



INFLUENCE OF POLYPHENOLS ON THE INTEGRATED POLYPHENOL-MAILLARD REACTION HUMIFICATION PATHWAY AS CATALYZED BY BIRNESSITE

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SUPPLEMENTARY MATERIALS

Table S1 The pH, redox potential (pH + pE), Mn concentration and visible absorbances at 400 and 600 nm of the supernatants of the integrated reaction systems at the equimolar ratio of polyphenol to Maillard reagents incubated at 25°C or 45°C at the end of a 15-day period, both in the presence or absence of birnessite.

Reaction system		pH	pH + pE	Mn (mmol L ⁻¹)	Visible absorbance	
					400 nm	600 nm
<i>Presence of birnessite</i>	Pyrogallol-Maillard 25°C	7.04	8.11	16.37	52.63	10.73
	Pyrogallol-Maillard 45°C	6.53	7.16	31.83	85.14	12.57
	Resorcinol-Maillard 25°C	8.35	10.62	114.49	170.28	18.93
	Resorcinol-Maillard 45°C	7.97	7.18	215.67	224.88	26.94
<i>Absence of birnessite</i>	Pyrogallol-Maillard 25°C	5.08	11.15	^a NA	11.60	0.40
	Pyrogallol-Maillard 45°C	4.81	10.21	NA	15.89	1.60
	Resorcinol-Maillard 25°C	6.45	12.43	NA	0.54	0.03
	Resorcinol-Maillard 45°C	6.23	8.60	NA	10.66	3.21

^aNot applicable

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Table S2 Assignments of FTIR absorption bands of the solid residues of the Maillard, integrated pyrogallol-Maillard and resorcinol-Maillard reaction, and pyrogallol and resorcinol only systems. Interpretation is based on previous works [1-3].

Fig. S2 (a) and (b), Maillard reaction and pyrogallol-Maillard systems with 0.0025 mole pyrogallol		Fig. S2 (c), (d) and (e), Pyrogallol-Maillard systems with 0.025, 0.05 and 0.10 mole pyrogallol		Fig. S2 (f) , 0.05 mole pyrogallol only system		Fig. S3 (b), (c), (d) and (e) , [†] Resorcinol-Maillard systems with 0.0025, 0.025, 0.05 and 0.10 mole resorcinol		Fig. S3 (f) , 0.05 mol resorcinol only system	
Wavenumber (cm ⁻¹)		Wavenumber (cm ⁻¹)		Wavenumber (cm ⁻¹)		Wavenumber (cm ⁻¹)		Wavenumber (cm ⁻¹)	
725	Carbonate C-O out of plane bend (rhodochrosite)	1079-1081	Aliphatic C-O stretching	860	Carbonate C-O stretch (rhodochrosite)	725	Carbonate C-O out of plane bend (rhodochrosite)	510, 598	Mn-O vibrations * (manganite, hausmannite)
860	Carbonate C-O stretch (rhodochrosite)	1315	C-O stretch and bending of COOH	1086	Carbonate C-O stretch (rhodochrosite)	860	Carbonate C-O stretch (rhodochrosite)	861, 1079	Carbonate C-O stretch (rhodochrosite)
1077-1079	Carbonate C-O stretch (rhodochrosite)	1397-1406	Asymmetrical COO ⁻ stretch, C-H deformation of CH ₂ & CH ₃ , OH deformation of phenols	1315	C-O stretch and bending of COOH	1077-1079	Carbonate C-O stretch (rhodochrosite)	1151	Mn-O vibrations (manganite, hausmannite)
1408	Asymmetric COO ⁻ stretch, C-H deformation of CH ₂ & CH ₃ , OH deformation of phenols	1498-1500	NH ₃ ⁺ symmetrical bending band, aromatic C=C stretch	1402	Asymmetric COO ⁻ stretch, C-H deformation of CH ₂ & CH ₃ , OH deformation of phenols	1408	Asymmetrical COO ⁻ stretch, C-H deformation of CH ₂ & CH ₃ , OH deformation of phenols	1410	Asymmetric COO ⁻ stretch, C-H deformation of CH ₂ & CH ₃ , OH deformation of phenols
1445	Carbonate symmetric C-O stretch (rhodochrosite), asymmetrical bending of CH ₂ & CH ₃	1592	Symmetric COO ⁻ stretch, N-H deformation + C=N amide II band	1463	Carbonate symmetric C-O stretch (rhodochrosite), Assymetrical bending of CH ₂ & CH ₃	1446	Carbonate symmetric C-O stretch (rhodochrosite), asymmetrical bending of CH ₂ & CH ₃	1461	Carbonate symmetric C-O stretch (rhodochrosite), asymmetrical bending of CH ₂ & CH ₃
1594	Symmetric COO ⁻ stretch, N-H deformation + C=N amide II band	3355-3358	OH stretch	1580	Symmetric COO ⁻ stretch	1594	Symmetric COO ⁻ stretch, N-H deformation + C=N amide II band	1613	C=C aromatic ring stretch, symmetric COO ⁻ stretch
3360	OH stretch			3358	OH stretch	3355	OH stretch	2052, 2710, 3378	Ketone, aldehyde OH stretch

*Presence of trace amounts of birnessite; [†]Fig. S3 (a) Maillard reaction is the same as Fig. S2 (a)

Table S3 Assignments of FTIR absorption bands of humic acids isolated from the supernatants of the Maillard, integrated pyrogallol-Maillard and resorcinol-Maillard, and pyrogallol- and resorcinol only systems. Interpretation is based on previous works [1-3].

Fig. S4 (a) and S5 (a) Maillard reaction system		Fig. S4 (b) & (c), Pyrogallol- Maillard systems with 0.05 and 0.10 mole pyrogallol		Fig. S4 (d) 0.05 mole pyrogallol only system		Fig. S5 (b) & (c) Resorcinol-Maillard systems with 0.05 and 0.10 mole resorcinol		Fig. S5 (d) 0.05 mole resorcinol only system	
Wavenumber (cm ⁻¹)		Wavenumber (cm ⁻¹)		Wavenumber (cm ⁻¹)		Wavenumber (cm ⁻¹)		Wavenumber (cm ⁻¹)	
883	Out of plane aromatic C-H bend	1084	Aliphatic C-O stretching	1072	Aliphatic C-O stretching	843, 1081-1107	Aliphatic C-O stretching	841, 963, 1149	Aliphatic C-O stretching
1091	Aliphatic C-O stretching	1253	C-O stretch and bending of COOH, C-O stretch of phenols or aryl ethers	1252	C-O stretch and bending of COOH, C-O stretch of phenols or aryl ethers	1226	C-O stretch and bending of COOH, C-O stretch of phenols or aryl ethers	1295	C-O stretch and bending of COOH, C-O stretch of phenols or aryl ethers
1218	C-O stretch and bending of COOH, C-O stretch of phenols or aryl ethers	1383	OH deformation and C-O stretch of phenols, C-H deformation of CH ₂ & CH ₃ , asymmetrical stretch of COO ⁻	1382	OH deformation and C-O stretch of phenols, C-H deformation of CH ₂ & CH ₃ , asymmetrical stretch of COO ⁻	1298	C-O stretch and bending of COOH, C-O stretch of phenols or aryl ethers	1358	OH deformation and C-O stretch of phenols, C-H deformation of CH ₂ & CH ₃ , asymmetrical stretch of COO ⁻
1380	OH deformation and C-O stretch of phenols, C-H deformation of CH ₂ & CH ₃ , asymmetrical stretch of COO ⁻	1444 -1445	Assymetrical bending of CH ₂ & CH ₃ , C=C aromatic ring stretch	1427	Assymetrical bending of CH ₂ & CH ₃ deformation band, C=C aromatic ring stretch	1392-1398	OH deformation and C-O stretch of phenols, C-H deformation of CH ₂ & CH ₃ , asymmetrical stretch of COO ⁻	1461	Assymetrical bending of CH ₂ & CH ₃ , C=C aromatic ring stretch
1580	Symmetric C-O stretch of COO ⁻ , N-H deformation + C=N amide II band	1510	Symmetric C-O stretch of COO ⁻ , N-H deformation + C=N amide II band	1511	Symmetric C-O stretch of COO ⁻	1460	Assymetrical bending of CH ₂ & CH ₃ , C=C aromatic ring stretch	1499	Symmetric C-O stretch of COO ⁻
1621	Aromatic C=C ring stretch	1605-1613	Aromatic C=C stretch, symmetric C-O stretch of COO ⁻ (shoulder)	1597	Aromatic C=C stretch, symmetric C-O stretch of COO ⁻ (shoulder)	1501	Symmetric C-O stretch of COO ⁻	1617	Aromatic C=C stretch
1712	Symmetric C=O stretch of COOH	1715	Symmetric C=O stretch of COOH	1711	Symmetric C=O stretch of COOH	1617	Aromatic C=C ring stretch	1713	Symmetric C=O stretch of COOH
2942	Aliphatic C-H stretch	2942	Aliphatic C-H stretch	3380	OH stretch	1713	Symmetric C=O stretch of COOH	3345	OH stretch
3269	OH or N-H stretch	3380	OH stretch			2942	Aliphatic C-H stretch		
3406	OH stretch					3349	OH stretch		

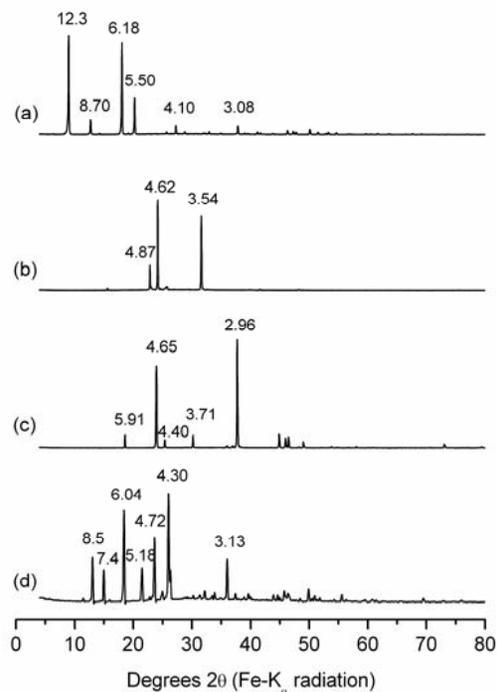


Figure S1

X-ray diffractograms of unreacted biomolecules: (a) pyrogallol, (b) resorcinol, (c) glycine and (d) glucose. D-spacings are indicated in Å. The spectrum of the unreacted pyrogallol (Fig. S1a) shows the typical pyrogallol d-values at 12.3, 8.70 and 5.50 Å [4]. In addition, there was a crystalline product present which has been identified as poly[(phenyl-p-phenylene)-co-(terephthalate)-co-(p-hydroxy-benzoate)] with d-values of 12.3, 6.18, 4.10 and 3.08 Å [4], which was probably formed as a result of pyrogallol transformation in reaction to the heat of the X-rays. There was also visible evidence of this transformation, as the initially white pyrogallol crystals mounted on the glass slide turned light brown in the center area that was exposed to the X-ray beam. Resorcinol (Fig. S1 b), glycine (Fig. S1 c) and glucose (Fig. S1 d) show their respective typical d-values [4] and appeared not to be affected by the X-rays.

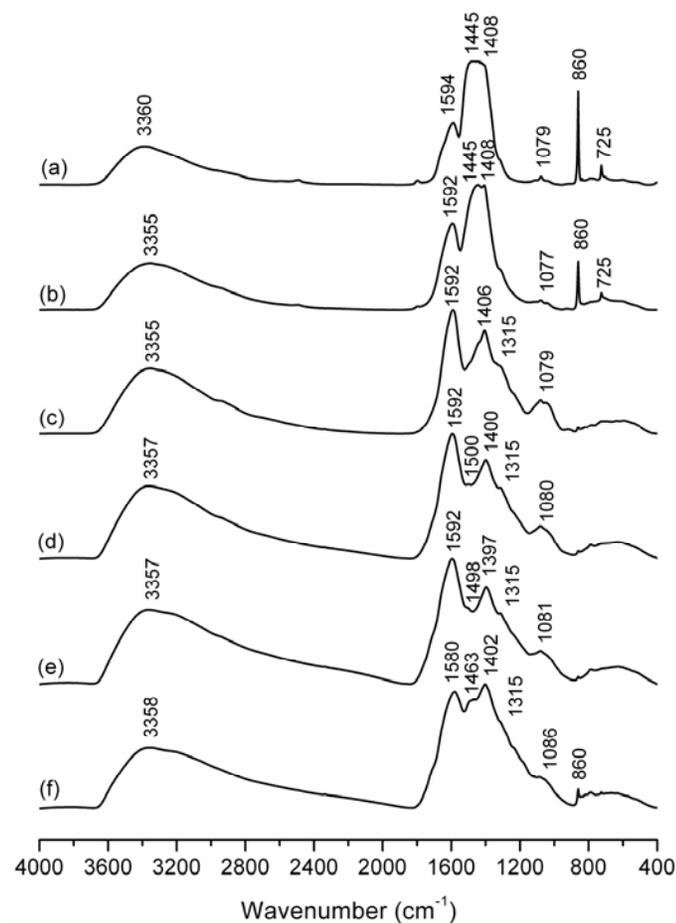


Figure S2 FTIR spectra of the solid residues formed in the presence of birnessite from (a) the Maillard reaction system; (b-e) the integrated pyrogallol-Maillard reaction systems with: (b) 2.5 mmole pyrogallol, (c) 25 mmole pyrogallol, (d) 50 mmole pyrogallol, (e) 100 mmole pyrogallol; and (f) the 50 mmole pyrogallol only system.

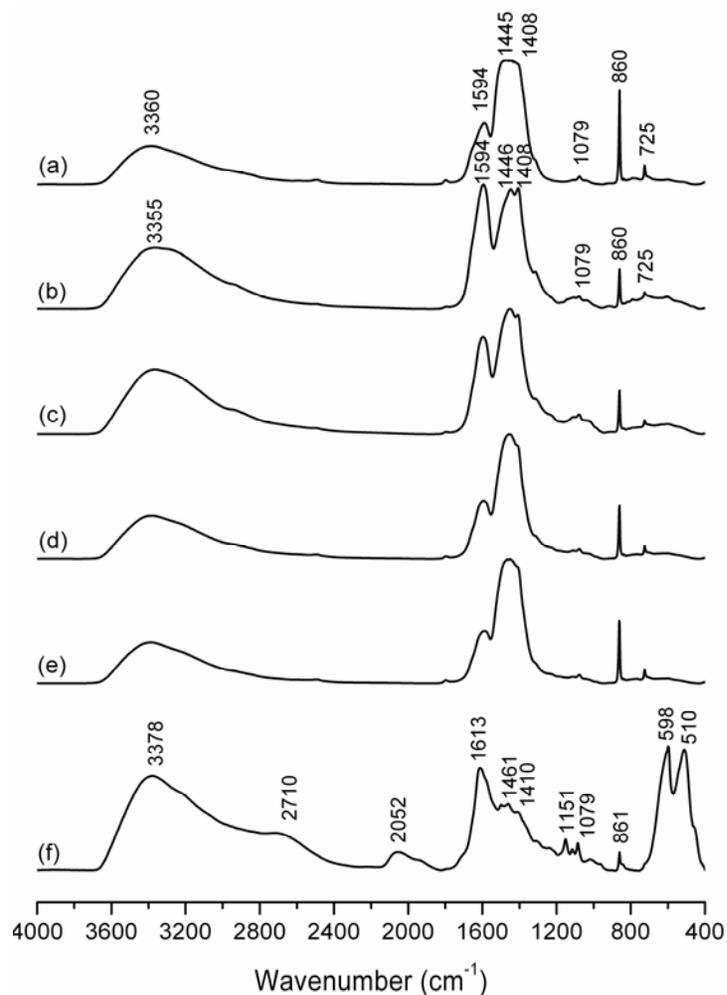


Figure S3 FTIR spectra of the solid residues formed in the presence of birnessite from (a) the Maillard reaction system; (b-e) the integrated resorcinol-Maillard reaction systems with: (b) 2.5 mmole resorcinol, (c) 25 mmole resorcinol, (d) 50 mmole resorcinol, (e) 100 mmole resorcinol; and (f) the 50 mmole resorcinol only system.

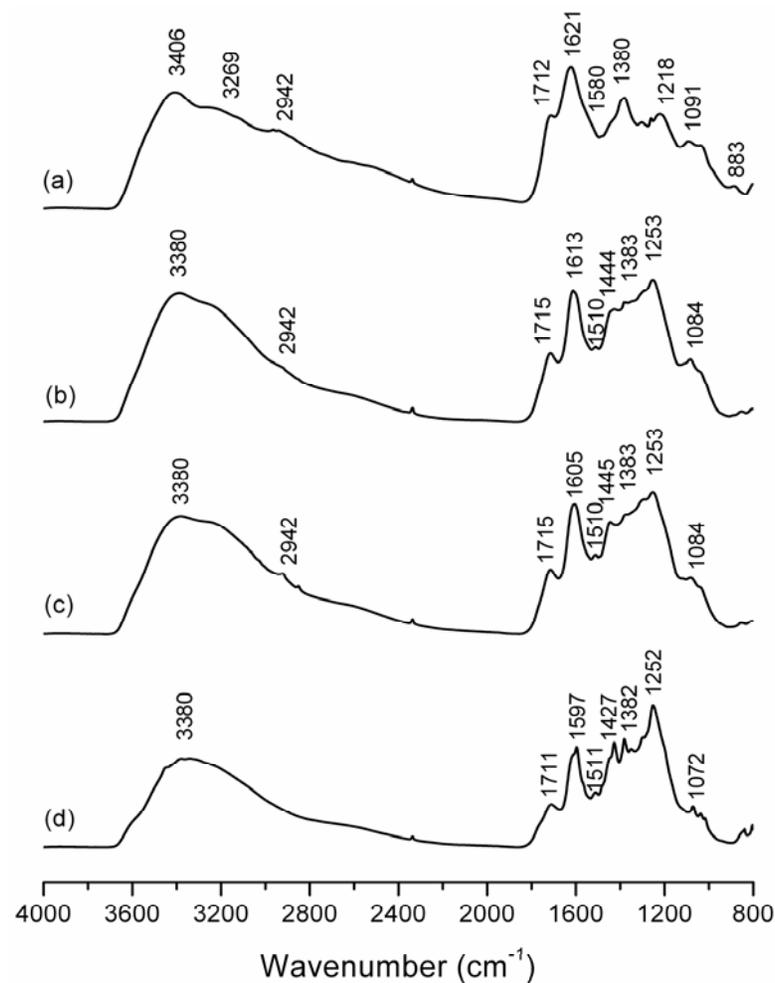


Figure S4 FTIR spectra of the humic acids isolated from the supernatants of reaction systems catalyzed by birnessite: (a) the Maillard reaction; integrated pyrogallol-Maillard reaction systems with: (b) 50 mmole pyrogallol and (c) 100 mmole pyrogallol; and (d) 50 mmol pyrogallol only system.

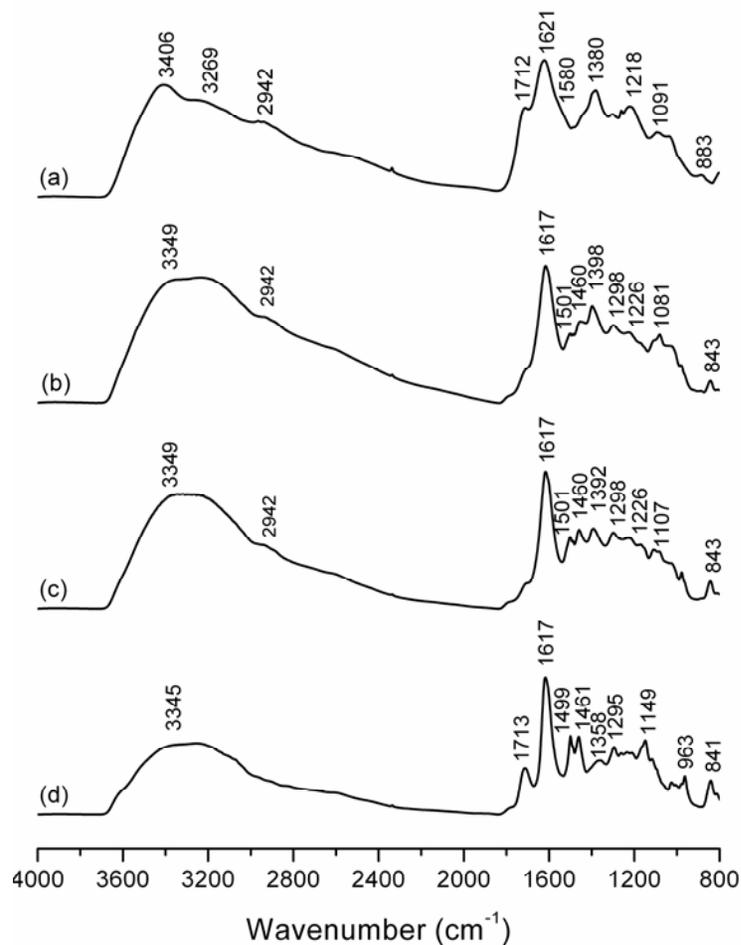


Figure S5 FTIR spectra of the humic acids isolated from the supernatants of reaction systems catalyzed by birnessite: (a) the Maillard reaction; integrated resorcinol-Maillard reaction systems with: (b) 50 mmole resorcinol and (c) 100 mmole resorcinol; and (d) 50 mmol resorcinol only system.

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