

## Supporting Information

# Preparation of concrete water-reducer via fractionation and modification of lignin extracted from pine wood by formic acid

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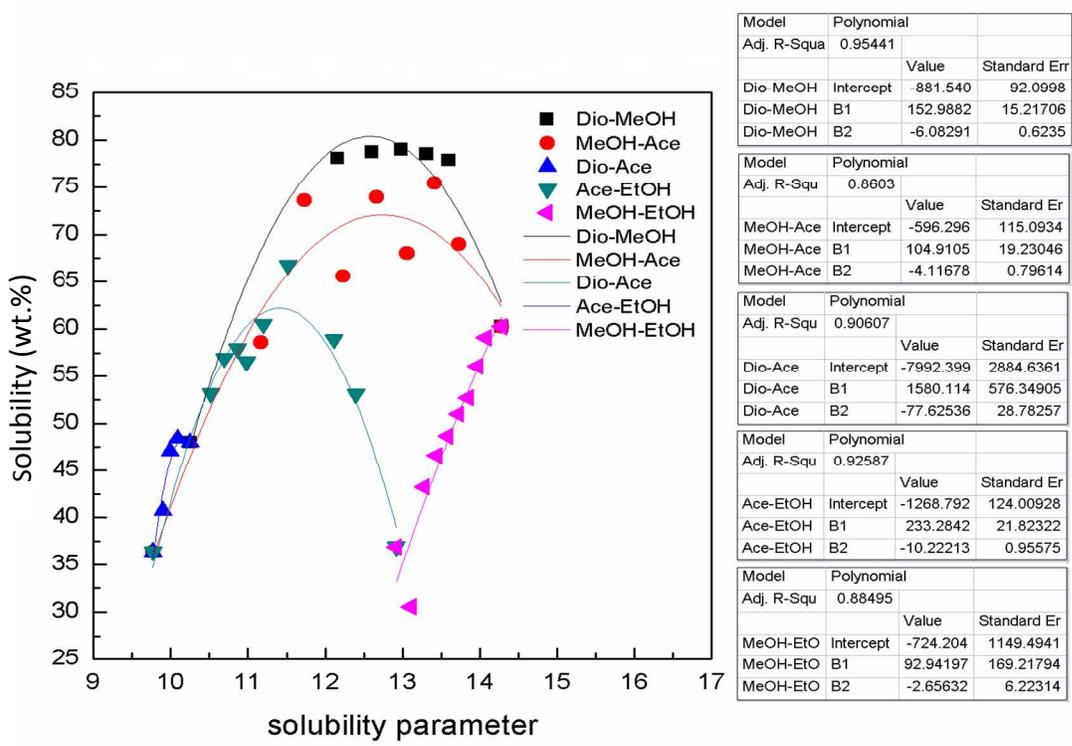
Including:

Pages S1-S4; Figure S1; Tables S1-S2.

**Table S1** Solubility of alkaline lignin in different organic solvents

| <b>Solvents</b>   | <b>Volume ratio</b> | <b>Mole ratio</b> | <b>Solubility parameter (<math>\delta</math>)</b> | <b>Solubility (wt.%)</b> |
|-------------------|---------------------|-------------------|---|--------------------------|
| Dioxane: Methanol | 6:4                 | 0.71143           | 12.60475  | 78.72                    |
| Dioxane: Methanol | 4:6                 | 0.31619           | 13.31186  | 78.53                    |
| Dioxane: Methanol | 3:7                 | 0.20327           | 13.59922  | 77.89                    |
| Dioxane: Methanol | 7:3                 | 1.10667           | 12.16297  | 78.08                    |
| Dioxane: Methanol | 5:5                 | 0.47429           | 12.98352  | 79.00                    |
| Methanol: Acetone | 7:3                 | 4.18213           | 13.4097   | 75.46                    |
| Methanol: Acetone | 6:4                 | 2.68851           | 13.05728  | 68.00                    |
| Methanol: Acetone | 5:5                 | 1.79234           | 12.66487  | 73.96                    |
| Methanol: Acetone | 4:6                 | 1.19489           | 12.22523  | 65.58                    |
| Methanol: Acetone | 3:7                 | 0.76815           | 11.72931  | 73.60                    |
| Methanol: Acetone | 8:2                 | 7.16936           | 13.72794  | 68.98                    |
| Methanol: Acetone | 2:8                 | 0.44809           | 11.16554  | 58.61                    |
| Dioxane: Acetone  | 3:7                 | 0.36478           | 9.898296  | 40.74                    |
| Dioxane: Acetone  | 5:5                 | 0.85116           | 9.990703  | 47.09                    |
| Dioxane: Acetone  | 7:3                 | 1.98604           | 10.08925  | 48.40                    |
| Acetone: Ethanol  | 2:8                 | 0.20081           | 12.39322  | 53.10                    |
| Acetone: Ethanol  | 3:7                 | 0.34425           | 12.11331  | 58.91                    |
| Acetone: Ethanol  | 6:4                 | 1.20489           | 11.19865  | 60.50                    |
| Acetone: Ethanol  | 2:1                 | 1.60651           | 10.97851  | 56.58                    |
| Acetone: Ethanol  | 3:1                 | 2.40977           | 10.69382  | 56.94                    |
| Acetone: Ethanol  | 4:1                 | 3.21303           | 10.51768  | 53.17                    |
| Acetone: Ethanol  | 1:1                 | 0.80326           | 11.51684  | 66.74                    |
| Acetone: Ethanol  | 7:3                 | 1.87427           | 10.86593  | 57.94                    |
| Methanol: Ethanol | 8:2                 | 5.77197           | 14.07917  | 59.11                    |
| Methanol: Ethanol | 7:3                 | 3.36698           | 13.96857  | 56.09                    |
| Methanol: Ethanol | 6:4                 | 2.16449           | 13.85023  | 52.72                    |
| Methanol: Ethanol | 5:5                 | 1.44299           | 13.72331  | 51.00                    |
| Methanol: Ethanol | 4:6                 | 0.96200           | 13.58683  | 48.67                    |
| Methanol: Ethanol | 3:7                 | 0.61843           | 13.43968  | 46.63                    |
| Methanol: Ethanol | 2:8                 | 0.36075           | 13.28055  | 43.26                    |
| Methanol: Ethanol | 1:9                 | 0.16033           | 13.10792  | 30.56                    |
| Dioxane           | -                   | -                 | 10.25   | 47.99                    |
| Methanol          | -                   | -                 | 14.28   | 60.24                    |
| Acetone           | -                   | -                 | 9.77  | 36.37                    |

|                  |   |   |       |       |
|------------------|---|---|-------|-------|
| Ethanol          | - | - | 12.92 | 36.92 |
| n-propyl alcohol | - | - | 11.97 | 23.55 |



**Figure S1** The relationship between solubility of alkaline lignin and solvent solubility parameter

**Table S2** Properties and performance of FAL samples as water reducer

| Solvents                           | Solubility<br>wt. % | Lignin<br>fraction | Mw       | Mn      | PDI        | SD <sup>a</sup><br>(mmol/g) | Fluidity (mm)           |                       |
|------------------------------------|---------------------|--------------------|----------|---------|------------|-----------------------------|-------------------------|-----------------------|
|                                    |                     |                    |          |         |            |                             | Unmodified <sup>b</sup> | Modified <sup>c</sup> |
| Dioxane:<br>methanol<br>=1:1(v/v)  | 80.5                | I-FAL              | 3528±150 | 1093±21 | 3.226±0.08 | 1.37±0.03                   | 105 ± 1                 | 160 ± 1               |
|                                    |                     | S-FAL              | 1786±40  | 620±10  | 2.881±0.01 | 1.64±0.04                   | 86 ± 1                  | 177 ± 2               |
| Methanol:<br>acetone=<br>7:3 (v/v) | 43.5                | I-FAL              | 2343±60  | 621±10  | 3.771±0.04 | 1.14±0.02                   | 91 ± 1                  | 136 ± 1               |
|                                    |                     | S-FAL              | 1295±40  | 484±12  | 2.675±0.03 | 1.40±0.01                   | 130 ± 1.5               | 167 ± 2               |
| Acetone<br>(pure)                  | 30.2                | I-FAL              | 5879±160 | 1024±25 | 5.739±0.02 | 1.32±0.01                   | 122 ± 1.5               | 158 ± 1.5             |
|                                    |                     | S-FAL              | 844±30   | 293±10  | 2.881      | 1.63±0.04                   | 93 ± 1                  | 178 ± 2               |
| Methanol<br>(pure)                 | 21.8                | I-FAL              | 4254±140 | 841±15  | 5.054±0.08 | 1.63±0.05                   | 85 ± 1                  | 172 ± 2               |
|                                    |                     | S-FAL              | 832±25   | 338±10  | 2.461      | 0.98±0.01                   | 115 ± 1                 | 122 ± 1               |
| Ethanol<br>(pure)                  | 16.1                | I-FAL              | 5000±170 | 1027±20 | 4.87±0.06  | 1.38±0.02                   | 95 ± 1                  | 162 ± 2               |
|                                    |                     | S-FAL              | 1855±45  | 539±15  | 3.441±0.02 | 0.79±0.01                   | 92 ± 1                  | 98 ± 1                |
| -                                  | -                   | FAL <sup>d</sup>   | 1750±40  | 492±15  | 3.561±0.03 | 1.22±0.02                   | 117 ± 1                 | 147 ± 2               |

<sup>a</sup> Sulfonation degree; <sup>b</sup> The fluidity with unmodified FAL; <sup>c</sup> The fluidity with modified FAL; <sup>d</sup> the one without fractionation by organic solvents.