Supplementary Information (SI) for Sustainable Energy & Fuels.

Advancing Hydrothermal Liquefaction of Canadian Forestry Biomass for Sustainable Biocrude Production: Co-Solvent Integration, Co-Liquefaction, and Process Optimization

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Table S1. Proximate, ultimate, and fiber analysis of different Canadian-grown softwoods

Softwood species	Fiber Analysis (wt. %)			Proximate Analysis (wt. %)					Ultimate Analysis (wt. %)				
	Cellulose	Hemi cellulose	Lignin	Moisture	Ash	Extractives	FC	VM	C	H	N	S	O
Tamarack	46	18.10	23.20	6.50	0.30	12.50	13.50	79.70	48.30	6.40	0.50	B. D	45.10
Pine	42.30	16.10	26	5.30	0.10	15.60	15.60	79.00	50.40	6.60	0.20	B. D	42.70
Spruce	50.30	18.60	26	6.20	0.20	4.80	11.50	82.10	51.20	6.70	0.00	0.10	41.80
Fir	42	15	32.50	4.30	0.50	10.20	10.90	84.30	50.00	6.30	0.30	B. D	42.90
Cedar	44.10	13.20	29.40	4.60	0.50	12.90	16.30	78.60	49.80	6.20	0.20	B. D	43.30

Average values are reported in the table. B.D: Below detection

Table S2. Biocrude yield and their Elemental analysis of different Canadian-grown Softwoods.

Hardwood species	Biocrude yield (Wt. %)	Elemental Analysis (wt. %)				
		C	H	N	S	O
Tamarack	23.90	72.40	7.00	0.10	B. D	20.50
Pine	23.90	70.60	7.10	0.10	0.10	22.10
Spruce	25.10	72.30	6.90	0.20	0.10	20.50
Fir	26.10	71.20	6.70	0.00	0.10	22.00
Cedar	31.30	69.80	6.90	0.00	B. D	23.30

Average values are reported in the table, B.D: Below the detection, Reaction Condition: 70 g feedstock, biomass to solvent/water ratio (W/V) =1:10, T = 300°C, 5 wt. % K_2CO_3 catalyst, t = 30 min, Initial Reaction Pressure = 100 Psi, Final pressure: 1500 Psi, extraction solvent for biocrude: ethanol.

Table S3. Proximate, ultimate, and fiber analysis of different Canadian-grown hardwoods

Hardwood Species	Fiber Analysis (wt. %)			Proximate Analysis (wt. %)					Ultimate Analysis (wt. %)				
	Cellulose	Hemicellulose	Lignin	Moisture	Ash	Extractives	FC	VM	C	H	N	S	O
Aspen	54.20	24.50	11.60	5.40	0.30	9.40	13.00	81.30	47.10	6.40	0.10	B. D	46.10
Red Birch	52.10	25.80	10.10	6.20	0.30	11.70	11.10	82.40	47.50	6.40	0.20	0.10	45.50
White Birch	46.60	29.00	10.30	4.00	0.80	13.30	14.70	80.50	49	6.60	0.30	0.04	43.30
Maple	53	17.20	19.90	4.10	1.00	9	12.80	82.10	48.10	6.10	0.40	0.10	44.30
Oak	48.30	23.40	15.20	4.00	1.00	12.10	13.30	81.70	48.00	6.20	0.20	B. D	44.60
Poplar	59.80	20.50	9.90	6.50	0.70	9.10	10.80	82.00	46.20	6.40	0.00	0.02	46.70

Average values are reported in Table, B.D: Below the detection

Table S4. Biocrude yield and Elemental analysis of different Canadian-grown hardwoods

Hardwood species	Biocrude yield (Wt. %)	Elemental Analysis (wt. %)				
		C	H	N	S	O
Aspen	24.40	71.70	7.00	0.10	0.04	21.20
Red Birch	26.60	69.20	7.40	0.20	B. D	23.20
White Birch	27.30	73.40	7.60	1.00	0.10	17.90
Maple	25.90	72.10	6.80	0.04	0.02	21.04
Oak	23.60	71.20	6.70	0.04	0.02	22.04
Poplar	24.20	72.30	6.70	0.10	0.10	21.00

Average values are reported in the table. B.D: Below detection, Reaction Condition: 70g feedstock, biomass to solvent/water ratio (W/V) =1:10, T=300℃, 5 wt. % K_2CO_3 catalyst, t=30min, Initial Reaction Pressure=100 Psi, Final pressure: 1500Psi, extraction solvent for biocrude: ethanol

Table S5. Different pre-treatment methods are employed for spruce wood

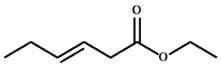
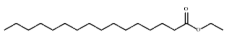
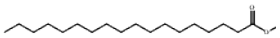
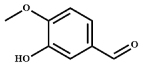
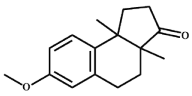
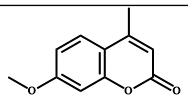
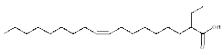
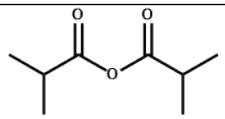
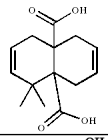
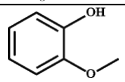
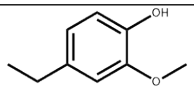
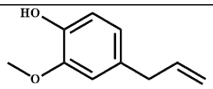
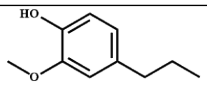
Code	Pretreatment Method
1	Spruce wood is mixed with 12 wt. % NaOH and 20 wt. % Urea in 700 mL of water and kept at -10℃ for 24h, The pH of the mixture is 14.
2	Spruce wood is mixed with 5 wt. % NaOH in 700 mL of water at RT and stirred overnight. The pH of the mixture is 12.
3	Spruce wood is mixed with 7.5 wt.% K_2CO_3 in 700 mL of water at 65 ℃ for 4 h with constant stirring, The pH of the mixture is 10
4	Spruce wood is mixed with 5 wt.% NaOH in 700 mL of water at,65 ℃ for 4 h with constant stirring, The pH of the mixture is 12

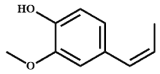
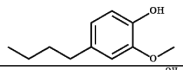
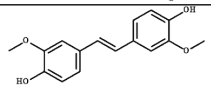
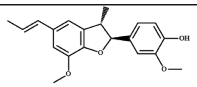
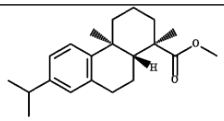
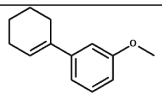
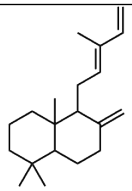
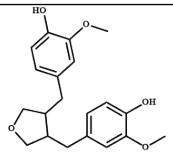
Table S6. Influence of catalyst and co-solvent on HTL of spruce wood at optimised reaction conditions

Reaction variables	Biocrude Yield	C	H	N	S	O	Hydrochar yield
				Wt.%			
No catalyst, no co-solvent	13.80	68.20	6.50	0.00	0.00	25.30	35.60
No Cat, with co-solvent	26.80	67.60	7.10	0.30	0.30	24.70	15.70
No co-solvent, with catalyst	23.80	67.20	7.00	0.00	0.10	25.70	18.40
With Cat, with co-solvent	31.00	71.10	7.50	0.00	0.10	21.30	7.10

Reaction Condition: 70g feedstock, biomass to solvent/water ratio (W/V) =1:10, 30% ethanol co-solvent, 5 wt. % K_2CO_3 catalyst T=280℃, Initial Reaction Pressure=100 PSI, extraction solvent for biocrude: acetone

Table S7. Chemical compounds identified by the GCMS analysis of biocrude obtained by the HTL of Spruce wood at optimum reaction conditions**.**

Functional groups	Chemical Compounds	Molecular Structure	Molecular formula	Molecular weight	Peak Area (%)
Esters	3-Hexenoic acid, ethyl ester, (E)-		$C_8H_{14}O_2$	142.20	2.00
	Hexadecanoic acid ethyl ester		$C_{18}H_{36}O_2$	284.48	2.50
	Octadecanoic acid ethyl ester		$C_{20}H_{40}O_2$	312.54	1.50
Aldehydes	3-Hydroxy-4-methoxy benzaldehyde		$C_8H_8O_3$	152.15	4.70
Ketones	7-Methoxy-3a,9b-dimethyl-1,2,3a,4,5,9b-hexahydro-3H-cyclopenta[a]naphthalen-3-one		$C_{16}H_{20}O_2$	244.33	2.60
	7-Methoxy-4-methylcoumarin		$C_{11}H_{10}O_3$	190.20	2.60
Acids	Ethyl oleic acid		$C_{20}H_{38}O_2$	310.50	14.30
Anhydrides	Propanoic acid, 2-methyl-, anhydride		$C_8H_{14}O_3$	158.20	3.10
	dimethyl 1,4,5,8-tetrahydronaphthalene-4a,8a-dicarboxylic acid		$C_{14}H_{18}O_4$	250.30	0.60
Phenols	2-methoxy Phenol		$C_7H_8O_2$	124.14	7.90
	Phenol, 4-ethyl-2-methoxy-		$C_9H_{12}O_2$	152.19	14.50
	Eugenol		$C_{10}H_{12}O_2$	164.20	2.90
	2-Methoxy-4-propylphenol		$C_{10}H_{14}O_2$	166.22	5.30

	Phenol, 2-methoxy-4-(1-propenyl)-, (Z)-		$C_{10}H_{12}O_2$	164.20	13.60
	4-Butyl-2-methoxy phenol		$C_{11}H_{16}O_2$	180.24	6.20
	(E)-3,3'-dimethoxy-4,4'-dihydroxy stilbene		$C_{16}H_{16}O_4$	272.30	3.90
	2-methoxy-4-[(2S,3S)-7-methoxy-3-methyl-5-[(E)-prop-1-enyl]-2,3-dihydro-1-benzofuran-2-yl] phenol		$C_{20}H_{22}O_4$	326.40	1.90
Others	Methyl dehydroabietate		$C_{21}H_{30}O_2$	314.50	3.50
	1-(cyclohex-1-en-1-yl)-3-methoxybenzene		$C_{13}H_{16}O$	188.26	1.00
	Naphthalene, decahydro-1,1,4a-trimethyl-6-methylene-5-(3-methyl-2,4-pentadienyl)		$C_{20}H_{32}$	272.47	1.30
	3,4 divanyllyltetrahydrofuran		$C_{20}H_{24}O_5$	344.41	3.90

Reaction Condition: 70g feedstock, biomass to solvent ratio (W/V) =1:10, 30% ethanol co-solvent, 5 wt. % K_2CO_3 catalyst, T=280℃, Initial Reaction Pressure=100 psi, Final pressure: 1500 Psi, extraction solvent for biocrude: acetone

Table S8. Chemical compounds identified by the GCMS analysis of biocrude obtained by the HTL of Poplar wood at optimum reaction conditions.

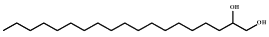
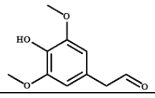
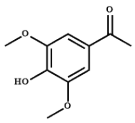
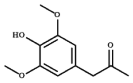
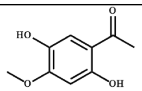
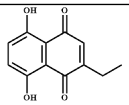
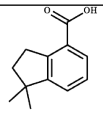
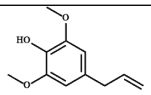
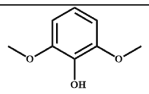
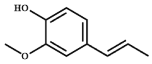
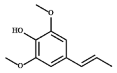
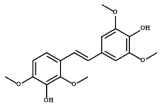
Functional groups	Chemical Compounds	Molecular Structure	Molecular formula	Molecular weight	Peak Area (%)
Alcohols	1,2 Nonadecanediol		$C_{19}H_{40}O_2$	300.50	3.10
Aldehydes	Homosyringaldehyde		$C_{10}H_{12}O_4$	196.20	9.70
Ketones	Ethanone, 1-(4-hydroxy-3,5-dimethoxy phenyl)		$C_{10}H_{12}O_4$	196.20	5.30
	Syringyl acetone		$C_{11}H_{14}O_4$	210.20	10.20
	2',5'-Dihydroxy-4'-methoxy acetophenone		$C_9H_{10}O_4$	182.20	9.70
	5,8-Dihydroxy-1,4-naphthoquinone		$C_{10}H_6O_4$	190.10	1.50
Acids	2,3-Dihydro-1,1-dimethyl-1H-indene-4-carboxylic acid		$C_{12}H_{14}O_2$	190.20	6.10
Phenols	2-methoxy Phenol		$C_7H_8O_2$	124.10	16.60
	4-(2-propenyl) 2,6-dimethoxy-Phenol		$C_{11}H_{14}O_3$	194.20	3.10
	2,6 Dimethoxy phenol		$C_8H_{10}O_3$	154.16	4.90
	4-(1-propenyl) 2-methoxy-Phenol		$C_{10}H_{12}O_2$	164.20	4.20
	2,6-dimethoxy-4-[(E)-prop-1-enyl] phenol		$C_{11}H_{14}O_3$	194.20	21.30
	(E)-3-(4-hydroxy-3,5-dimethoxystyryl)-2,6-dimethoxy phenol		$C_{18}H_{20}O_6$	332.40	2.80
Alkanes	Heptadecane		$C_{19}H_{40}O_2$	300.50	3.10

Table S9. ICP-OES analysis for biocrude obtained from Spruce and Poplar wood HTL tests. Values in [ppm]

Metal	Spruce	Poplar	Co-liquefaction (50:50 wt.%)
Li	0.849	0.56	0.33
Na	6.78	6.88	7.54
Mg	0.59	0.40	0.16
K	87.03	35.85	76.65
Ca	1.47	1.52	1.01
Sr	0.01	0.01	0.00
Ba	0.01	0.01	0.01
Cr	0.023	0.03	0.02
Mn	0.027	0.04	0.01
Fe	1.67	0.87	0.56
Co	0.01	0.00	0.00
Ni	0.02	0.06	0.08
Cu	0.07	0.09	0.08
Zn	0.16	0.55	0.25
Mo	0.17	0.02	0.02
B	0.28	0.13	0.18
Al	1.37	2.16	1.23
Ti	0.02	0.04	0.42
Si	0.59	0.50	0.57
Pb	0.03	0.00	0.00
P	0.08	0.09	0.00
As	0.19	0.15	0.00
S	7.29	6.84	7.60

Table S10. Calorific values and textural properties of the hydrochar obtained by the HTL of spruce and poplar at optimum conditions.

Name of the wood hydrochar	**Elemental analysis (wt. %)**			**HHV (MJ/Kg)**	**BET Surface Area (m^2/g)**	**Pore Volume (cm^3/g)**	**Pore size (Å)**
	C	**H**	**O**				
Spruce	66.60	7.10	27.70	27.30	329.90	0.15	30.96
Poplar	57.10	5.90	37	22.90	267.40	0.13	35.18

The values of N and S are less than 0.1 wt. %

Table S11. Percentage composition of gaseous products obtained during the hydrothermal liquefaction of spruce wood and poplar wood at optimum conditions.

HTL Feedstock	Gas composition and quantity (mol. %)	
Spruce wood	CO_2	68.60
	CO	21.70
	H_2	8.63
	O_2	0.80
	CH_4	0.31
	C_2H_2	0.02
Poplar wood	CO_2	65.60
	CO	18.00
	H_2	11.20
	O_2	5.00
	CH_4	0.20
	C_2H_2	0.06

Reaction Condition: 70g feedstock, biomass to solvent ratio (W/V) =1:10, 10% ethanol co-solvent, 5 wt. % K_2CO_3 catalyst, T=260°C, Initial Reaction Pressure=100 psi, Final pressure: 1150 Psi, extraction solvent for biocrude: acetone

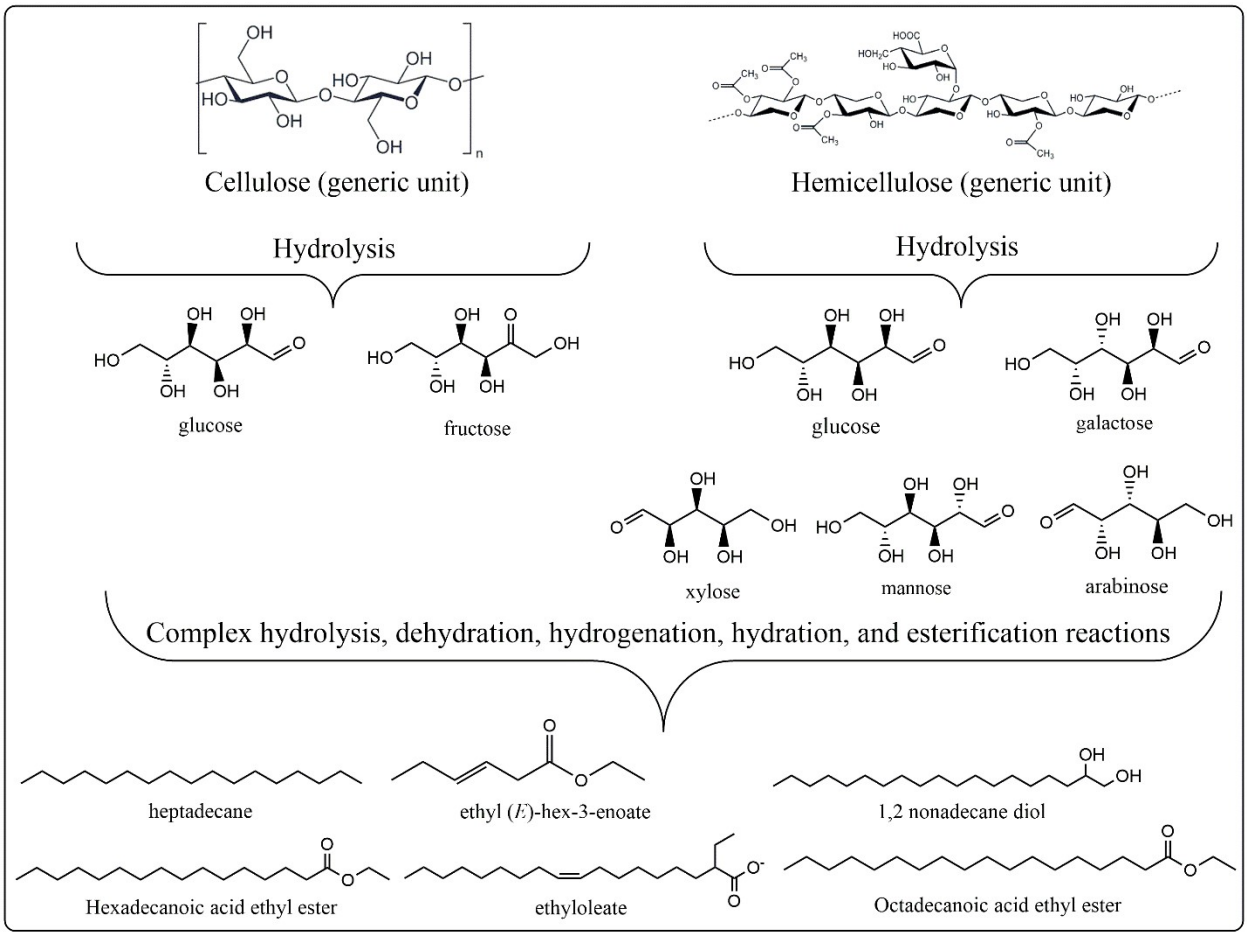


Fig S1. Plausible decomposition pathways of lignocellulosic biomass macromolecules cellulose, and hemicellulose under HTL conditions. [61-63]

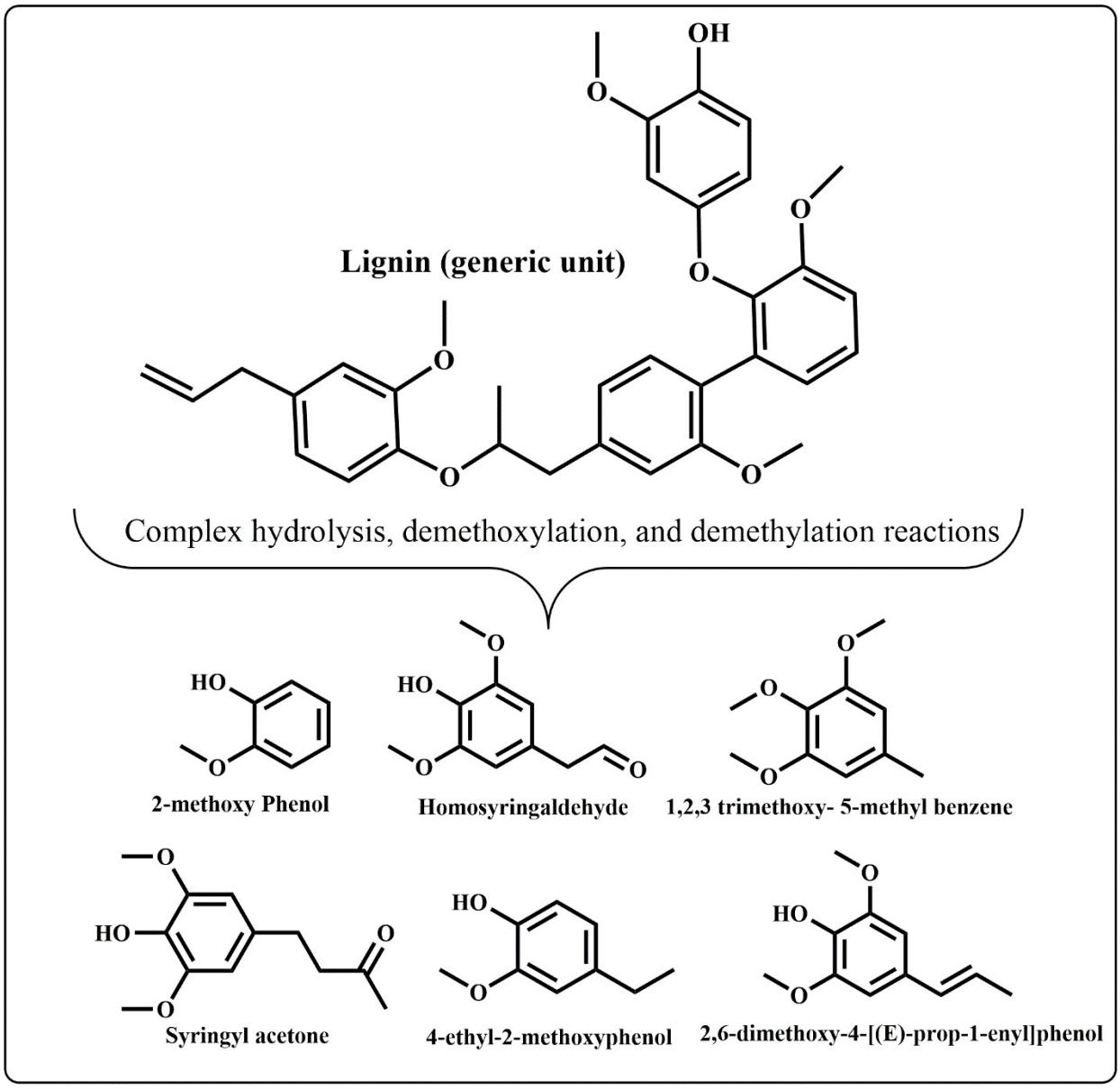


Fig S2. Plausible decomposition pathways of lignocellulosic biomass macromolecule lignin, under HTL conditions.[61-63]