Supplementary Information for:

A Mild Approach for Bio-oil Stabilization and Upgrading: Electrocatalytic Hydrogenation Using Ruthenium Supported on Activated Carbon Cloth

Zhenglong Li[a,b], Shantanu Kelkar[a,b], Lauren Raycraft[a], Mahlet Garedew[a], James E. Jackson[c], Dennis J. Miller[b], Christopher M. Saffron[a,b,d,*]

Table S1 Properties of the bio-oil derived from fast pyrolysis of poplar DN34

		Weight % *
Elements	C	34.3
	H	8.2
	O	57.5
	N	<0.01
Solids (methanol insoluble)		0.7
pH		2.8
Density		1.12 g/mL
Water content		36.6

* as received.

[a]Department of Biosystems & Agricultural Engineering, Michigan State University, East Lansing, MI 48824, US; [b]Department of Chemical Engineering & Materials Science, Michigan State University; [c]Department of Chemistry, Michigan State University; [d]Department of Forestry, Michigan State University.
* Corresponding author at: Department of Biosystems & Agricultural Engineering, Michigan State University, East Lansing, MI, 48824, United States. Tel.: +1 517 432 7414; fax: +1 517 432 2892.
E-mail address: saffronc@egr.msu.edu (C.M. Saffron).

Table S2 Quantification of major compounds in bio-oil via GC/MS and HPLC

Compounds in bio-oil	Group	Method	wt% in whole bio-oil
Cellulose/hemicellulose derived compounds			
Acetic acid	Acids	GC/MS	6.2
Acetol	Misc. Oxygenates	GC/MS	5.6
1-Hydroxy-2-butanone	Misc. Oxygenates	GC/MS	3.1
Furfural	Furans	GC/MS	0.4
Furfuryl alcohol	Furans	GC/MS	0.3
Cyclopentanone	Ketones	GC/MS	0.3
3-Methyl-2-cyclopentenone	Ketones	GC/MS	0.4
3-Methyl-1,2-cyclopentanedione	Ketones	GC/MS	1.1
Levoglucosan	Sugars	GC/MS	3
Glucose	Sugars	HPLC	0.3
Xylose	Sugars	HPLC	0.3
Lignin derived compounds			
Phenol	Phenols	GC/MS	1
2-Methylphenol	Phenols	GC/MS	0.3
Guaiacol	Phenols	GC/MS	0.5
Cresol	Phenols	GC/MS	0.5
4-Ethyl-guaiacol	Phenols	GC/MS	0.4
Eugenol	Phenols	GC/MS	0.2
Isoeugenol	Phenols	GC/MS	1.2
Methoxyeugenol	Phenols	GC/MS	2.3
Syringol	Phenols	GC/MS	1.4

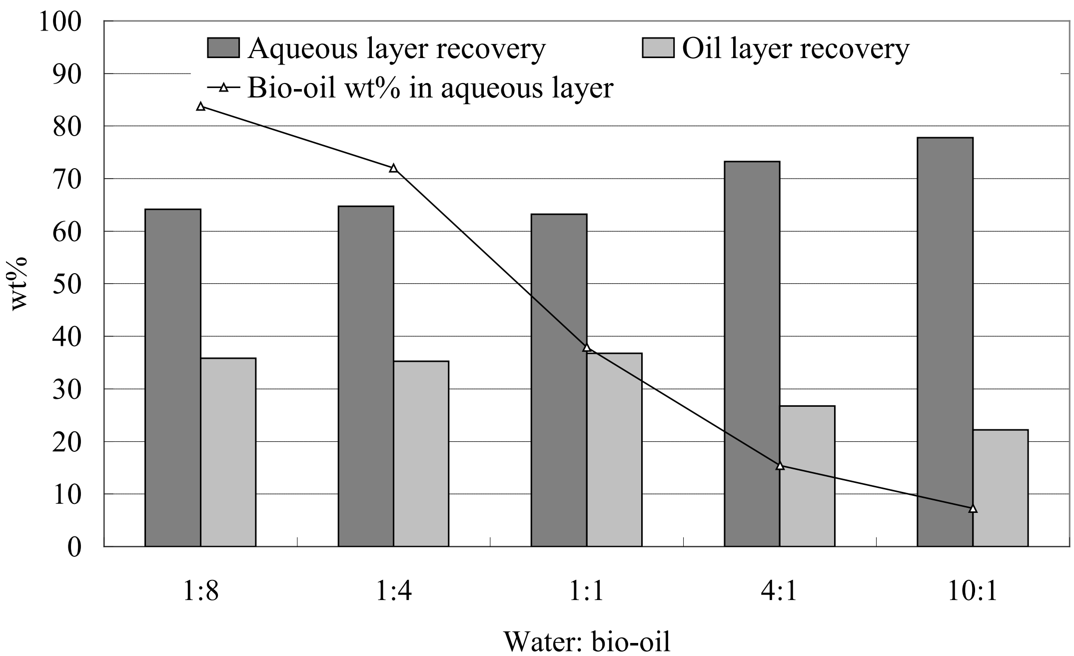

Fig. S1 Separation of bio-oil using water with different water/bio-oil ratio

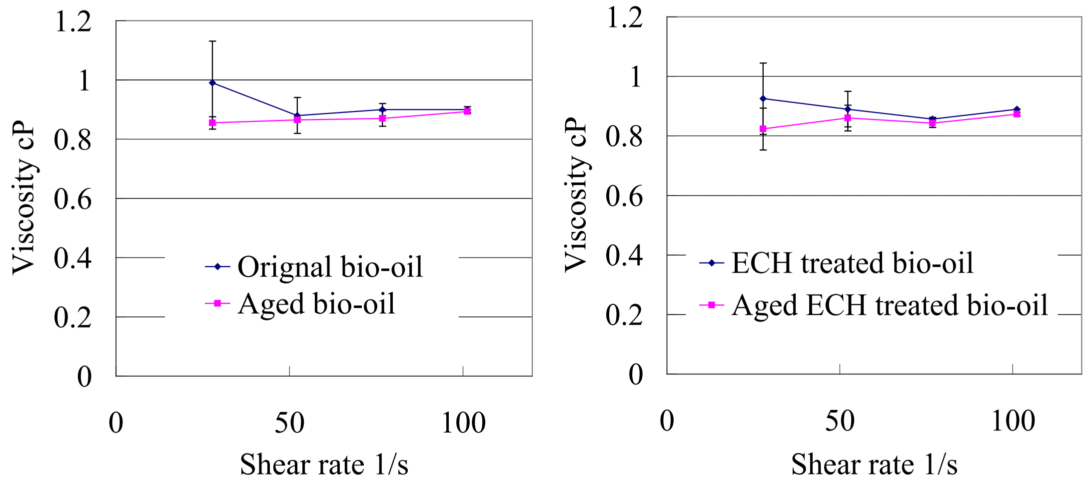

Fig. S2 Viscosity change for original bio-oil and ECH treated bio-oil after aging for 48 h at 80°C

Strategies for System Optimization in the ECH of WSBO

(1) Material balance

Material balance for ECH of water-soluble bio-oil is shown in Fig. S3. All the calculations are based on the experiments shown in the paper. After ECH, the mass change of stabilized water-soluble bio-oil (SWSBO) compared to WSBO, includes the increase due to hydrogenation and the loss from the migration of small molecules to the anode chamber. The increase from hydrogenation is equal to the hydrogen used for the hydrogenation, calculated by the difference between theoretical hydrogen yield and measured hydrogen yield. Loss of SWSBO is not known and assumed to be x percentage of WSBO. Thus the final SWSBO is (0.73(1-x%)+0.005) Kg. Oxygen is produced in the anode chamber (0.58 Kg) due to the oxidation of water, resulting in water decrease in the anode chamber. The water loss is calculated based on generated oxygen according to:

$$2H_2O \rightarrow 2H_2 + O_2$$

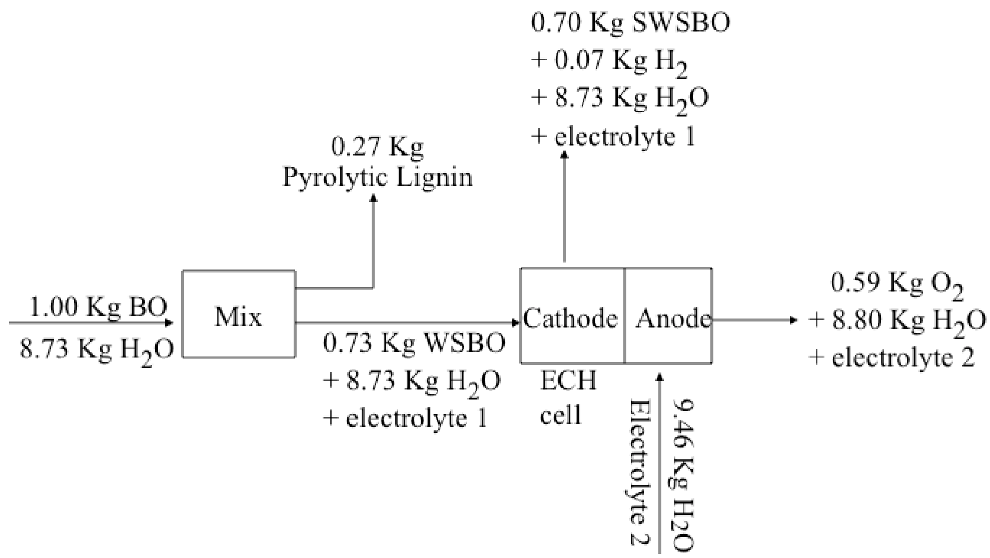

Fig. S3 Material balance for ECH of water-soluble bio-oil with water to bio-oil ratio at 8.73:1. BO: bio-oil; WSBO: water-soluble bio-oil; SWSBO: stabilized water-soluble bio-oil. (Assuming WSBO loss is 5%)

(2) Energy balance

The energy balance for ECH process is shown in Fig. S4. W_e is the electrical energy input to the ECH system, and W_e can be calculated according to $W_e = U\ I\ t$, and U is the applied voltage, I is the current and t is the time for the ECH. The energy content of WSBO (E_1) is the energy difference between bio-oil and pyrolytic lignin. The energy content of SWSBO (E_2) is contributed by the loss of WSBO and hydrogenation, thus $E_2 = 5.6(1\text{-}x\%) + 0.7$, 0.7 MJ is the energy content of hydrogen added into the SWSBO.

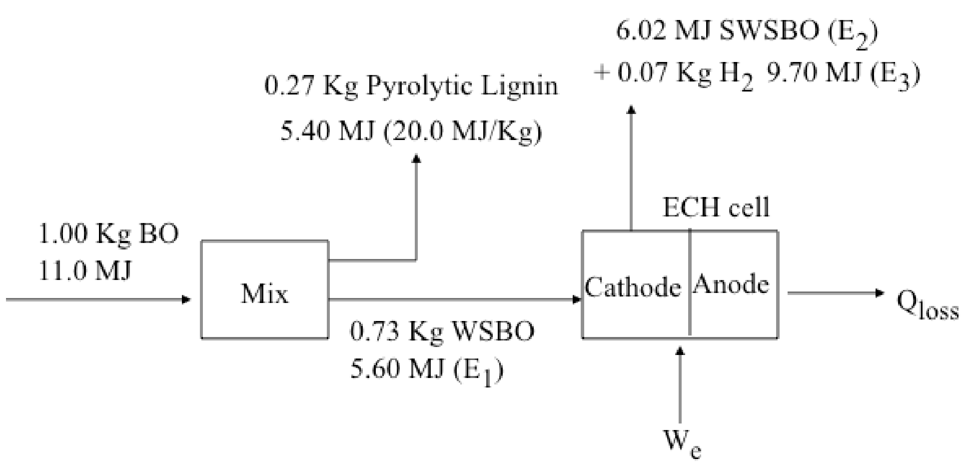

Fig. S4 Energy balance for ECH of water-soluble bio-oil with water to bio-oil ratio at 8.73:1. (Assuming WSBO loss is 5%)