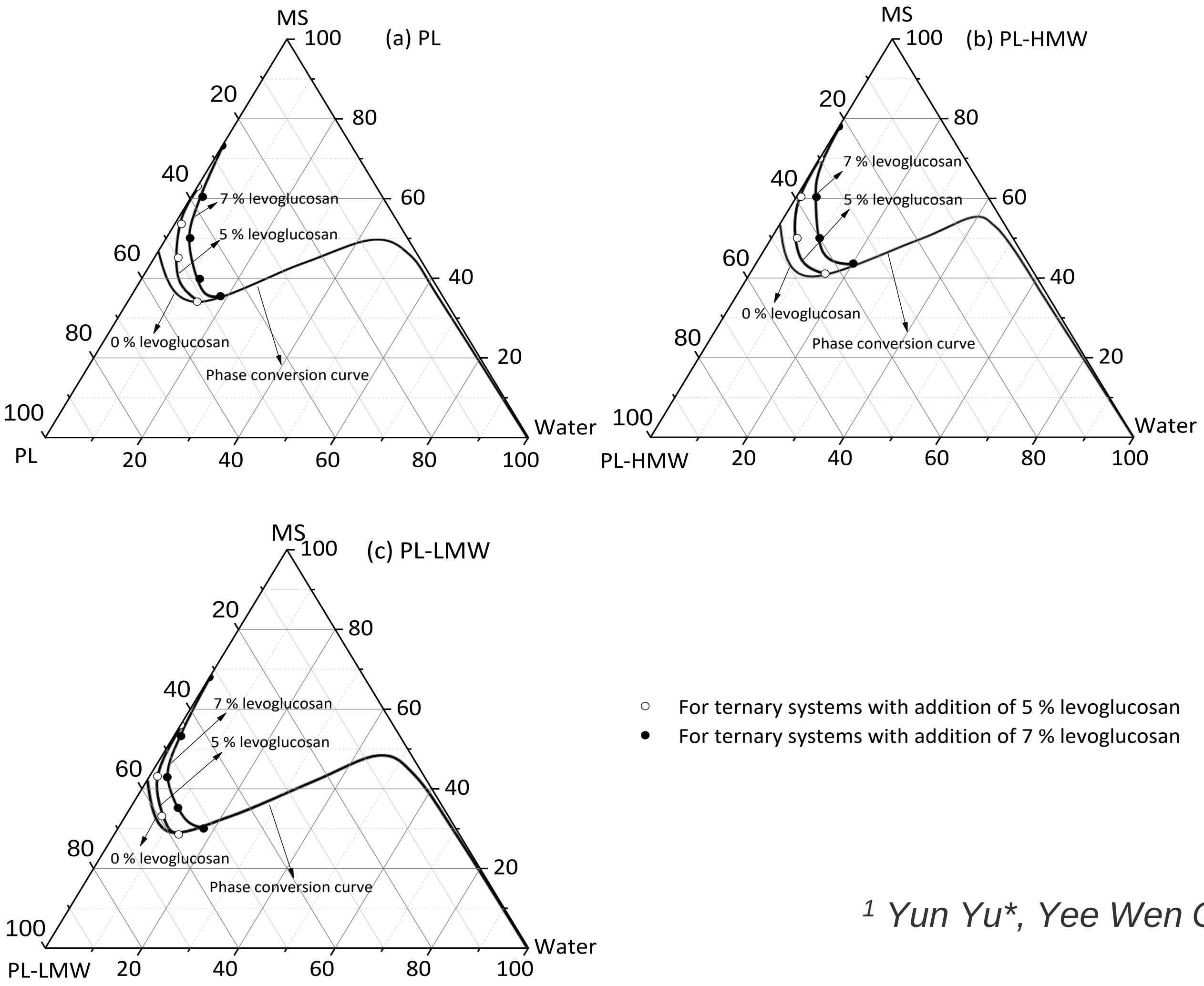
Effect of Sugar on Ternary Phase Diagrams of PL and Its Fractions.



- ~5−7 wt % of sugar (mainly in the form of levoglucosan) could be present in the bio-oil used in this study. [1]
- The phase conversion curves of the PL/MS/water systems can be greatly affected by the presence of levoglucosan in the system when the water content in the ternary system is low

[1] *Yun Yu*, Yee Wen Chua, and Hongwei Wu* Energy Fuels, 2016, 30 (5), pp 4145–4149.*

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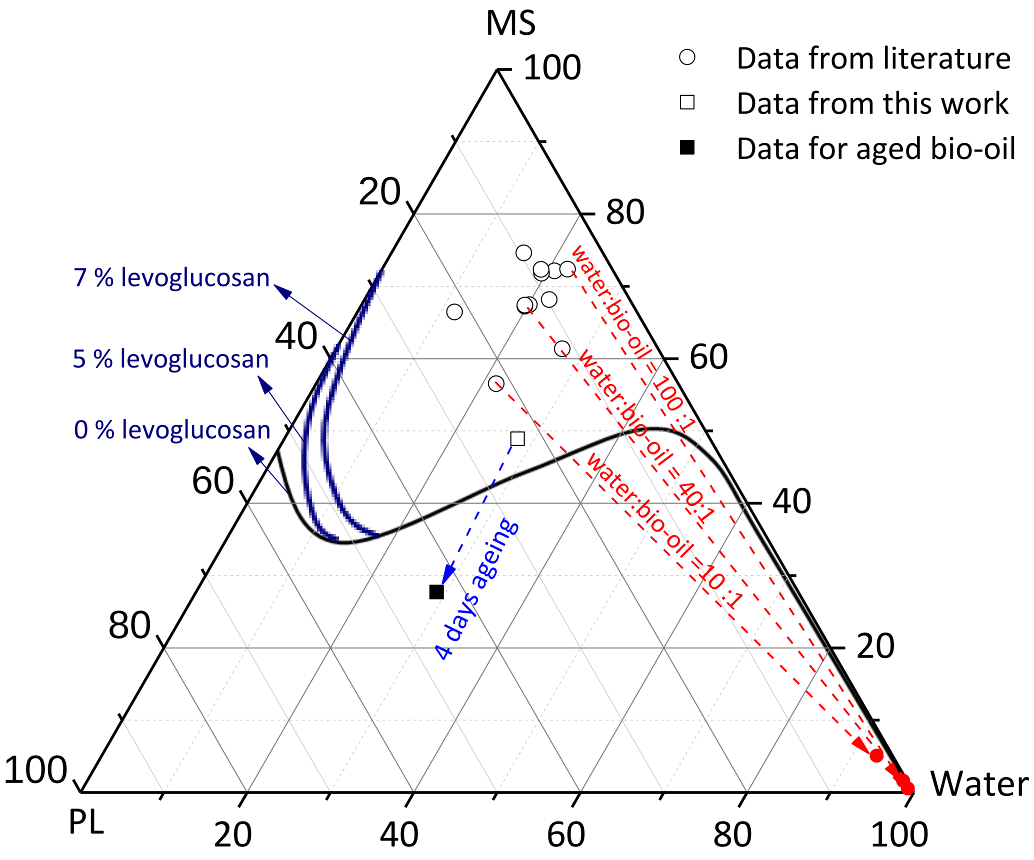
Applications of the Ternary Phase Diagram.



- A two-phase bio-oil was easily formed even at a low water-to-oil ratio of 10/1
- Accelerated aging experiment of the bio-oil sample was carried out at 80 °C for 4 days.
- The ternary phase diagrams can be very useful in estimating the aging process of bio-oil and the amount of solvent required to prevent phase separation during bio-oil storage

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Conclusion

- A mixed solvent (MS) is developed based on the composition of bio-oils in the existing literature
- Several ternary phase diagrams of PL/MS/water systems are constructed for PL and its fractions, and their solubilities in various MS/water mixtures are also estimated.
- The solubilities of different PL fractions indicate that PL solubility is influenced by its average molecular weight
- The presence of free sugar (i.e., levoglucosan) also affects the phase stability of the PL/MS/water system, but only at low water content.

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THANK YOU!