Supplementary Information File

Life Cycle Inventory:

Life cycle data were collected from literature sources and evaluated using data quality indicators, as described by the modified Weidema method in Table S1.¹ The scoring range is from 1-5, with 1 indicating that the data is most reliable while 5 is least reliable. Each item was qualified using a 6-digit score, with each digit ranging from 1 to 5. Each digit represents the reliability of the data in each of the 6 categories, with the first digit representing evaluation criteria A and the last digit representing criteria F, respectively.

	Evaluation criteria	Description	Scoring range
Α	Acquisition method	Method of acquiring the data,	1: measured data
		whether measured directly or	5: non-qualified estimate
		estimated based on assumptions	
В	Independence of data	Source of information and its	1: independent verified source
	supplier	bias towards the concerned	5: unverified source with bias
		study	
С	Representativeness	Degree of application of data to	1: representative data from
		even out fluctuations	sufficiently large samples
			5: incomplete data from
			relatively small samples
D	Data age	Temporal relevance of data	1: less than 3 years
			5: unknown or greater than 20
			years
E	Geographical	Spatial relevance of data	1: data from area under study
	correlation		5: data from area unknown or
			different conditions
F	Technological	Technological relevance of data	1: data from processes under
	correlation	with processes in study	study
			5: data from related processes
			but different technology

Table S1: Evaluation criteria in the modified Weidema method and description of scores (adapted from Couillard et al.).²

Table S2: Life cycle input data for both Py-ECH and CE systems with their source and data quality indicator score.

Parameter	Value	Source	Data quality indicator (ABCDEF)
Technical data for Py-ECH system		Lam et al. ³	211111
Technical data for CE system		Humbird et al.	211321
Annual C sequestration rate	0.174 Mg C/ha/yr	GREET ⁴	211321
Corn stover storage losses	8.40%	GREET ⁴	211321
Corn stover transport losses	2.00%	GREET ⁴	211321
Corn stover farm handling losses	2.00%	GREET ⁴	211321
Diesel for harvesting corn stover	3.58 gallons/acre	GREET ⁴	211321
Fraction of N leached to surface waters	24% of total applied N	GREET ⁴	211321
Fraction of P leached to surface waters	7% of total applied P	Powers et al. ⁵	311421
Fraction of fertilizer N emitted as NO	0.8% of total applied N	GREET ⁴	211321
Fraction of fertilizer N emitted as NH ₃	10% of total applied N	IPCC ⁶	211421
Fraction of fertilizer N emitted as N ₂ O	1.5% of total applied N	GREET ⁴	211321
Corn stover yield	2.39 dry ton/acre	GREET ⁴	211321
Distance from field to refinery for CE system	50 miles	Kim et al. ⁷	212122
Weight limitation on trucks	80,000 lbs	Edwards et al. ⁸	221311
Distance from refinery to pumps for both Py-ECH and CE systems	110 miles	Kumar et al. ⁹	212322

Using the life cycle data in Table S2, the technical data from our previous work,³ and the Humbird et al. report,¹⁰ the contribution of all operations to each impact category was calculated for the Py-ECH and CE systems, respectively. These have been tabulated in Tables S3, S4, and S5.

Table S3: Contribution of different operations to greenhouse gas emissions (GHG) for CE and Py-ECH systems.

Operations	Allocation Method 1		Allocation Method 2	
	CE Py- FCH(F)		CE	Py- ECH(F)

	(g CO ₂ /	MJ)	(g CO	O_2/MJ
Supply Chain:				
Harvesting	5.51	2.09	5.51	2.09
Fertilizer Application	3.09	1.17	1.26	4.78
Fertilizer Production	3.15	1.19	8.33	7.36
Below ground C Sequestration	0.00	0.00	-13.70	-5.19
Feedstock Biomass to Energy	-235.00	-64.20	-235.00	-64.20
Corn Stover Losses	5.35	2.03	5.35	2.03
Processing				
Heat and Power	132.00	12.40	132.00	12.40
Fermentation CO ₂	39.50	0.00	39.50	0.00
Feedstock Biomass to Biochar	0.00	-13.30	0.00	-13.30
Electricity	-12.40	84.80	-12.40	84.80
Transport				
Transportation	1.46	0.37	1.46	0.37
Combustion				
Fuel Combustion	71.00	64.10	71.00	64.10

Table S4: Contribution of different operations to eutrophication potential (EUP) for CE and Py-ECH systems.

Operations	Allocation Method 1		Allocation	n Method 2
	СЕ	Py- ECH(F)	CE	Py- ECH(F)
	(mg CO	2/MJ	(mg C	O_2/MJ
Supply Chain:				
Harvesting	4.18	1.58	4.18	1.58
Fertilizer Application	6.86	2.60	28.00	10.60
Nitrogen Runoff	111.00	42.00	452.00	171.00
Phosphorus Runoff	70.20	26.60	139.00	52.70
Fertilizer Production	0.35	0.13	0.80	0.66
Processing				
Refinery Operations	15.10	0.66	15.10	0.66
Electricity	-0.43	2.94	-0.43	2.94
Transport				
Transportation	1.46	0.37	1.46	0.37
Combustion				
Fuel Combustion	71.00	64.10	71.00	64.10

Operations	Allocation Method 1		Allocation	Method 2
	CE	Py-	CE	Py-
		ECH(F)		ECH(F)
	(LH_2O/L)	MJ)	$(L H_2)$	0/MJ)
Supply Chain:				
Farming	0.00	0.00	12.80	4.85
Fertilizer Production	0.006	0.002	0.009	0.004
Processing				
Refinery Operations	2.42	0.38	2.42	0.38
Electricity	-0.32	2.18	-0.32	2.18
Transport				
Transportation	0.00	0.00	0.00	0.00
Combustion				
Fuel Combustion	0.00	0.00	0.00	0.00

Table S5: Contribution of different operations to water scarcity footprint (WSF) for CE and Py-ECH systems.

Table S6: Life cycle impact summary for the CE process. Allocation methods 1 and 2 are reported to observe the effects of avoiding allocation and applying minimal allocation to cultivation.

	GHG		EUP		WSF	
Allocation	1	2	1	2	1	2
	g CO2 eq /MJ		g N eq/MJ		L H ₂ O/MJ	
Supply Chain	-2.18E+02	-2.17E+02	1.92E-01	6.24E-01	5.98E-02	1.29E+01
Processing	1.60E+02	1.60E+02	1.46E-02	1.46E-02	2.10E+00	2.10E+00
Transport	1.46E+00	1.46E+00	3.02E-05	3.02E-05	0	0
Combustion	7.10E+01	7.10E+01	1.11E-03	1.11E-03	0	0
TOTAL	1.44E+01	1.54E+01	2.08E-01	6.39E-01	2.16E+00	1.50E+01

Table S7: Life cycle impact summary for the Py-ECH process. Allocation methods 1 and 2 are reported to observe the effects of avoiding allocation and applying minimal allocation to cultivation.

	GHG		EUP		WSF	
Allocation	1	2	1	2	1	2
	g CO2 eq /MJ		g N eq/MJ		L H ₂ O/MJ	

Supply Chain	-5.77E+01	-5.31E+01	7.29E-02	2.37E-01	2.27E-02	4.89E+00
Processing	8.11E+01	8.11E+01	3.60E-03	3.60E-03	2.56E+00	2.56E+00
Transport	3.68E-01	3.68E-01	7.61E-06	7.61E-06	0	0
Combustion	6.41E+01	6.41E+01	1.07E-03	1.07E-03	0	0
TOTAL	8.78E+01	8.82E+01	7.76E-02	2.41E-01	2.58E+00	7.45E+00
	0.1.02.01	0.022101		01	=::::=:::::::::::::::::::::::::::::::::	



Figure S1: Sensitivity of system RF and ER_f with % renewable heat at refinery. Fossil electricity implies all the electricity is provided by the MRO-West electrical grid; Renewable electricity implies that all the electricity being provided is from renewable sources. The breakeven is at about 25% renewable heat and 100% renewable electricity.



Figure S2: Net GHG emissions of Py-ECH and CE processes using allocation method 1 on a "per MJ fuel energy" basis; 'F' indicates 2020 electrical grid including 70.8% fossil electricity and 'R' refers fully renewable power. Excess land area of ~0.2 million hectares. The annual rate of carbon accumulation in forests can vary from 0.8 tonnes/ha/yr to 5.1 tonnes/ha/yr, depending on the type of forest.¹¹ The CCLUB model from GREET estimates an annual carbon sequestration rates from forests in the United States at 2.4 tonnes C/ha/yr, which is well within this range. The annual carbon sequestration rate for forests have been assumed conservatively to be 0.8 tonnes/ha/yr.



Figure S3: Net GHG emissions of Py-ECH and CE processes using allocation method 1 on a "per kg corn stover processed" basis; 'F' indicates 2020 electrical grid including 70.8% fossil electricity and 'R' refers fully renewable power. Excess fuel energy of of ~11-12 MJ is produced in the Py-ECH process per kg corn stover processed. An energy allocation percentage of~ 38% has been applied as the fuel energy of the primary product must be made equal to the fuel energy of the CE process, which is about ~7 MJ/kg corn stover processed.

References:

- 1. M. W. Toffel and A. Horvath, *Environmental Science & Technology*, 2004, **38**, 2961-2970.
- 2. S. Couillard, G. Bage and J.-S. Trudel, *Comparative Life Cycle Assessment (LCA) of Artificial vs Natural Christmas Tree*, Report 1043-RF3-09, 2009.
- C. H. Lam, S. Das, N. C. Erickson, C. D. Hyzer, M. Garedew, J. E. Anderson, T. J. Wallington, M. A. Tamor, J. E. Jackson and C. M. Saffron, *Sustainable Energy & Fuels*, 2017, 1, 258-266.
- 4. M. Wang, *The Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation Model*, Argonne National Laboratory, Argonne, Illinois, 1999.
- 5. S. E. Powers, *Quantifying Cradle-to-Farm Gate Life-Cycle Impacts Associated with Fertilizer Used for Corn, Soybean, and Stover Production* NREL, Golden, Colorado, 2005.

- 6. IPCC, Revised 1996 IPCC Guidelines for National Greenhouse Gas Inventories, 1996.
- 7. S. Kim, X. Zhang, B. E. Dale, A. D. Reddy, C. D. Jones, K. Cronin, R. C. Izaurralde, T. Runge and M. Sharara, *Biofuels, Bioproducts & Biorefining*, 2018, **12**, 203-212.
- 8. W. Edwards, *Economics of Harvesting and Transporting Corn Stover* Iowa State University, 2014.
- 9. D. Kumar and G. Murthy, *The International Journal of Life Cycle Assessment*, 2012, **17**, 388-401.
- D. Humbird, R. Davis, L. Tao, C. Kinchin, D. Hsu, A. Aden, P. Schoen, J. Lukas, B. Olthof and M. Worley, *Process design and economics for biochemical conversion of lignocellulosic biomass to ethanol: dilute-acid pretreatment and enzymatic hydrolysis of corn stover*, Report NREL/TP-5100-47764, National Renewable Energy Laboratory (NREL), Golden, CO., 2011.
- 11. S. Brown, J. Sathaye, M. Cannell and P. E. Kauppi, *Management of Forests for Mitigation of Greenhous Gas Emissions*, 1995.