

Experimental and computer aided solubility quantification of diverse lignins and performance prediction

Olumoye Ajao^a, Marzouk Benali^{†a} and Naïma El Mehdi^b

^aNatural Resources Canada, CanmetENERGY, P.O. Box 4800, Varennes, Quebec J3X 1S6, Canada

^bCEPROCQ, 6220 Sherbrooke East, Montreal, Quebec, H1N 1C1, Canada

[†]E-mail address: marzouk.benali@canada.ca (M. Benali)

Electronic Supplementary Information (ESI) for Chemical Communications

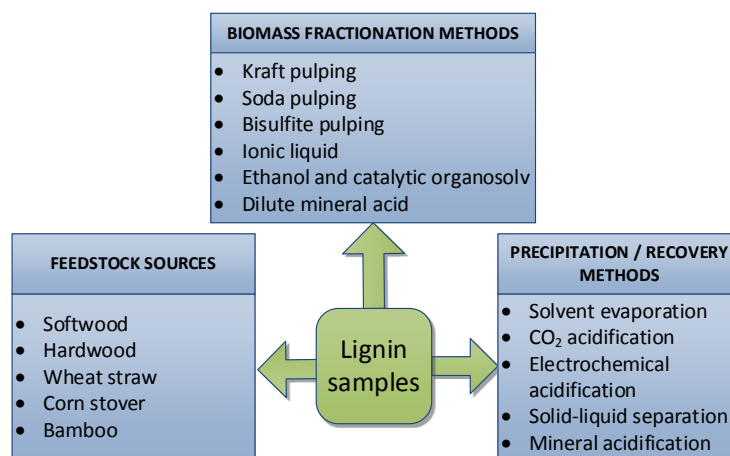


Figure ESI-1. Overview of the feedstock, fractionation and recovery methods for the investigated lignins

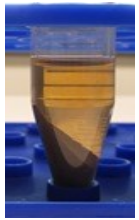
Lignin	Insoluble (Hexane)	Partially Soluble (Butanol)	Soluble (Aniline)
CO ₂ precipitated Kraft lignin 1-softwood			
Ionic Liquid Lignin			
CO ₂ precipitated Kraft lignin 2-softwood			

Figure ESI-2. Examples of approach for classifying different lignins as insoluble, partially soluble and soluble

Hansen Solubility Parameter in Practice (HSPiP) calculation approach

The default algorithm embedded in the software for determining the Hansen Solubility Parameters (sphere centre coordinates and radius) is based on the quality of fit or desirability function as described by Hansen^I and Gharagheizi^{II}. The input data (soluble “1”, insoluble “0” or partially soluble “2”) originates from experimental evaluation. The form of the function is as shown:

$$Data\ Fit = \sqrt[n]{A_1 \times A_2 \times A_3 \times \dots \times A_n}$$

With n representing the number of solvents represented by experimental data in the correlation, the *Data Fit* tends to 1 with improving fit and reaches 1.0 when all good solvents are included within the sphere and all bad solvents are outside because:

$$A_i = e^{(error\ distance)}$$

The sensitivity of the sphere to the uncertainties represented by the solvents in which each lignin is partially soluble is validated by alternating the results between soluble and insoluble to ensure their impact is negligible.

The total solubility parameter (δ_T) of a compound can be determined from the three-dimensional solubility parameters using equation (1). The solubility parameter difference (R_a) is used to compare two substances (within the Hansen space and is defined in equation (2)). Lastly, another essential parameter known as the RED number is also used to characterise solute-solvent interactions and can be calculated using equation (3). The term R_0 is frequently known as the radius of a Hansen solubility sphere. Suitable solvents for a specific solute will have $RED \leq 1$.

$$\delta_T^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \quad (1)$$

$$R_a = \sqrt{4(\delta_{D2} - \delta_{D1})^2 + (\delta_{P2} - \delta_{P1})^2 + (\delta_{H2} - \delta_{H1})^2} \quad (2)$$

$$RED = \frac{R_a}{R_0} \quad (3)$$

^I C. M. Hansen, Hansen solubility parameters: a user's handbook, CRC press, Boca Raton, 2007.

^{II} F. Gharagheizi, Journal of Applied Polymer Science, 2007, 103, 31–36.

Table ESI-1. List of lignins used to characterise the differences in the *Hansen* solubility parameters, and their molecular weight distributions

Lignin sample number	Biomass fractionation	Feedstock source	Molecular weight				Solubility parameters			
			M _n (g/mol)	M _w (g/mol)	M _z (g/mol)	M _w /M _n	δ _D	δ _P	δ _H	R _O
1	Kraft	Softwood	1497	7319	85310	4.90	20.93	16.98	15.71	15.00
2	Kraft	Softwood	2051	14899	137380	7.30	21.24	16.80	15.39	15.20
3	Kraft	Hardwood	1397	6393	88910	4.60	20.95	17.22	15.13	15.20
4	Kraft	Softwood	1294	8992	121200	6.90	19.72	18.42	16.23	13.50
5	Organosolv	Hardwood	1245	4488	74640	3.60	21.83	21.26	11.93	19.90
6	Kraft	Softwood	1409	12161	174290	8.60	24.40	15.31	20.03	19.90
7	Kraft	Softwood	1515	8554	94470	5.60	20.89	16.34	15.39	14.40
8	Kraft	Softwood	1537	7301	95570	4.80	20.45	16.54	15.42	13.90
9	Soda	Wheat straw	1096	5210	111520	4.70	20.48	16.39	15.58	13.90
10	Kraft	Softwood	2053	14684	129990	7.20	20.90	16.82	15.44	14.50
11	Dilute mineral acid	Wheat straw	1447	11384	151910	7.90	18.65	15.89	12.37	9.50
12	Dilute mineral acid	Softwood	1566	9840	153660	6.30	20.04	18.92	16.14	14.00
13	Kraft	Softwood	1329	5276	40650	4.00	21.24	16.34	15.33	14.90
14	Kraft	Softwood	1824	11341	87930	6.22	12.41	24.24	24.04	19.90
15	Bisulfite	Softwood	N.D.	N.D.	N.D.	N.D.	12.17	20.80	30.16	14.60
16	Dilute mineral acid	Softwood	549	2745	41870	5.01	19.82	15.19	17.44	11.20
17	Dilute mineral acid	Wheat straw	656	3237	55020	4.94	14.89	22.18	19.80	13.50
18	Dilute mineral acid	Wheat straw	830	5236	79640	6.31	20.48	19.58	16.55	14.80
19	Dilute mineral acid	Bamboo	1274	9546	106480	7.49	14.94	22.19	19.73	13.50
20	Dilute mineral acid	Bamboo	1406	11620	102430	8.27	20.48	19.33	16.56	14.60
21	Kraft	Softwood	1425	10615	92450	7.45	21.19	2.39	33.45	19.90
22	Kraft	Softwood	1316	7983	76170	6.07	26.60	8.33	19.92	19.30
23	Kraft	Softwood	1812	8292	49180	4.58	20.98	16.58	15.58	14.70
24	Kraft	Softwood	2045	11747	73200	5.74	20.18	18.07	15.95	13.90
25	Ionic Liquid	Corn Stover	754	1625	3460	2.16	13.30	24.00	17.11	14.50
26	Ionic Liquid	Corn Stover	1335	4708	61000	3.53	18.83	11.62	15.37	7.60
27	Kraft	Softwood	2488	16716	95630	6.72	20.49	17.02	15.65	14.30
28	Kraft	Softwood	2127	19337	124960	9.09	14.08	26.34	25.26	19.90
29	Biological	Softwood	1024	5041	70150	4.92	18.95	10.95	9.78	5.80
30	Steam explosion	Hardwood	1469	6103	70110	4.15	20.09	18.16	16.06	13.90
31	Kraft	Softwood	2093	9025	53150	4.31	20.74	16.74	15.69	14.60
32	Kraft	Softwood	1848	7336	48840	3.97	20.75	16.66	15.63	14.50
33	Kraft	Hardwood	1226	4361	59690	3.56	19.21	22.86	11.35	19.90
34	Organosolv	Hardwood	1382	3340	28140	2.42	20.75	20.60	13.57	17.80
35	Mechanical	Hardwood	4185	22993	89190	5.49	14.20	19.71	15.60	9.80
36	Kraft	Softwood	2108	10989	68050	5.21	21.97	19.35	15.78	16.70
37	Kraft	Softwood	N.D.	N.D.	N.D.	N.D.	11.98	20.55	30.32	14.50
38	Kraft	Hardwood	1285	3761	46610	2.93	20.52	17.31	15.19	14.70
39	Kraft	Softwood	2006	10174	52540	5.07	20.38	16.84	14.95	14.10
40	Kraft	Softwood	2057	13352	84250	6.49	22.59	16.78	14.60	17.30
41	Kraft	Softwood	2459	14216	82780	5.78	21.26	24.09	14.56	19.40
42	Kraft	Softwood	781	2532	32400	3.24	12.17	20.81	30.48	14.60
43	Kraft	Hardwood	1441	6188	56290	4.29	21.13	16.96	15.53	15.20
44	Biorefinery	Softwood	N.D.	N.D.	N.D.	N.D.	14.62	19.55	15.69	9.8
45	Biorefinery	Softwood	N.D.	N.D.	N.D.	N.D.	21.25	12.34	17.05	12.40

Table ESI-2. List of solvents used for lignin Hansen Solubility Parameters estimation, their respective HSPs and the experimental observation (S: Soluble; I: Insoluble; and P: Partially Soluble), the descriptions of the lignin sample number remain the same as stated in Table ESI-1.

Solvent	HSP			Lignin sample number																																												
	δ_D	δ_P	δ_H	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Acetic acid	14.5	8.0	13.5	I	I	I	I	I	I	I	I	I	I	P	I	I	I	I	I	I	I	I	P	P	I	I	I	I	P	P	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	P	P
Acetic anhydride	16.0	11.7	10.2	P	P	P	P	P	P	P	P	P	I	P	P	I	I	I	I	P	I	I	I	I	P	P	I	I	P	I	I	P	P	P	S	P	I	P	I	S	P	P	P	I	P	P	P	
Acetone	15.5	10.4	7.0	S	P	S	S	S	S	P	P	S	S	P	P	S	S	I	P	P	P	P	P	P	P	P	P	P	S	S	I	P	P	S	S	S	P	P	P	S	S	S	S	P	P	S	P	P
Acetonitrile	15.3	18.0	6.1	P	P	P	P	S	P	P	P	P	P	I	I	P	I	I	I	I	I	I	P	P	P	P	I	P	P	P	I	P	P	P	S	S	I	P	I	S	P	P	P	I	P	P	P	
Aniline	20.1	5.8	11.2	S	S	S	P	S	P	S	S	S	S	P	P	S	I	I	I	I	I	I	I	I	S	S	I	P	S	I	I	S	S	S	S	S	P	P	I	S	S	S	S	I	S	P	S	
Benzaldehyde	19.4	7.4	5.3	P	P	S	P	S	P	P	P	P	P	I	I	P	I	I	I	I	I	I	I	I	P	P	I	I	P	I	I	P	P	P	S	S	I	P	I	S	S	P	P	I	S	P	P	
Bromonaphthalene	20.6	3.1	4.1	S	S	S	P	S	S	S	P	S	S	I	P	S	I	I	I	I	I	I	I	I	S	P	I	P	S	I	I	P	S	S	S	S	P	P	I	S	S	S	P	I	S	P	P	
butanol	16.0	5.7	15.8	S	S	S	P	S	P	S	S	S	S	I	P	S	I	I	I	I	I	I	I	I	S	S	I	P	P	I	-	P	S	S	S	S	I	S	I	S	S	S	P	I	S	P	P	
Chloroform	17.8	3.1	5.7	I	I	I	I	S	P	I	I	P	I	I	I	P	I	I	S	I	I	I	I	S	S	I	I	I	I	I	I	I	I	P	I	I	P	P	I	I	I	P	P	I	I	I	P	P
Cyclohexane	16.8	0.0	0.2	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I		
Dichloromethane	17.0	7.3	7.1	P	P	S	P	S	P	P	I	P	P	I	I	P	I	I	I	I	I	I	I	I	P	I	I	I	I	I	I	I	P	P	P	S	S	I	P	I	P	P	P	P	I	P	P	
Diethyl ether	14.5	2.9	4.6	P	I	I	I	P	I	I	I	I	I	I	I	P	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	-	I	I	P	P	P	I	I	I	P	P	I	I	I	I	I	
Diethylene glycol monomethyl ether	16.2	7.8	12.6	S	S	S	S	S	S	S	S	S	S	P	S	S	S	I	P	P	P	P	P	P	P	S	S	P	P	S	P	-	S	S	S	S	S	P	S	I	S	S	S	S	I	S	P	S
Dimethyl carbonate	15.5	8.6	9.7	P	P	P	P	S	P	P	P	P	P	I	I	P	I	I	I	I	I	I	I	I	P	P	I	I	P	I	-	P	P	P	S	P	I	P	I	P	P	P	P	I	P	P	P	
Dimethyl formamide (DMF)	17.4	13.7	11.3	S	S	S	S	S	S	S	S	S	S	S	S	S	S	P	S	S	S	S	S	P	P	S	S	P	S	S	P	P	S	S	S	S	S	P	S	P	S	S	S	S	I	S	P	S
Dimethyl sulfoxide (DMSO)	18.4	16.4	10.2	S	S	S	S	S	S	S	S	S	S	S	S	S	S	P	S	S	S	S	S	P	S	S	S	S	S	S	S	P	S	S	S	S	S	P	S	P	S	S	S	S	P	S	S	
Distilled Water	15.5	16.0	42.3	I	I	I	P	I	S	I	I	I	I	I	I	I	S	S	P	P	P	P	P	S	S	I	I	P	P	I	S	P	I	I	I	I	I	I	I	S	I	I	P	I	S	I	I	I
Ethanol	15.8	8.8	19.4	S	P	S	P	S	P	S	S	S	S	P	P	S	I	I	I	I	P	P	P	I	I	S	P	I	P	P	I	I	P	S	S	S	S	I	P	I	S	S	P	P	I	S	P	P
Ethanolamine	17.0	15.5	21.0	S	S	S	S	S	S	S	S	S	S	S	S	S	S	P	S	S	S	S	S	P	P	S	S	S	S	S	S	-	S	S	S	S	S	P	S	P	S	S	S	S	P	S	S	S
Ethyl acetate	15.8	5.3	7.2	P	P	P	P	P	P	P	P	P	P	I	I	P	I	I	I	I	I	I	I	I	P	P	I	I	P	I	I	P	P	P	S	P	I	P	I	P	P	P	P	I	P	P	P	
Ethylene glycol	17.0	11.0	26.0	S	S	S	S	S	S	S	S	S	S	P	S	S	S	S	S	S	S	S	S	S	S	S	S	P	P	S	S	-	P	S	S	S	S	P	S	S	S	S	S	S	S	S	P	S
Formic acid a 90%	14.6	10.0	14.0	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	P	S	S	S	S	S	S	S	S	S	S	S	
Glycerol	17.4	11.3	27.2	S	S	S	P	S	S	I	P	P	S	I	-	S	P	P	P	P	P	P	P	S	P	S	P	P	P	S	S	-	S	S	S	S	S	P	S	I	S	P	P	P	P	S	I	P
Hexane	14.9	0.0	0.0	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	I	
Isopropanol	15.8	6.1	16.4	P	P	P	P	P	I	P	P	P	P	I	P	P	I	I	I	I	I	I	I	I	P	P	I	I	P	I	I	I	P	P	P	P	I	P	I	P	P	P	P	I	P	P	P	
Methanol	14.7	12.3	22.3	S	S	S	S	S	S	S	S	S	S	P	P	S	S	P	P	P	P	P	P	P	P	S	S	P	P	S	S	I	S	S	S	S	S	P	P	P	S	S	S	S	P	S	P	P
Methyl isobutyl ketone	15.3	6.1	4.1	P	P	P	P	P	P	P	I	P	P	I	I	P	I	I	I	I	I	I	I	I	P	P	I	I	P	I	I	P	P	P	S	P	I	P	I	P	P	P	P	I	P	P	P	
Pyridine	19.0	8.8	5.9	S	S	S	S	S	S	S	S	S	S	S	S	S	I	I	P	P	S	P	S	I	I	S	S	P	P	S	I	-	S	S	S	S	S	P	S	I	S	S	S	S	I	S	S	S
THF (tetrahydrofuran)	16.8	5.7	8.0	S	S	S	P	S	S	S	S	S	S	P	P	S	I	I	P	I	P	I	I	I	I	S	S	I	P	S	I	-	S	S	S	S	S	I	S	I	S	S	S	S	I	S	P	S

Acknowledgements

The authors are grateful to all companies that provided the lignin samples used in this study and for the financial support received from the Program on Energy Research and Development (PERD-3A03-003) and the Forest Innovation Program of the Canadian Forest Service (FIB-BC-.3), at Natural Resources Canada. The authors are also grateful for the technical support provided by Andrea M. Restrepo and Amel Mouda Azzem from the Quebec Research Centre of Chemical Processes (CEPROCQ).