Techno-economic and Greenhouse Gas Emission Assessment of Carbon Negative Pyrolysis Technology

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1. Electronic Supplementary Calculations and corresponding Tables

Supplementaty computational methods regarding calculation of CO_2 removal analysis for phenolic oil (or bioasphalt) and biochar emissions (related to Table 6 of the paper):

1.1 Phenolic oil (PO) or Bioasphalt CO_2 removal analysis for corn stover (CS) or red oak (RO) or yellow pine (YP) fed conventional fast pyrolysis FP or autothermal pyrolysis ATP (no pretreatment) plant:

$$\mathrm{EF_{PO}} = \mathrm{EF_{bioasphalt}} * \frac{\mathrm{Y_{bioasphalt}}}{\mathrm{Y_{PO}}} - \mathrm{C_{PO_{CS/RO/YP}}} * \mathrm{CR_{bioasphalt}} * \mathrm{CF}$$

where, CF = $\frac{44\ \mathrm{kg\ CO_{2e}}}{12\ \mathrm{kg\ \ C}}$

Electronic Supplementary Table ES1. Values of the parameters for CO_2 removal analysis of phenolic oil or bioasphalt (Related to Table 6 in the paper)

Parameters	Value	Units	Comments	References
$\mathrm{C_{PO_{CS}}}$	0.621	$\frac{\mathrm{kg\ C}}{\mathrm{kg\ PO}}$	Carbon content of phenolic oil	Polin et al.[1]
$\mathrm{C_{PO_{RO}}}$	0.56			
$\mathrm{C_{PO_{YP}}}$	0.56			
$EF_{bioasphalt}$	0.16	$\frac{\mathrm{kg\ CO_{2e}}}{\mathrm{kg\ bioasphalt}}$	Emission factor of bioasphalt	Zhou et al.[2]
$Y_{bioasphalt}$	0.23	$\frac{\mathrm{kg\ bioasphalt}}{\mathrm{kg\ biomass}}$	Bioasphalt yield from biomass	
Y_{PO}	0.525	$\frac{\mathrm{kg\ PO}}{\mathrm{kg\ biomass}}$	Phenolic oil yield from biomass	
$CR_{bioasphalt}$	1	$\frac{\mathrm{kg\ C}}{\mathrm{kg\ C}}$	Carbon sequestration rate after 100 years	
$\mathrm{EF_{PO_{CS}}}$	-2.21	$\frac{\mathrm{kg\ CO_{2e}}}{\mathrm{kg\ PO}}$	Emission factor of phenolic oil	For this study
$\mathrm{EF_{PO_{RO}}}$	-1.98			
$\mathrm{EF_{PO_{YP}}}$	-1.98			

1.2 Biochar (BC) CO_2 removal analysis for corn stover (CS) or red oak (RO) or yellow pine (YP) fed conventional fast pyrolysis FP or autothermal pyrolysis ATP (no pretreatment) plant:

$$\mathrm{EF_{BC_{CS/RO/YP}}} = -\mathrm{C_{BC_{CS/RO/YP}}} * \mathrm{CR_{BC}} * \mathrm{CF}\ + \mathrm{D_{BC}}$$

where, CF = $\frac{44\ \mathrm{kg\ CO_{2e}}}{12\ \mathrm{kg\ \ C}}$

Electronic Supplementary Table ES2. Values of the parameters for CO_2 removal analysis of biochar (Related to Table 6 in the paper)

Parameters	Value	Unit	Comments	Reference
$C_{BC_{CS}}$	0.623	$\frac{\text{kg C}}{\text{kg BC}}$	Biochar carbon content	Polin et al.[1]
$C_{BC_{RO}}$	0.427			
$C_{BC_{YP}}$	0.427			
D_{BC}	0.00609	$\frac{\text{kg } CO_{2e}}{\text{kg BC}}$	Biochar distribution from pyrolysis plant (40 miles)	Wang et al.[3]
CR_{BC}	0.7	$\frac{\text{kg C}}{\text{kg C}}$	Carbon sequestration rate after 100 years	Tisserant, Cherubini[4]
$EF_{BC_{CS}}$	-1.59	$\frac{\text{kg of } CO_{2e}}{\text{kg of PO}}$	Emission factor of phenolic oil	For this study
$EF_{BC_{RO}}$	-1.09			
$EF_{BC_{YP}}$	-1.09			

1.2.1 Biochar (BC) CO_2 removal analysis for corn stover (CS) or red oak (RO) or yellow pine (YP) fed ATP (with $FeSO_4$ pretreatment) plant:

Note: The biochar carbon content for pretreated $FeSO_4$ ATP plants assumes that the $FeSO_4$ mass goes directly into biochar. Hence, we took the adjusted carbon content of biochar for all $FeSO_4$ treated biomass (CS or RO or YP)

$$\text{Adj } C_{BC_{CS/RO/YP}} = \frac{Y_{BC_{CS/RO/YP}} * C_{BC_{CS/RO/YP}}}{TY_{BC_{CS/RO/YP}}}$$

$$EF_{BC/RO/YP} = -\text{Adj } C_{BC_{CS/RO/YP}} * CR_{BC} * CF + D_{BC}$$

Electronic Supplementary Table ES3. Values of the parameters for CO_2 removal analysis of adjusted biochar for all $FeSO_4$ pretreatment scenarios (Related to Table 6 in the paper)

Parameters	Value	Unit	Comments	Reference
$C_{BC_{CS}}$	0.623	$\frac{\text{kg C}}{\text{kg BC}}$	Biochar carbon content	Polin et al.[1]
$C_{BC_{RO}}$	0.427			
$C_{BC_{YP}}$	0.427			
$TY_{BC_{CS}}$	14	$\frac{\text{kg BC}}{\text{kg CS}}$ (wt.%)	Total biochar yield including $FeSO_4$ from biomass used	Elliot et al.[5], Rollag et al.[6] and Dalluge et al.[7]
$TY_{BC_{RO}}$	11	$\frac{\text{kg BC}}{\text{kg RO}}$ (wt.%)		
$TY_{BC_{YP}}$	17	$\frac{\text{kg BC}}{\text{kg YP}}$ (wt.%)		
$Y_{BC_{CS}}$	6.5	$\frac{\text{kg BC}}{\text{kg CS}}$ (wt.%)	Actual biochar yield excluding $FeSO_4$ from biomass used	Rollag et al.[6]
$Y_{BC_{RO}}$	10	$\frac{\text{kg BC}}{\text{kg RO}}$ (wt.%)		
$Y_{BC_{YP}}$	16	$\frac{\text{kg BC}}{\text{kg YP}}$ (wt.%)		
$\text{Adj } C_{BC_{CS}}$	28.3	$\frac{\text{kg C}}{\text{kg BC}}$ (wt.%)		Quantified

Adj $C_{BC_{RO}}$	38.8		Adjusted biochar carbon content	
Adj $C_{BC_{YP}}$	38.8			
$EF_{BC_{CS}}$	-0.74	$\frac{\text{kg of } CO_{2e}}{\text{kg of BC}}$	Emission factor of biochar	For this study
$EF_{BC_{RO}}$	-0.99			
$EF_{BC_{YP}}$	-1.02			

1.3 Direct air capture:

Direct air capture results include carbon footprint (cradle to grave) involved for storage for obtaining CO_2 removal along with electricity, heat, and other requirements for the DAC plant.

$$\varepsilon_{\text{net\_DAC}} = \frac{\varepsilon_{\text{emission}}}{\varepsilon_{\text{energy}}}$$

$$\varepsilon_{\text{emission}} = (C_{\text{footprint\_Total}} - 1)$$

Electronic Supplementary Table ES4. Values of the parameters for DAC plant (Related to Figure 10 in paper)

Parameters	Global 2030 Value	Germany Value	Global 2050 Value	Unit	Comments	Reference
$C_{\text{footprint\_Total}}$	0.589	1.0025	0.2	$\text{kg } CO_{2e}$	Total CO_2 footprint from different energy sources for the DAC plant	Deutz et al.[8]
$\varepsilon_{\text{emission}}$	-0.411	0.0025	-0.8	$\frac{\text{kg } CO_2 \text{ emitted}}{\text{kg } CO_2 \text{ captured}}$	CO_2 footprint of carbon captured	
$\varepsilon_{\text{energy}}$	11	15.9	6.5	$\frac{\text{MJ of energy}}{\text{kg } CO_2 \text{ captured}}$	Energy requirement of carbon captured	
$\varepsilon_{\text{net\_DAC}}$	-0.04	0.00016	-0.12	$\frac{\text{kg } CO_2 \text{ emitted}}{\text{MJ energy}}$	CO_2 footprint of energy required by DAC plant	For this study

1.4 Conventional fast pyrolysis (FP) and Autothermal pyrolysis (ATP):

The corn stover or red oak or yellow pine fed CFP or ATP systems quantifies CO_2 footprint per MJ of energy (electricity for grinding), and CO_2 footprint per MJ of energy, when the source of electricity changes. The table SX shows for corn stover $FeSO_4$ pretreated ATP plant only. The calculation remains same for the rest of the seven scenarios.

$$\alpha_{\text{emission\_KWh}} = \alpha_{\text{emission\_st}} * \frac{\alpha_{\text{MJ\_bio}}}{\alpha_{\text{KWh}}}$$

$$\varepsilon_{\text{net\_ATP}} = \alpha_{\text{emission\_KWh}} * \text{Conv}_{\text{KWh-MJ}} * \text{Conv}_{\text{elect-MJ}}$$

where, $\mathrm{Conv_{Kwh-MJ}} = \frac{\mathrm{1\ KWh}}{\mathrm{3.6\ MJ\ electricity}}$

$$\mathrm{Conv_{elect-MJ}} = \frac{\mathrm{0.42\ MJ\ electricity}}{\mathrm{1\ MJ\ energy}}$$

$$\alpha_{\mathrm{KWh}} = \frac{\mathrm{KWhr\ electricity}}{\mathrm{kg\ biomass\ (CS/RO/YP)}} = 0.02$$

$$\alpha_{\mathrm{MJ\_bio}} = \frac{\mathrm{MJ\ lignocellulosic\ biomass}}{\mathrm{kg\ lignocellulosic\ biomass}} = 17.47$$

Electronic Supplementary Table ES5. Values of the parameters for CS $FeSO_4$ pretreated ATP plant (Related to Table 7 in paper)

Parameters	ATP-US National Electricity	ATP-Coal	ATP-Coal-fired Boiler (CHP)	ATP-Wind	ATP-PV	Unit	Comments	References
$\alpha_{\mathrm{emissiom\_st}}$	-0.022	-0.021	-0.022	-0.023	-0.023	$\frac{\mathrm{kg\ CO_{2e}}}{\mathrm{MJ\ stover}}$	Carbon footprint of MJ stover	Cai et al.[9] (Coal, CHP-NG), Deutz et al.[8] (Wind, PV)
$\alpha_{\mathrm{emission\_KWh}}$	-19.3	-18.74	-18.98	-19.8	-19.7	$\frac{\mathrm{kg\ CO_{2e}}}{\mathrm{KWh}}$	Carbon footprint of electricity	
$\varepsilon_{\mathrm{net\_ATP}}$	-2.25	-2.18	-2.21	-2.31	-2.3	$\frac{\mathrm{kg\ CO_{2e}}}{\mathrm{MJ\ energy}}$	Carbon footprint of total energy	This study

Electronic Supplementary Table ES6. Comparison in GHG emissions of red oak (RO) fed FP and ATP (without and with pretreatment) plants and DAC plant using different electricity resources (related to table 7 in the paper)

Electricity Supply	RO FP	RO ATP (No PT)	RO ATP (PT)	DAC Plant	References
		($kg\ CO_{2e}$/MJ energy)			
Global grid 2030	-	-	-	-0.037	Deutz et al.[8]
Global grid 2050	-	-	-	-0.12	
Germany grid	-	-	-	0.00016	
Renewable grid 1	-2.9	-3.0	-2.83	-	
Renewable grid 2	-2.87	-2.98	-2.8	-	
Fossil fuel grid 1	-2.7	-2.87	-2.7	-	GREET[9]
Fossil fuel grid 2	-2.7	-2.9	-2.74	-	
This study	-2.82	-2.94	-2.78	-	Calculated

Electronic Supplementary Table ES7. Comparison in GHG emissions of yellow pine (YP) fed ATP (without and with pretreatment) plants and DAC plants using different electricity resources (related to table 7 in the paper)

Electricity Supply	YP ATP (No PT)	YP ATP (PT)	DAC Plant	References
	($kg\ CO_{2e}$/MJ energy)			
Global grid 2030	-	-	-0.037	Deutz et al.[8]
Global grid 2050	-	-	-0.12	
Germany grid	-	-	0.00016	
Renewable grid 1	-2.82	-3.03	-	
Renewable grid 2	-2.8	-3.0	-	
Fossil fuel grid 1	-2.69	-2.90	-	GREET[9]
Fossil fuel grid 2	-2.72	-2.93	-	
This study	-2.76	-2.97	-	Calculated

1.5 Life cycle analysis (LCA) system boundary:

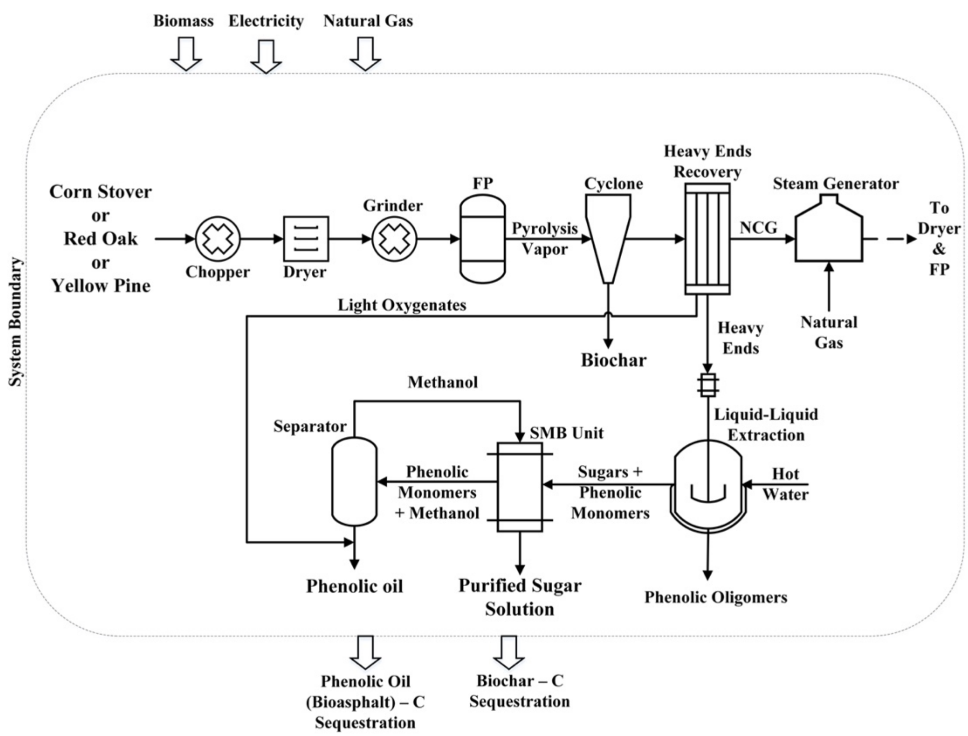

Figure ES1. Life cycle system boundary for 250 MTPD biomass fed FP system sugar production

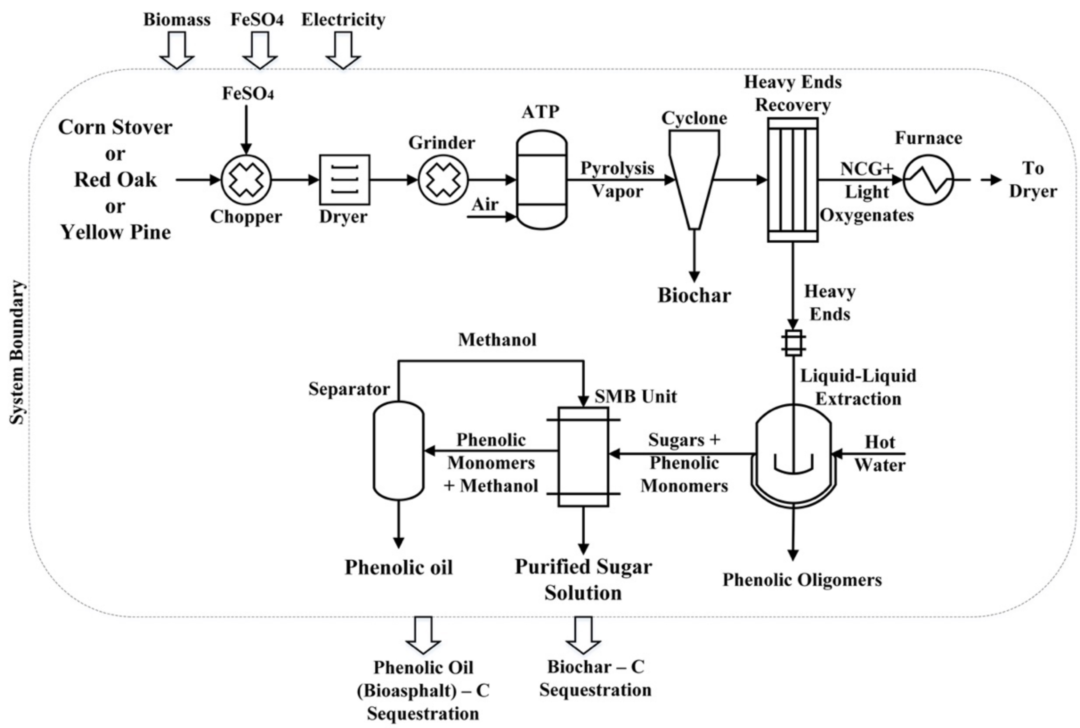

Figure ES2. Life cycle system boundary for 250 MTPD biomass fed ATP system sugar production

1.6 Annual operating costs and revenues incurred by 250 MTPD biomass (corn stover/red oak/yellow pine) fed fast pyrolysis and autothermal pyrolysis plants (with and without pretreatment) (all related to figure 4 in the paper):

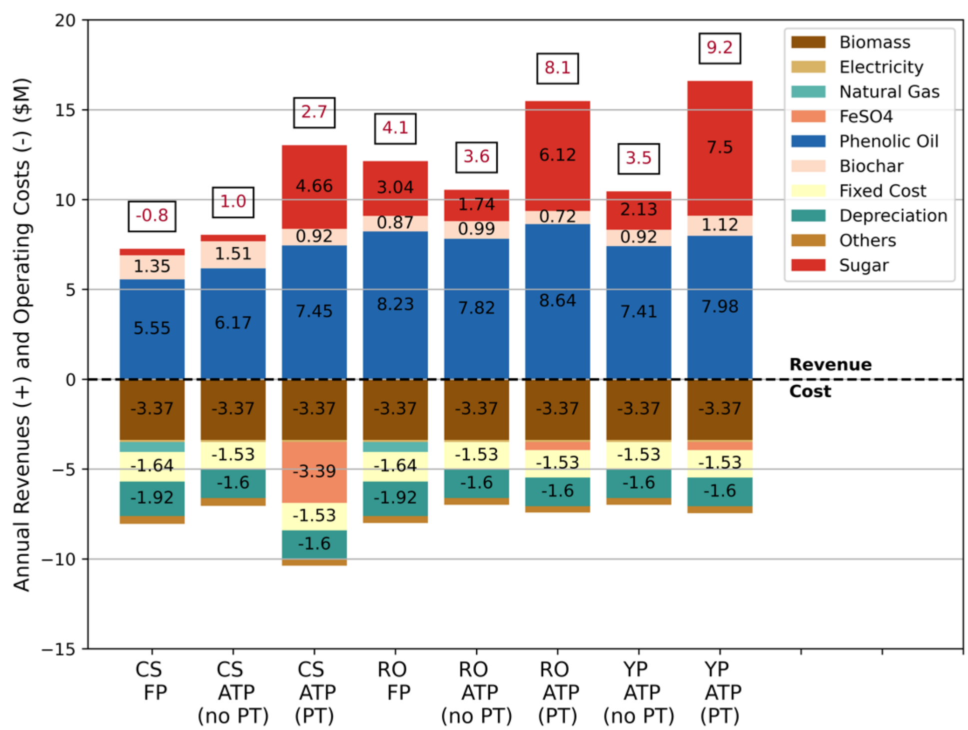

Figure ES3. Annual operating costs and revenues (at average sugar market price over the last 16 years) of 250 MTPD biomass-fed FP and ATP plant sugar production

1.1 Techno-economic analysis sensitivity for red oak and yellow pine FP and ATP (with and without pretreatment) scenarios (all related to figure 5 in the paper):

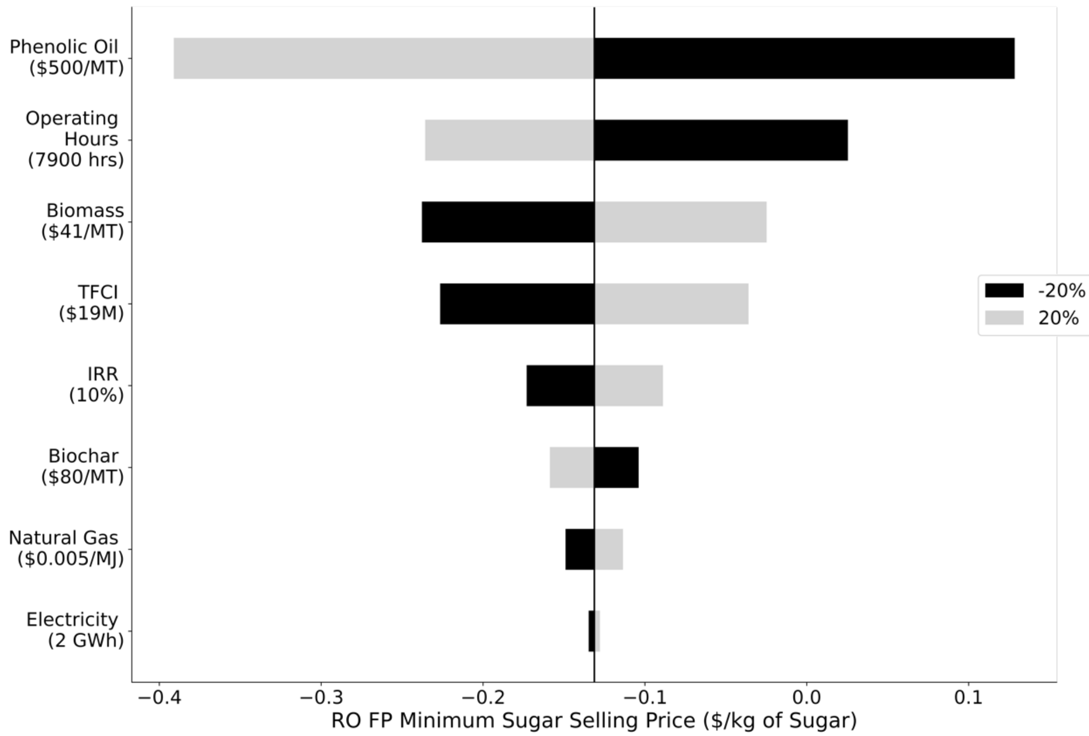

Figure ES4. Sensitivity analysis of red oak fed 250 MTPD FP plant sugar production with phenolic oil and biochar byproducts MSSP

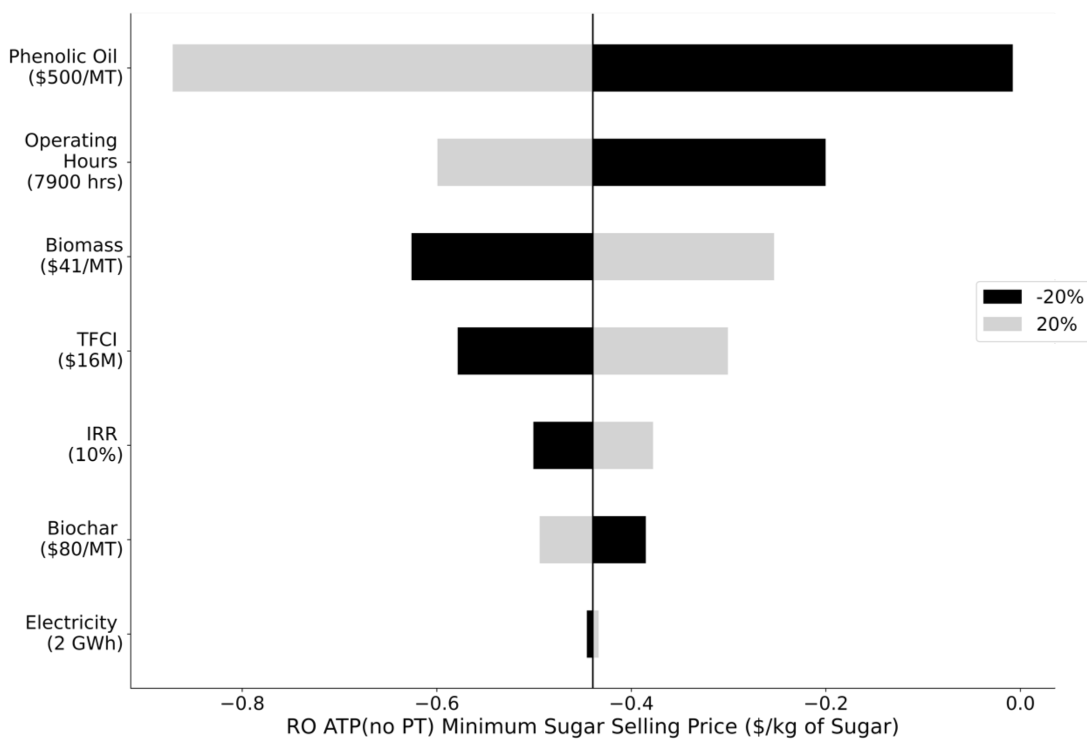

Figure ES5. Sensitivity analysis of red oak fed 250 MTPD ATP (no pretreatment) plant sugar production with phenolic oil and biochar byproducts MSSP

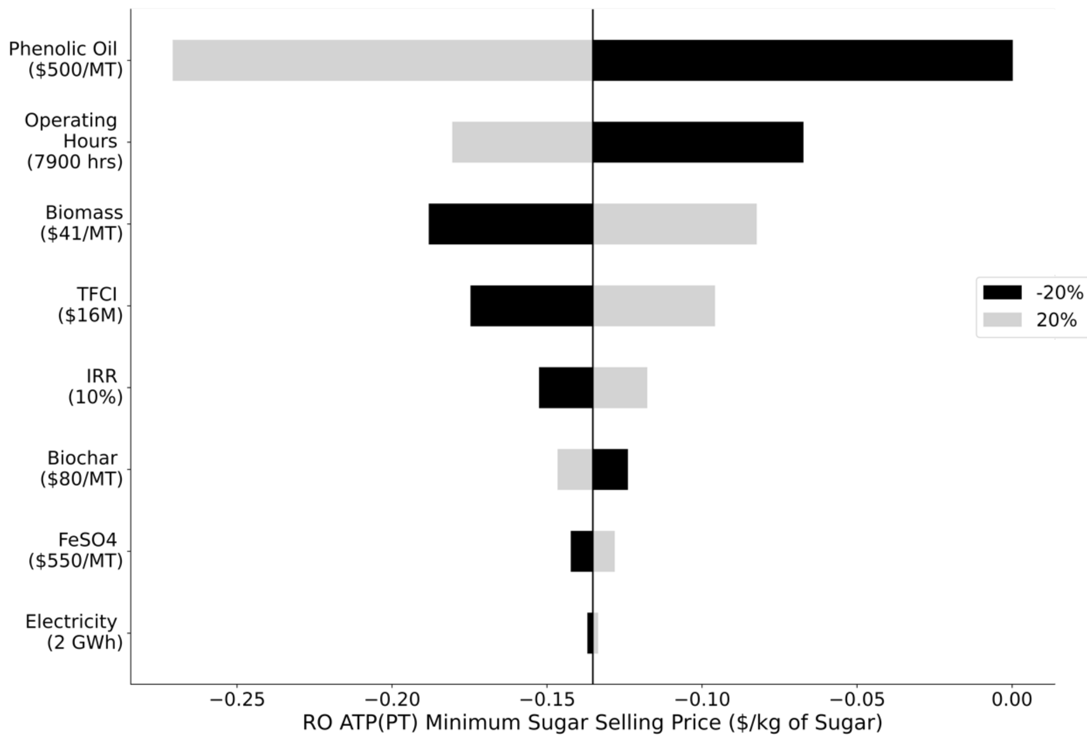

Figure ES6. Sensitivity analysis of red oak fed 250 MTPD ATP (with $FeSO_4$ pretreatment) plant sugar production with phenolic oil and biochar byproducts MSSP

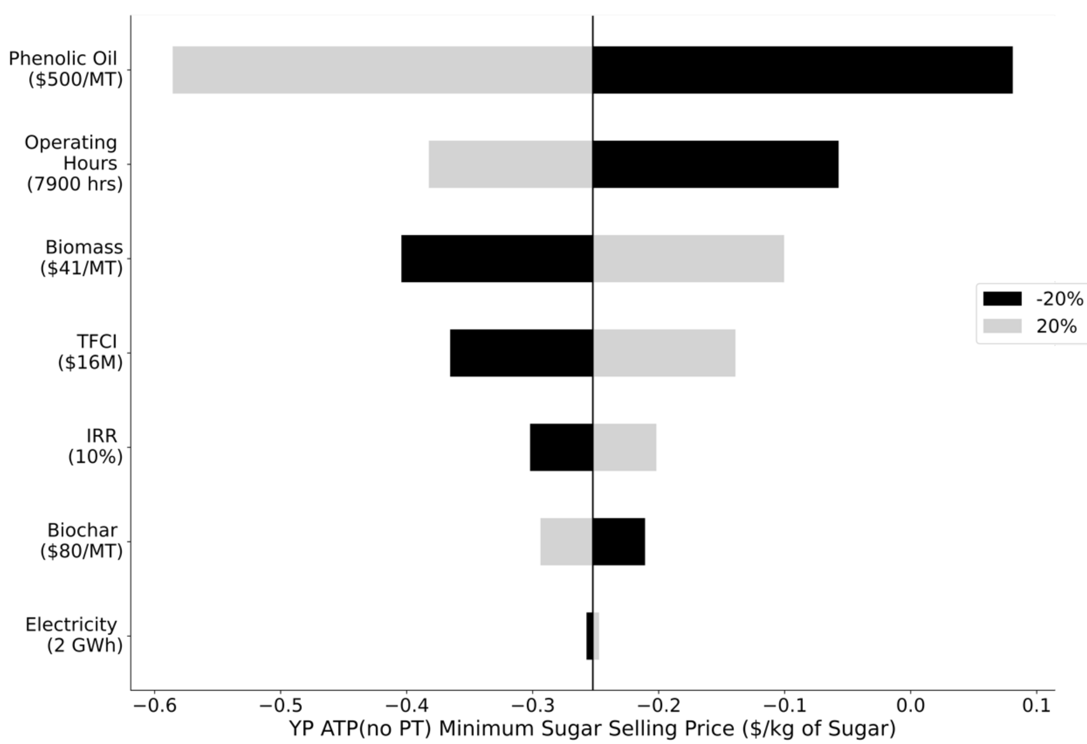

Figure ES7. Sensitivity analysis of yellow pine fed 250 MTPD ATP (without pretreatment) plant sugar production with phenolic oil and biochar byproducts MSSP

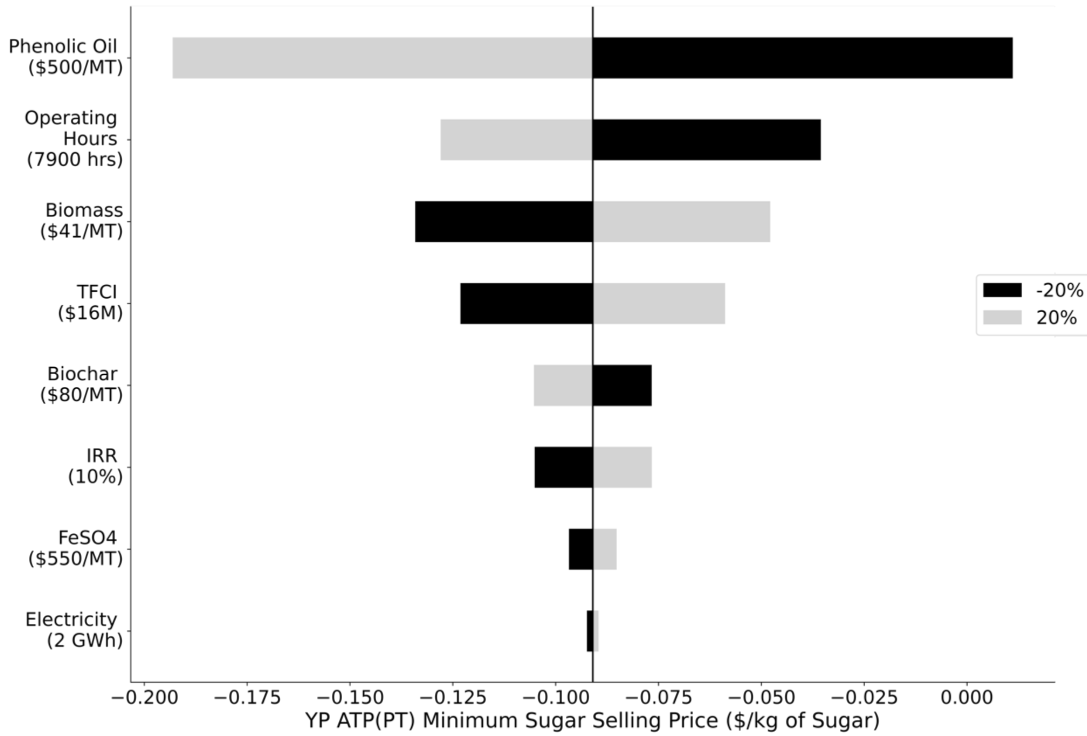

Figure ES8. Sensitivity analysis of yellow pine fed 250 MTPD ATP ($FeSO_4$ pretreatment) plant sugar production with phenolic oil and biochar byproducts MSSP

1.2 Life cycle sensitivity analysis for red oak and yellow pine FP and ATP (with and without pretreatment) scenarios (all related to figure 7 in the paper):

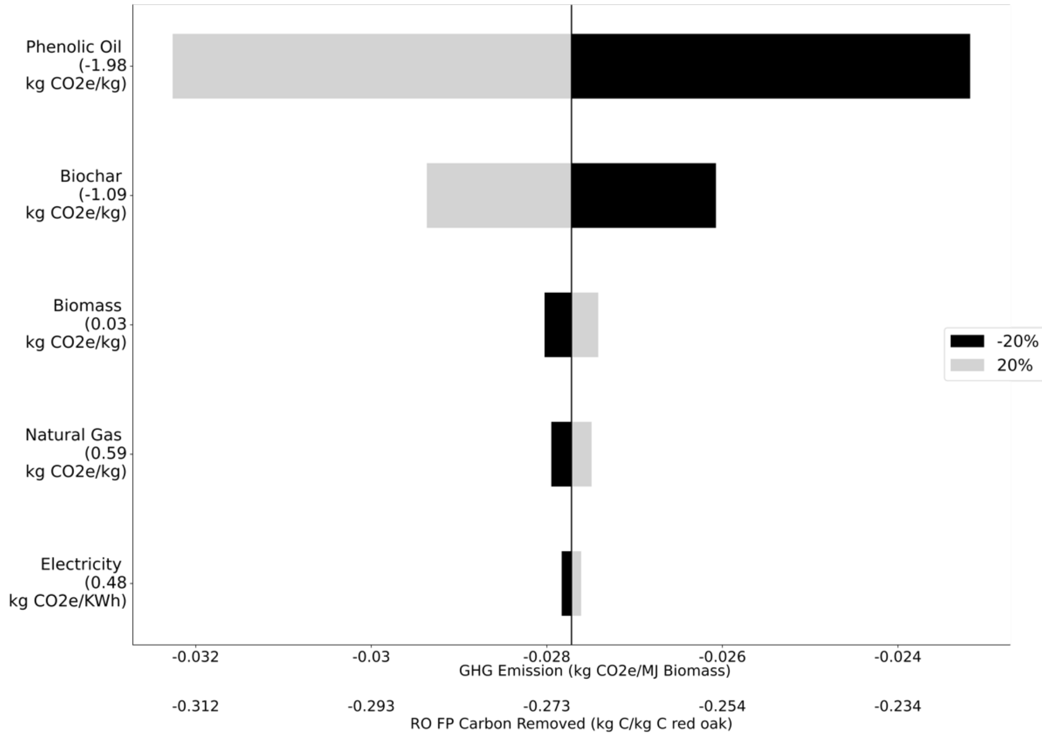

Figure ES9. Sensitivity analysis of GHG emissions (upper x-axis) and carbon removal (lower x-axis) for red oak fed 250 MTPD FP plant sugar production with phenolic oil and biochar byproducts

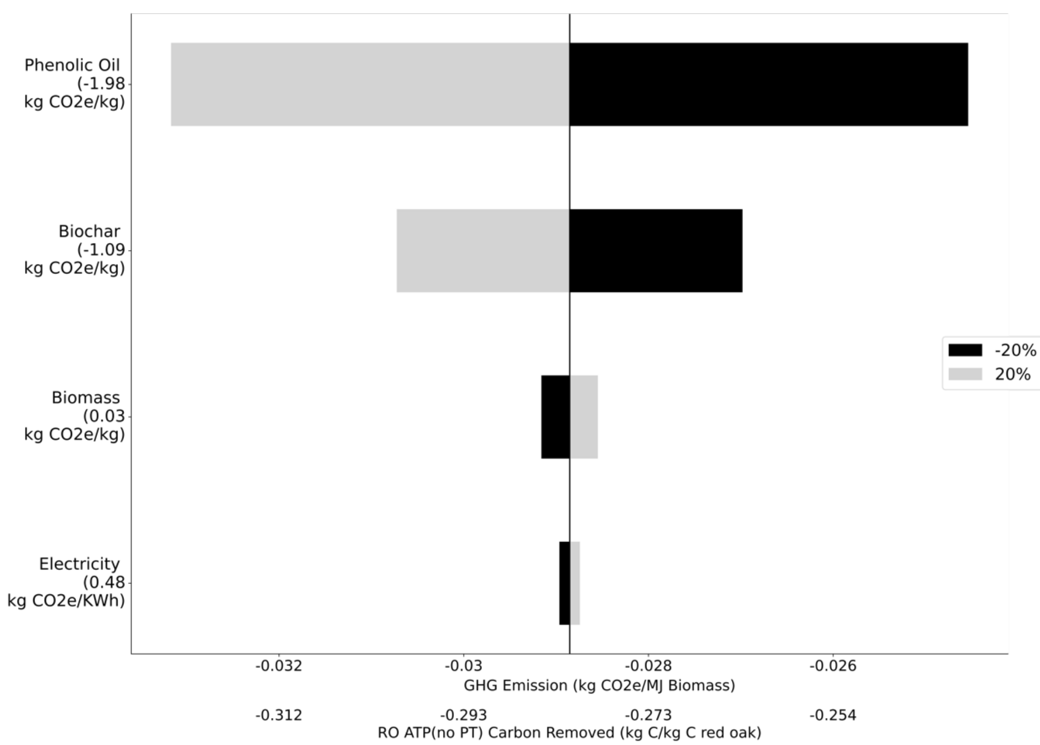

Figure ES10. Sensitivity analysis of GHG emissions (upper x-axis) and carbon removal (lower x-axis) for red oak fed 250 MTPD ATP (no pretreatment) plant sugar production with phenolic oil and biochar byproducts

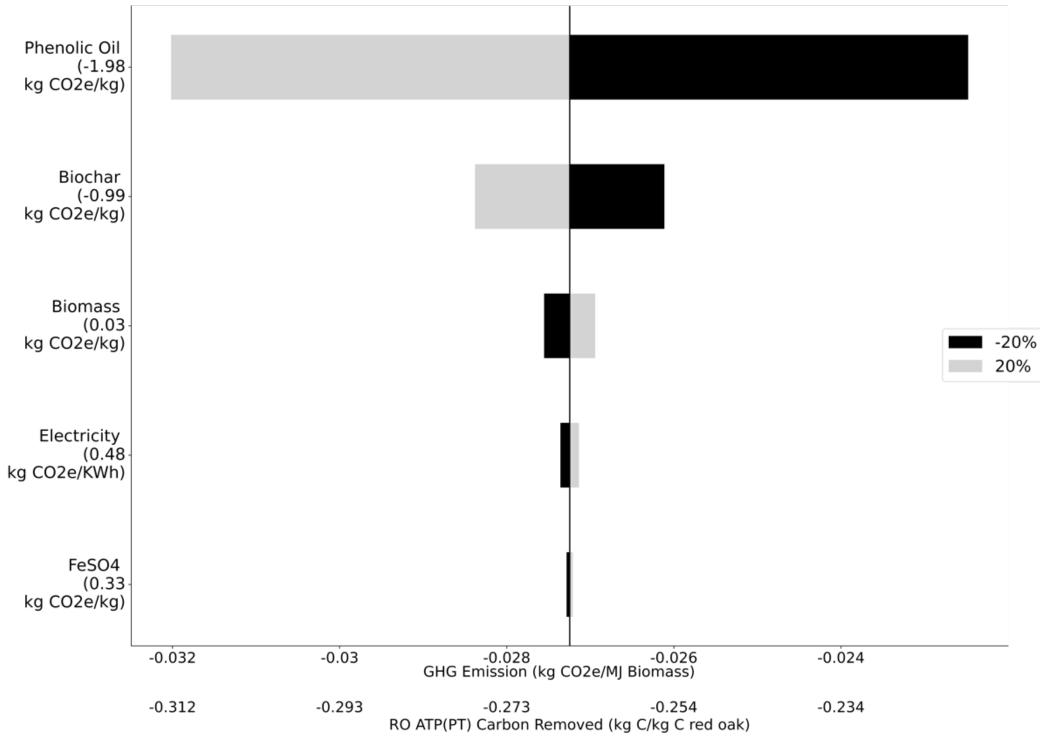

Figure ES11. Sensitivity analysis of GHG emissions (upper x-axis) and carbon removal (lower x-axis) for red oak fed 250 MTPD ATP ($FeSO_4$ pretreatment) plant sugar production with phenolic oil and biochar byproducts

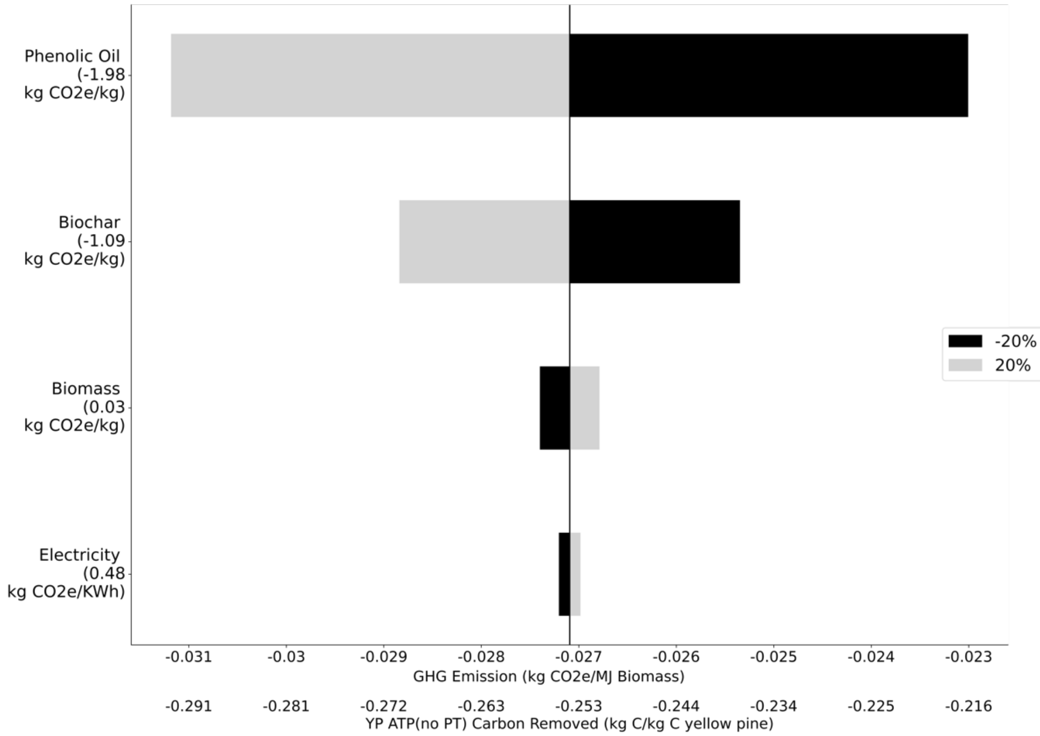

Figure ES12. Sensitivity analysis of GHG emissions (upper x-axis) and carbon removal (lower x-axis) for yellow pine fed 250 MTPD ATP (no pretreatment) plant sugar production with phenolic oil and biochar byproducts

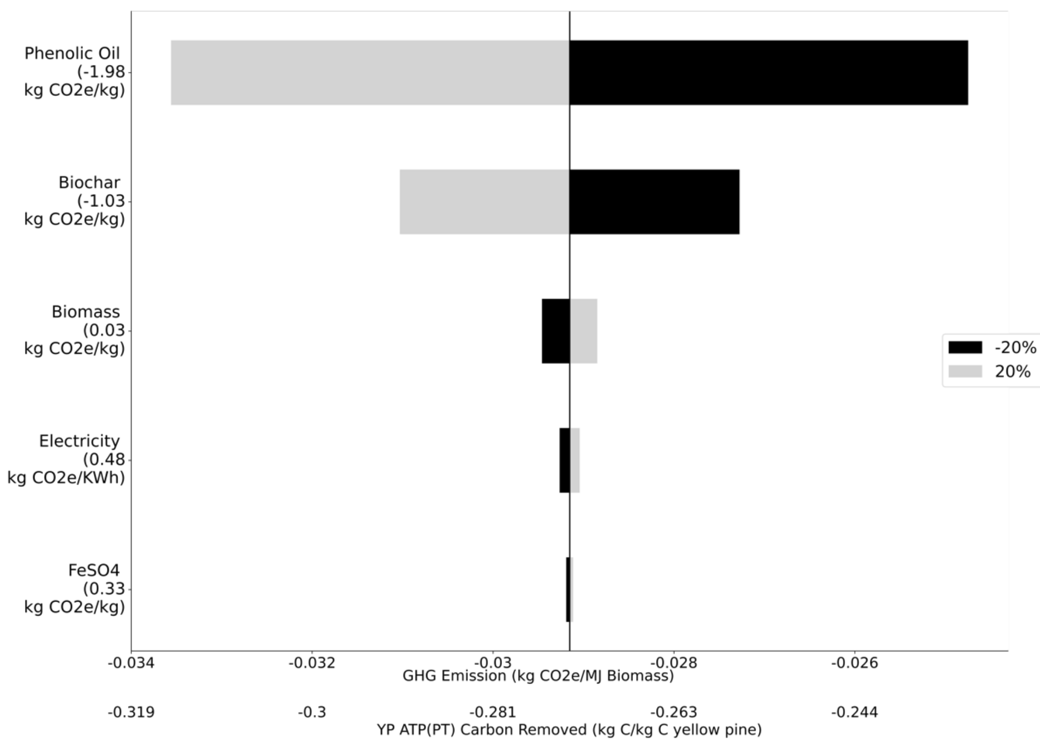

Figure ES13. Sensitivity analysis of GHG emissions (upper x-axis) and carbon removal (lower x-axis) for yellow pine fed 250 MTPD ATP ($FeSO_4$ pretreatment) plant sugar production with phenolic oil and biochar byproducts

1.8 Costs of CO_2 removal for corn stover/red oak/yellow pine fed 250 MTPD and 50 MTPD fast pyrolysis and autothermal pyrolysis plants with and without $FeSO_4$ pretreatment (all related to figure 11 in the paper)

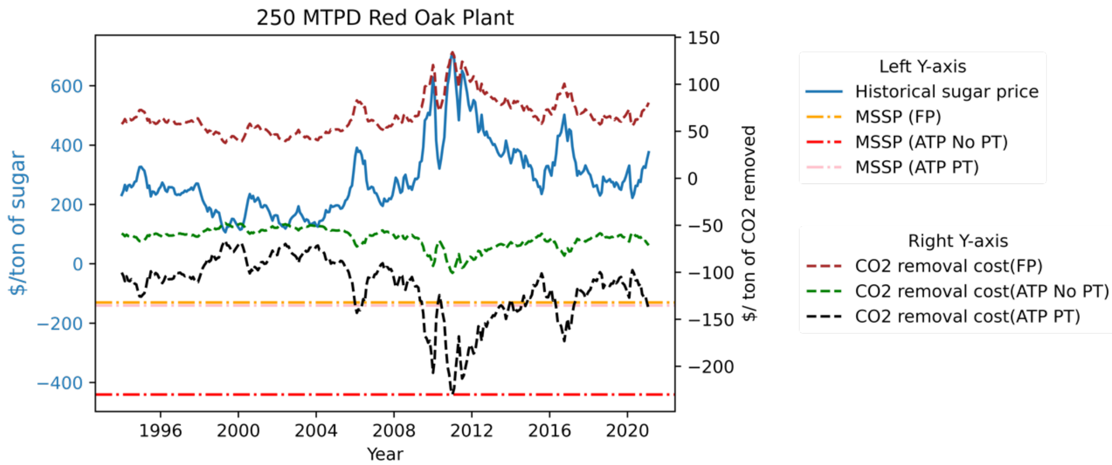

Figure ES14. Cost of CO_2 removal for a red oak fed autothermal and conventional fast pyrolysis system as function of sugar price

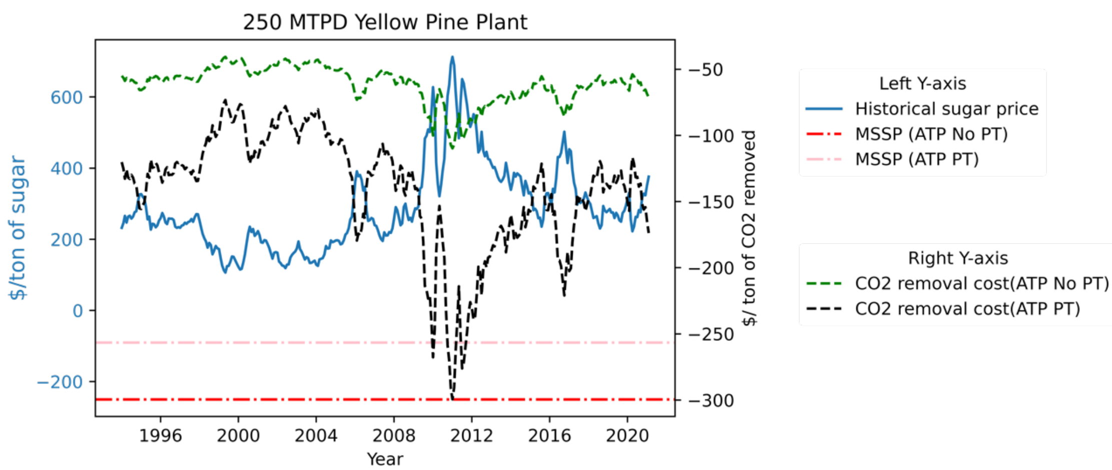

Figure ES15. Cost of CO_2 removal for a yellow pine fed autothermal systems (without and with $FeSO_4$ pretreatment) as a function of sugar price

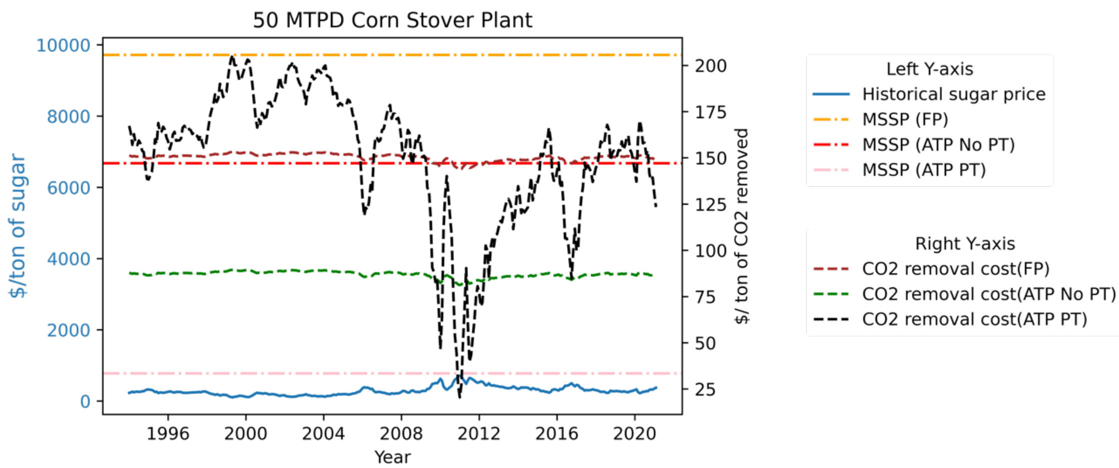

Figure ES16. Cost of CO_2 removal for a 50 MTPD corn stover-fed autothermal and conventional fast pyrolysis system as a function of sugar price

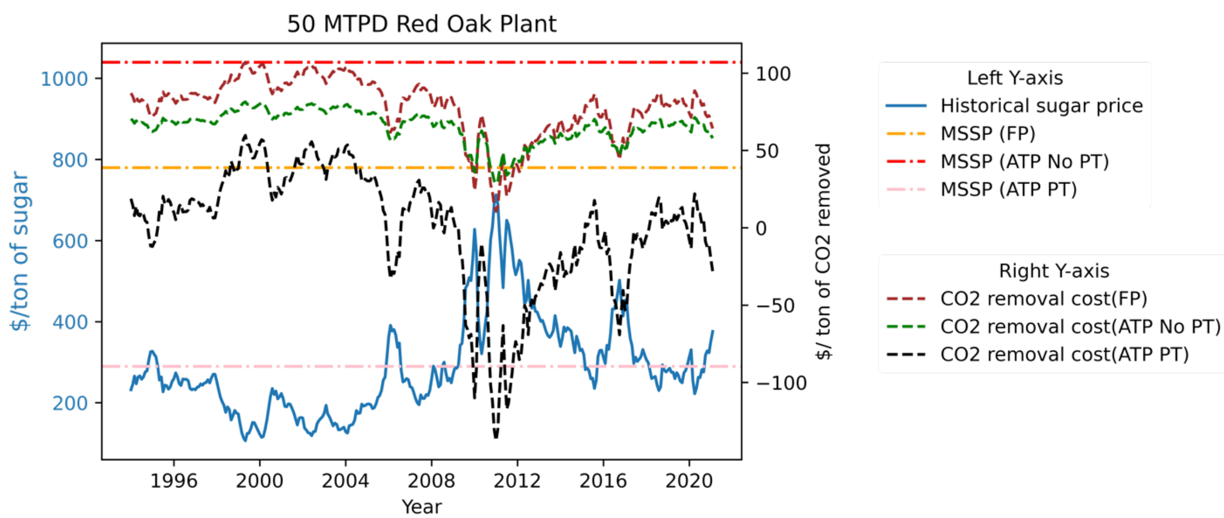

Figure ES17. Cost of CO_2 removal for a 50 MTPD red oak-fed autothermal and conventional fast pyrolysis system as a function of sugar price

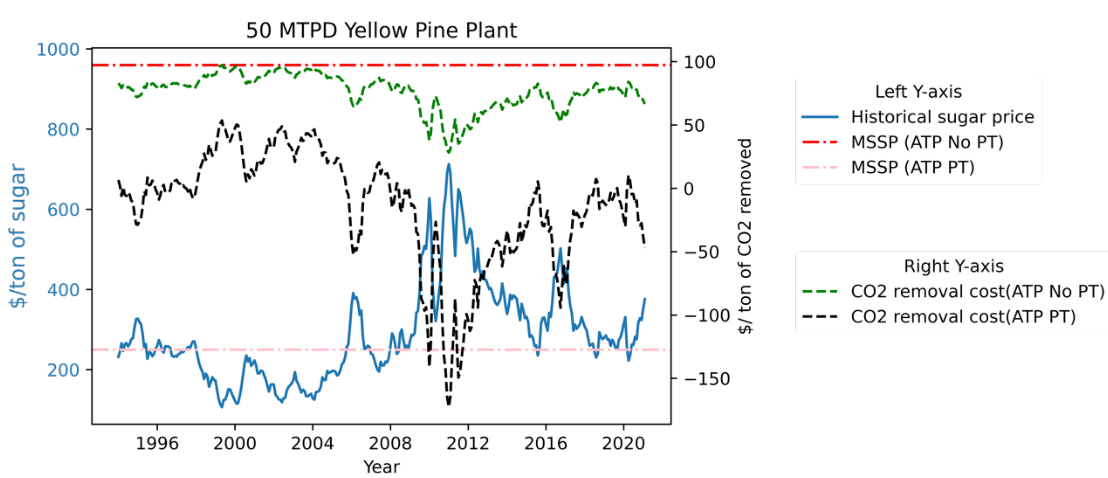

Figure ES18. Cost of CO_2 removal for a 50 MTPD yellow pine-fed autothermal systems (without and with $FeSO_4$ pretreatment) as a function of sugar price

Electronic Supplementary References:

1. Polin, J.P., Carr, H.D., Whitmer, L.E., Smith, R.G., and Brown, R.C. (2019). Conventional and autothermal pyrolysis of corn stover: Overcoming the processing challenges of high-ash agricultural residues. J. Anal. Appl. Pyrolysis *143*, 104679.

2. Zhou, X., Moghaddam, T.B., Chen, M., Wu, S., Adhikari, S., Xu, S., and Yang, C. (2020). Life Cycle Assessment of Biochar Modified Bioasphalt Derived from Biomass. ACS Sustain. Chem. Eng. *8*, 14568–14575.

3. Wang, Z., Dunn, J.B., Han, J., and Wang, M.Q. (2014). Effects of co-produced biochar on life cycle greenhouse gas emissions of pyrolysis-derived renewable fuels. Biofuels, Bioprod. Biorefining *8*, 189–204.

4. Tisserant, A., and Cherubini, F. (2019). Potentials, limitations, co-benefits, and trade-offs of biochar applications to soils for climate change mitigation. Land *8*.

5. Elliott, D.C., Wang, H., Rover, M., Whitmer, L., Smith, R., and Brown, R. (2015). Hydrocarbon Liquid Production via Catalytic Hydroprocessing of Phenolic Oils Fractionated from Fast Pyrolysis of Red Oak and Corn Stover. ACS Sustain. Chem. Eng. *3*, 892–902.

6. Rollag, S.A., Lindstrom, J.K., and Brown, R.C. (2020). Pretreatments for the continuous production of pyrolytic sugar from lignocellulosic biomass. Chem. Eng. J. *385*, 123889.

7. Dalluge, D.L., Daugaard, T., Johnston, P., Kuzhiyil, N., Wright, M.M., and Brown, R.C. (2014). Continuous production of sugars from pyrolysis of acid-infused lignocellulosic biomass. Green Chem. *16*, 4144–4155.

8. Deutz, S., and Bardow, A. (2021). Life-cycle assessment of an industrial direct air capture process based on temperature–vacuum swing adsorption. Nat. Energy *6*, 203–213.

9. Cai, H., Wang, M., Elgowainy, A. and Han, J. (2012). Updated greenhouse gas and criteria air pollutant emission factors and their probability distribution functions for electricity generating units.