## Supporting Information

## Synthesis and Characterization of Bio-pitch from Bio-oil

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#### 1. Properties of bio-oil and coal-tar-pitch used in the study

The biomass was fed into the reactor at a typical rate of typically 25–30 kg/h on a continuous basis. The average residence time of the solid particles inside the reactor was approximately 12–15 minutes. Detailed physical and chemical analysis of the bio-oil was performed at CanmetENERGY (Ottawa, Canada) and the results were summarized in Table S1.

Properties	Results	Method
Density @ 20 °C (g/cm <sup>3</sup> )	1.18	ASTM D4052
Kinetic viscosity @ 40 °C (Pa·s)	532.8	ASTM D445
Solid content by filtration (wt %)	0.46	ASTM D7579
pH	2.53	In house
Water content (wt %)	9.78	ASTM E203
Ash (wt %)	0.016	ASTM D482
C (wt %)	63	ASTM D5291 modified
H (wt %)	7.2	ASTM D5291 modified
N (wt %)	0.16	ASTM D5291 modified
O (wt %)	29.6	ASTM D5291 modified
Mn (g/mol)	164	GPC
Mw (g/mol)	306	GPC
Polydispersity Index (PDI)	1.9	GPC

Table S1. Properties of bio-oil used in the study <sup>a</sup>

<sup>*a*</sup> The method information is provided by CanmetENERGY (Ottawa, Canada).

The bio-pitch samples were synthesized using a vacuum distillation process, as drawn in Figure S1.



Figure S1. Set-up of the vacuum distillation of bio-oil used in this study

Table S2. Experimental conditions used in this study for synthesis bio-pitch samples

Experimental conditions	BP-1	BP-2	BP-3	BP-4	BP-5	BP-6	BP-7	BP-8	BP-9	BP-10
Final temperature (°C)	160	180	200	220	240	260	180	180	180	180
Holding time (h)	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	9.5	25.5
Pressure (Torr)	35	35	35	35	35	35	10	50	35	35

A typical CTP used in the carbon anode industry <sup>1-3</sup> was used as a reference pitch for comparison purpose. Its physical properties and chemical composition are characterized and given in Table S2.

#### Table S3. Physical properties and chemical composition of coal-tar-pitch

Pitch Softening properties point (°C)		Density Coking (g/cm <sup>3</sup> ) value	Coking value	Quinoline insoluble	Viscosity Elemental analysis (%) at 178 °C					Aromaticity	PAH (wt %)
properties	point (°C)	(g/cm/)	(wt %)	(wt %)	(Pa·s)	С	Н	0	N	-	
СТР	110.0	1.35	65.24	16.00	2.81	92.49	4.10	2.37	1.04	0.9995	12.12

#### 2. Characterization of bio-pitch

*Helium density*. The density of the samples was measured using a helium gas pycnometer (Micromeritics, AccuPyc II 1340). Before the analysis, the samples were crushed manually using a mortar and pestle, then the fraction passing a 150  $\mu$ m sieve was collected. Pitch samples (5–7 g) were weighed in a stainless-steel cell (10 mL) and placed in the pycnometer. The density was obtained by dividing the mass of the sample to the volume obtained by the pycnometer. For each type of pitch, an average of three different samples was reported.

*Softening point*. The produced bio-pitch samples were analyzed using the "Ring and Ball Method", ASTM D36/D36M-14 Standard Test in a glycerol bath. The bio-pitch sample (1 g) was used for each test. The heating rate of the glycerol bath used for softening point measurement was 5 °C/min.

*Quinoline insoluble*. Solubility of pitch in quinoline was determined according to ASTM D2318-15 standard method. The bio-pitch (1 g) was placed in a 100 mL flask with quinoline (25 mL), and then heated in a water bath to 75 °C for 20 min. The dry Celite Analytical Filter Aid (CAFA) (1 g) was used to filter out the insoluble solid particles. The solution was filtered with Celite Analytical Filter Aid (CAFA) and the residue washed with toluene and acetone for complete quinoline removal. Each experiment was repeated three times.

*Viscosity*. The rheological properties of samples were obtained using a Discovery Hybrid Rheometer (DHR-3), with a 20 mm Peltier Parallel plates geometry. The gap thickness was 1000  $\mu$ m. In this study, a typical CTP with softening point of 110 °C used in the carbon anode industry was used as a reference pitch for comparison purpose. As the mixing temperature during anode making process is 178 °C, the viscosity of the samples was measured at 178 °C.

*Coking value*. The produced bio-pitch sample (1 g) was heated for two hours at 550 °C in an electric furnace, outlined to ASTM D4715-98 standard test method. The percentage of residue was reported as the coking value. Each experiment was repeated three times.

*PAH*. The CTP or BP powder (0.1000 g) was sonicated in dichloromethane (5.00 mL) for 30 min to ensure the full extraction of PAH. The suspension was filtered through a membrane filter (0.45  $\mu$ m of aperture) to obtain a clear solution. The blank sample was prepared by the same method. Subsequently, the PAH content analysis was performed by using a gas chromatography (GC) system (Agilent Technologies, 6890N Network GC System). The calibration curve was built using PAH solution mix (0.2 mg/mL in CH<sub>2</sub>Cl<sub>2</sub>/MeOH (1:1)) obtained from Accustandard. The sample (1.0  $\mu$ L) was injected in the splitless mode at an injection temperature of 300 °C. The column temperature was initially held at 40 °C for 1 min, raised to 120 °C at the rate of 25 °C/min, then to 160 °C at the rate of 10 °C/min, and finally to 275 °C at the rate of 5 °C/min, then kept at final temperature for 15 min. The detector temperature was kept at 280 °C. Helium was used as carrier gas at a constant flow rate of 1 mL/min.

Gel permeation chromatography (GPC) analysis. GPC analysis were used to determine the molar mass distribution and the weight-average molar masses of the produced bio-pitches. Bio-pitch with lower polymerization degree showed almost total solubility in tetrahydrofuran (THF). The sample was dissolved in THF (0.5 mg/mL), THF was used at an elution flow rate of 1.0 mL/min and 1000 psi. Analyses were carried out in two PLgel 10 µm MIXED-B LS columns (Varian, Inc) coupled with a MODEL 441 UV absorbance detector (WATERS ASSOCIATEDS) at 254 nm and a Chromatopac integrator with a software (ASTRA) for GPC calculations. The polystyrene standards (Mw: 162–657000 g/mol) were used to build the calibration curve.

*Elemental analysis*. The elemental analysis was performed using a Thermo Scientific Flash 2000 Elemental Analyzer to determine the C, H, N, S contents and the C/H ratio of the produced biopitches. Oxygen content was calculated by the subtraction of C, H, N, and S elements from the total.

*FTIR analysis*. Infrared spectra of the produced bio-pitches were obtained using a Golden Gate single reflection attenuated total reflection system (Specac, Pleasantville, NY) fitted with a diamond crystal. The infrared spectra were recorded with a Nicolet iS50 Fourier transform spectrometer (Thermo-Nicolet, Madison, WI) equipped with a deuterated triglycine sulfate (DTGS) detector and a germanium coated KBr beam splitter. A total of 64 interferograms were acquired, co-added and Fourier transformed, using a Happ–Genzel apodization function to give a spectral resolution of 4 cm<sup>-1</sup> in the spectral range of 4000 to 500 cm<sup>-1</sup>. Each experiment was repeated twice.

<sup>1</sup>*H* NMR and <sup>13</sup>*C* NMR. The sample (50 mg) was dissolved in (CD<sub>3</sub>)<sub>2</sub>SO (0.5 mL) at room temperature. Subsequently, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Varian Inova 400 MHz spectrometer and a Bruker AC 300 MHz spectrometer at 25 °C, respectively. Relaxation time of 1 second, and 45° of pulse angle were used for the signal acquisition. For <sup>1</sup>H NMR, the scan range was -2.0-14.0 ppm with 64 scans. For <sup>13</sup>C NMR (decoupled with <sup>1</sup>H), the scan range was -15.0-235.0 ppm with 18000 scans. Chemical shifts are given in ppm, and residual solvent peaks ( $\delta_{\rm H} = 2.50$  ppm, and  $\delta_{\rm C} = 39.52$  ppm for (CD<sub>3</sub>)<sub>2</sub>SO) were used as reference. Different sets of parameters (e.g. relaxation times, acquisition times, pulse angle and temperatures from 25 °C to 110 °C) were tested, however, no obvious improvements of spectra quality (higher resolution and intensity) was observed. Thus, all NMR experiments were run under classical parameters as default. *GC-MS analysis*. Approximately 50 mg of condensed liquid was dissolved in 1 mL of  $CH_2Cl_2/MeOH$  (1:1). Then, the gas chromatography/mass spectrometry (GC-MS) analysis was performed on a Thermo Scientific ITQ 900 GC/MS instrument. The sample (2.0 µL) was injected by a TriPlus autosampler at an injection temperature of 220 °C with a split flow of 50 mL/min (split ratio 50%). The column temperature was raised from 80 °C to 280 °C at the rate of 20 °C/min, then kept at final temperature for 4 min. Helium was used as carrier gas at a constant flow rate of 1 mL/min. Electron impact ionization was used for the MS detection with the parameters as follows: starting time: 2 min, scan range of masses: 50–500, positive ion mode, ion source temperature: 200 °C.

*MALDI-TOF mass spectrometry and ESI-TOF mass spectrometry analysis.*<sup>49</sup> The MALDI-TOF (matrix assisted laser desorption ionization-time of flight) mass spectrum was carried out on a Shimadzu Biotech mass spectrometer using a nitrogen laser for MALDI (wavelength = 337 nm). 100 shots were accumulated for the spectra at a 20 kV source voltage with pulsed extraction at – 2.1 kV, and the reflectron lens potentials at 6.0 kV. Polyethylene glycol-2000 was used as external calibrant. The bio-pitch samples were dissolved in acetone at concentration of 4 mg/mL. 2,5-Dihydroxybenzoic acid (10 mg/mL in acetone) was used as matrix. LiCl (10 mg/mL in methanol) was used as cationization agent. Trifluoroacetic acid (TFA, 0.5 vol % in EtOH) was used as additive. 20  $\mu$ L of bio-pitch solution, 20  $\mu$ L of matrix solution, 20  $\mu$ L of test solution and 10  $\mu$ L of TFA solution were mixture together to obtain the test solution. 1  $\mu$ L of test solution was dropped on the MALDI-TOF steel plate and dried. Subsequently, the spectrum was recorded in positive ion mode. ESI-TOF (electrospray ionization time-of-flight) mass spectrometry was performed on an Agilent 6210 mass spectrometer using electrospray ionization at 4 kV and fragment voltage at 175 V in positive ion mode. 5 mmol/L of ammonium formats in methanol/H<sub>2</sub>O (75:25) was used

as eluent. The bio-pitch samples were dissolved in EtOH at concentration of 0.1 mg/mL for the test.

## 3. PAH content in pitch samples from GC



Figure S2. Structure for coal-tar-pitch.<sup>10</sup>

#### Table S4. The PAH content in pitch samples from GC <sup>a</sup>

Sample Name	СТР	BP-1	BP-2	BP-3	BP-4	BP-5	BP-6	BP-7	BP-8	BP-9	BP-10
Napthalene (wt %)	-	-	-	-	-	0.18	-	-	-	-	-
Acenaphthalene (wt %)	0.21	0.24	0.41	0.32	0.19	-	-	0.61	0.35	0.41	-
Acenaphthene (wt %)	-	-	-	-	0.13	-	-	-	-	-	-
Fluorene (wt %)	-	-	-	-	-	-	-	-	-	-	-
Phenanthrene (wt %)	0.18	-	-	-	-	-	-	-	-	-	-
Anthracene (wt %)	-	0.69	0.91	0.72	0.70	0.59	0.31	1.00	0.77	0.61	0.30
Fluoranthene (wt %)	0.79	-	0.08	0.07	-	-	-	-	-	-	-
Pyrene (wt %)	0.88	-	-	-	-	-	-	-	-	-	-
Benz[ <i>a</i> ]anthracene (wt %)	1.21	-	-	-	-	-	-	-	-	-	-
Chrysene (wt %)	0.74	-	0.09	0.08	0.12	0.06	0.05	0.03	0.10	0.12	0.05
Benz[b]fluoranthene (wt %)	1.78	0.79	-	-	-	-	-	-	-	-	-
Benz[k]fluoranthene (wt %)	0.79	-	-	-	-	-	-	-	-	-	-
Benz[ <i>a</i> ]pyrene (wt %)	1.85	-	-	-	-	-	-	-	-	-	-
Indeno[ <i>1,2,3,c,d</i> ]-pyrene (wt %)	1.86	-	-	-	-	-	-	-	-	-	-

Total PAH (wt%)	12.19	1.71	1.50	1.20	1.14	0.83	0.36	1.64	1.22	1.14	0.35
Benz[ $g,h,i$ ]perylene (wt%)	1.69	-	-	-	-	-	-	-	-	-	-
Dibenz[ <i>a</i> , <i>h</i> ]anthracene (wt %)	0.21	-	-	-	-	-	-	-	-	-	-

<sup>a</sup>"-" means not detected by GC.

## 4. <sup>1</sup>H NMR and <sup>13</sup>C NMR of bio-pitch obtained from different vacuum distillations



**Figure S3.** <sup>1</sup>H NMR (400 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) of bio-pitch samples from various vacuum distillation

conditions.



Figure S4.  $^{13}$ C NMR (75 MHz, (CD<sub>3</sub>)<sub>2</sub>SO) of bio-pitch obtained from different vacuum distillations.

#### 5. Assignments for the main infrared absorptions of bio-oil and bio-pitches

Table S5.	Assignments	for the	e main	infrared	absor	ptions (	of bio	-oil and	bio-	pitches
	<u> </u>									4

Chemical groups	BO	BP-2	BP-9	BP-10
Moisture	3412	3366	3365	3368
C-H stretching of -CH <sub>3</sub>	2980, 2959	2958, 2927	2957, 2927	2958, 2928
C-H stretching of -CH <sub>2</sub>	2959, 2867	2927, 2870	2927, 2870	2928, 2871
C–H stretching of –CH	2867	2870	2870	2871
C-H bending of -CH <sub>3</sub>	1471, 1383	1449, 1357	1449, 1357	1450, 1358
C-H bending of -CH <sub>2</sub>	1450	1440	1440	1440
C=C stretching of aromatic groups	1625, 1523	1601, 1513	1602, 1513	1603, 1514
C–H bending of aromatic groups	690–600	690–600	690–600	690–600
C-OH stretching of -COOH	3412	-	_	_
C=O stretching of -COOH/aldehyde/ketone	1731	_	_	_
C-O stretching of -COOH	1238, 1122	_	_	_
C-OH bending of -COOH	908	-	_	_
C–O stretching in phenols	1294	1265	1268	1268
C–O–C stretching of aliphatic ethers	1070	1033	1033	1033
C–O stretching in secondary alcohols	1122	1121	1116	1115
C-H stretching of aromatic groups	885, 837, 773	816, 790, 765	812, 789, 765	812, 785, 750

## 6. MALDI-TOF full spectrum and ESI-TOF mass spectrum of bio-pitch



Figure S5. MALDI-TOF full spectrum of bio-pitch.



Figure S6. ESI-TOF mass spectrum of bio-pitch.



## 7. <sup>1</sup>H NMR spectra of distilled fractions from bio-oil

Figure S7. <sup>1</sup>H NMR spectra (400 MHz, CDCl<sub>3</sub>) of distilled fractions from bio-oil.

# 8. Possible structures for the detected molecular formula in GC-MS spectra (BP-10)

Table S6. Pos	sible structures <b>f</b>	for the	detected	molecular	formula in	GC-MS a	spectra
10010 0001 000							

Retention time (min.)	Possible structures for the detected molecular formula	Retention time (min.)	Possible structures for the detected molecular formula
2.16	O C <sub>6</sub> H <sub>8</sub> O <i>m/z</i> : 96.06	2.48	OH C <sub>6</sub> H <sub>6</sub> O <sub>2</sub> OH m/z: 110.04
2.75	C <sub>6</sub> H <sub>6</sub> O <i>m/z</i> : 94.04	3.08	0 C <sub>7</sub> H <sub>12</sub> O <i>m/z</i> : 112.09
3.21	0 C <sub>7</sub> H <sub>6</sub> O m/z: 106.04	3.34	HO C <sub>7</sub> H <sub>8</sub> O m/z:108.06
3.49	OH C <sub>7</sub> H <sub>8</sub> O <sub>2</sub> C <sub>8</sub> H <sub>12</sub> O m/z: 124.05 m/z: 124.09	3.83	С <sub>8</sub> H <sub>10</sub> O С <sub>8</sub> H <sub>10</sub> O С <sub>9</sub> H <sub>10</sub> O С <sub>9</sub> H <sub>10</sub> O m/z: 122.07 m/z: 122.07 m/z: 122.07
4.16	острон но острон на поставите и	4.44	O C <sub>8</sub> H <sub>8</sub> O <sub>3</sub> <i>m/z</i> : 152.05
4.73	$\begin{array}{c} & & HO \\ & & HO \\ C_8H_8O_3 \\ m/z: 152.05 \\ m/z: 152.08 \end{array} OH$	5.06	0 C <sub>10</sub> H <sub>6</sub> O <sub>3</sub> <i>m/z</i> : 174.03
5.26	HO HO C <sub>9</sub> H <sub>8</sub> O <sub>3</sub> m/z: 164.05 C <sub>10</sub> H <sub>12</sub> O <sub>2</sub> m/z: 164.08	5.34	HO HO C <sub>g</sub> H <sub>10</sub> O <sub>3</sub> <i>m/z</i> : 166.06 HO HO C <sub>g</sub> H <sub>6</sub> O <sub>4</sub> HO HO <i>C</i> <sub>g</sub> H <sub>6</sub> O <sub>4</sub> <i>m/z</i> : 166.03
5.58	0 C <sub>12</sub> H <sub>10</sub> O <sub>3</sub> O <i>m/z</i> : 202.06	5.60	$\begin{array}{c} & & & \\ & & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & &$
5.90	OH C <sub>11</sub> H <sub>14</sub> O <sub>2</sub> <i>m/z</i> : 178.10	6.10	H C <sub>13</sub> H <sub>17</sub> O m/z: 189.13 C <sub>13</sub> H <sub>16</sub> O <sub>2</sub> m/z: 204.12



#### 9. GC-MS analysis of the distilled fractions



Figure S8. MS for the component at 2.16 min in GC.



Figure S9. MS for the component at 2.48 min in GC.



Figure S10. MS for the component at 2.75 min in GC.



Figure S11. MS for the component at 3.08 min in GC.



Figure S12. MS for the component at 3.21 min in GC.



Figure S13. MS for the component at 3.34 min in GC.



Figure S14. MS for the component at 3.49 min in GC.



Figure S15. MS for the component at 3.83 min in GC.



Figure S16. MS for the component at 4.16 min in GC.



Figure S17. MS for the component at 4.44 min in GC.



Figure S18. MS for the component at 4.73 min in GC.



Figure S19. MS for the component at 5.06 min in GC.



Figure S20. MS for the component at 5.26 min in GC.



Figure S21. MS for the component at 5.34 min in GC.



Figure S22. MS for the component at 5.58 min in GC.



Figure S23. MS for the component at 5.60 min in GC.



Figure S24. MS for the component at 5.90 min in GC.



Figure S25. MS for the component at 6.10 min in GC.



Figure S26. MS for the component at 6.12 min in GC.



Figure S27. MS for the component at 6.19 min in GC.



Figure S28. MS for the component at 6.25 min in GC.



Figure S29. MS for the component at 6.37 min in GC.



Figure S30. MS for the component at 6.47 min in GC.



Figure S31. MS for the component at 7.23 min in GC.



Figure S32. MS for the component at 7.27 min in GC.



Figure S33. MS for the component at 8.16 min in GC.



Figure S34. MS for the component at 8.86 min in GC.



Figure S35. MS for the component at 9.07 min in GC.



Figure S36. MS for the component at 9.57 min in GC.

#### 10. Simulation analysis of proposed bio-pitch structure

Gaussian is a general-purpose computational chemistry software.<sup>11</sup> The method, density functional theory (DFT) used in this study to simulate the IR of one of the  $\beta$ -O-aryl ether oligomers, is a computational quantum mechanical modelling method used in physics, chemistry

and materials science to investigate the electronic structures (or nuclear structure) of many-body systems, in particular atoms, molecules, and the condensed phases. Using this theory, the properties of a many-electron system can be determined by using functionals, i.e. functions of another function, which in this case is the spatially dependent electron density. The DFT calculation has been frequently used to simulate IR spectra of inorganic <sup>12</sup> and organic molecules,<sup>13-16</sup> which good results have been obtained.

One of the possible stereo-configurations of the chiral centers is indicated in Figure S37.<sup>17</sup> The simulated IR spectrum of the oligomer and the experimental IR spectrum results were shown in Figure S38. It was found that the calculated wavenumbers of the  $\beta$ -*O*-aryl ether oligomer are linearly and well correlated with the experimental wavenumbers of the bio-pitch (BP-2) (Figure S39). It indicates that the bio-pitch samples are enriched in  $\beta$ -*O*-aryl ether polymers, furthermore, this result can be used to support the proposed structure of bio-pitch.

![](_page_26_Figure_2.jpeg)

**Figure S37.** Optimized structure of  $\beta$ -*O*-aryl ether oligomer calculated at B3LYP/6-31G\* level.

![](_page_27_Figure_0.jpeg)

**Figure S38.** Experimental IR of BP-2 and simulated IR of  $\beta$ -*O*-aryl ether oligomer.

![](_page_27_Figure_2.jpeg)

Caculated wavenumber of β-O-aryl ether oligomer (cm<sup>-1</sup>)

**Figure S39.** Correlation graphs of calculated wavenumbers of  $\beta$ -*O*-aryl ether oligomer and experimental wavenumbers of BP-2.

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