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Supplementary Information

Negative-carbon drop-in transport fuels produced via catalytic hydropyrolysis of woody biomass with CO_2 capture and storage

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Appendix A. Composition of feedstocks

The composition and heating value assumed for woody biomass residues in our process simulations is given in Table A1. The biomass arrives at the plant gate with a moisture content of 30 wt%. The "as-fed" moisture content refers to the moisture content of the biomass as it enters the pyrolysis reactor.

The composition assumed for natural gas is given in Table A2.

Table A1. Biomass composition.[1]

	Mixed wood (wt%)		
	as fed	dry	m.a.f.
Moisture	10.00%		
C	44.73%	49.70%	49.95%
H	5.22%	5.80%	5.83%
O	39.47%	43.86%	44.08%
N	0.10%	0.11%	0.11%
S	0.03%	0.03%	0.03%
Ash	0.45%	0.50%	
LHV (MJ/kg)	16.29	18.37	18.47
HHV (MJ/kg)	17.68	19.64	19.74

Table A2. Natural gas composition.[2]

Component	***Wt%***
CH_4	93.90
C_2H_6	3.20
C_3H_8	0.70
C_4H_{10}	0.40
CO_2	1.00
N_2	0.80
LHV (MJ/kg)	49.01
HHV (MJ/kg)	54.34

Appendix B. Estimation of H_2 flow

Published estimates of the H_2 flow required for a 3,425 t/d_{dry} biomass fluidized-bed catalytic hydropyrolysis reactor are not available, so the H_2 flow was estimated for purposes of the process simulations undertaken in this work. In developing the estimate, it was recognized that the H_2 serves three roles:

1) As a reactant in the pyrolysis process;
2) As the fluidizing agent;
3) As a thermal regulator.

The flow of H_2 required for each of these roles was estimated separately, and the largest of the three flow rates was adopted as the assumed flow for the system simulations reported in the main text.

Reactant

According to GTI publications,[1,3] **0.049 kg H_2/kg biomass$_{MAF}$** is needed as reactant. For the design reactor capacity in our simulations (39.4 kg/s biomass$_{MAF}$), the required reaction H_2 is 1.95 kg/s. Since this is the amount of H_2 that reacts during pyrolysis, the actual H_2 input would need to be higher than this in order to maintain a sufficient partial pressure driving force for the reactions.

Fluidizing agent

The H_2 flow needed for fluidization of the bed was calculated assuming that the reactor behaves as an ideal fluidized bed and using the following equations and input assumptions:

Table B1. Data, assumptions and equations for ideal fluidization flow calculation.

Symbol (unit)	Name	Value	Source
Equations			
F_{H2} (kg/s)	Design minimum H_2 mass flow rate	$v * A * \rho_g$	4
v (m/s)	Design fluidization velocity	$2*v_{mf}$	5
v_{mf} (m/s)	Minimum fluidization velocity	$\frac{Re * \mu}{d_p * \rho_g}$	4
Re (dimensionless)	Reynolds number	$\frac{Ar}{1502}$	4
Ar (dimensionless)	Archimedes number	$\frac{d_p^3 * \rho_g * (\rho_s - \rho_g)}{\mu^2}$	4
D (m)	Bed diameter	$\sqrt{\frac{A}{\frac{1}{4}\pi}}$	
A (m^2)	Bed cross-sectional area	$\frac{W * g}{\Delta p}$	4
W (kg)	Bed weight	F_{Bio} / WHSV *3600	4
Equation input assumptions			
WHSV (kg bio/ (kg cat*h))	Weight Hourly Space Velocity	1.62	3
F_{Bio} (kg bio$_{as\ fed}$/s)	Biomass flow	44.04	Assumed plant size
Δp (bar)	Pressure drop over entire bed	0.5	5
d_p (m)	Particle size [a)]	$300*10^{-6}$	5
ρ_s (kg/m^3)	Catalyst particle density	1,500	5
ρ_b (kg/m^3)	Bed bulk density at rest	1,000	5
ρ_g (kg/m^3)	H_2 density in reactor at 22.4 bar	1.66	Aspen Plus
μ (kg/(m*s))	H_2 dynamic viscosity in reactor	$1.5*10^{-5}$	6
g (m/s^2)	Gravity	9.81	

a) This is the assumed average catalyst particle size as it is assumed that the majority of particles inside the reactor are from the catalyst.

The resulting calculated minimum H_2 flow rate (F_{H2}) is 3.80 kg/s. Since this is the H_2 flow leaving the reactor, the H_2 consumed as reactant should be added, resulting in a total H_2 input flow of 5.73 kg/s, or a H_2/biomass ratio of **0.15 kg H_2/kg biomass$_{MAF}$**.

Thermal regulator

An energy balance across the catalytic hydropyrolysis reactor is the basis for estimating the H_2 flow required for thermal regulation. It is assumed that the conversion of biomass into pyrolysis products occurs at 104°C (biomass input temperature). The pyrolysis products are then heated to the reactor exit temperature of 389°C. Assuming that the pyrolysis reactor is adiabatic, the energy balance is

$$E_{Therm,input} + E_{Chem,input} = E_{Therm,output} + E_{Chem,output}$$

where E_{Therm} are thermal energy flows and E_{Chem} are chemical energy flows. Some chemical energy is released as heat during pyrolysis and this energy is assumed to heat all of the pyrolysis products to the temperature of 389°C at which they leave the reactor. The H_2 flow rate is the only unknown in this equation. Solving this balance for the H_2 flow rate gives the H_2 flow required for thermal regulation. An adjustment is made later to account for input H_2 converted to other compounds.

The thermal flows for all inputs and outputs other than H_2 are calculated from their known temperatures and heat capacities and chemical energy estimates are based on the heat of combustion (ΔH_c):

$$Chemical\ energy\ (MW): E_{Chem} = \sum (F_i * \Delta H_{c_i}) \quad \textbf{Eq. 1}$$

$$Thermal\ energy\ (MW): E_{Therm} = \sum (F_i * c_p * \Delta T) \quad \textbf{Eq. 2}$$

where F represents mass flow rate and the subscript i denotes different molecules or compounds. c_p values were estimated from the literature, and ΔH_c for heterogeneous compounds (biomass, condensable hydrocarbons, light and heavy liquid products, and char) were estimated using the following equation:[7]

$$\Delta H_C\,(MJ/kg) = 34.9 * C + 118 * H - 10.3 * O - 1.51 * N + 10.1 * S - 2.11 * Ash \quad \textbf{Eq. 3}$$

where C, H, O, N, S and Ash are elemental weight fractions of compounds of interest (e.g., for CH_4 the equation would give 34.9 * 0.75 + 118 * 0.25 = 55.7 MJ/kg).

Other values used in the calculation:

- ΔH_c for H_2 = 141.8 MJ/kg;$^{\text{Aspen Plus}}$
- ΔH_c for CO = 10.1 MJ/kg;$^{\text{Aspen Plus}}$
- ΔH_c for CH_4 = 55.5 MJ/kg;$^{\text{Aspen Plus}}$
- ΔH_c for C_2H_6 = 51.9 MJ/kg;$^{\text{Aspen Plus}}$
- ΔH_c for C_3H_8 = 50.3 MJ/kg;$^{\text{Aspen Plus}}$
- ΔH_c for biomass$_{dry}$ = 19.6 MJ/kg;$^{\text{Eq. 3}}$
- ΔH_c for condensable hydrocarbons = 43.6 MJ/kg;$^{\text{Eq. 3}}$
- ΔH_c for gasoline = 44.7 MJ/kg;$^{\text{Eq. 3}}$ (used to represent the light fraction of the output liquids)
- ΔH_c for diesel = 43.1 MJ/kg;$^{\text{Eq. 3}}$ (used to represent the heavy fraction of the output liquids)

- ΔH_c for char = 23.8 MJ/kg;[Eq. 3]
- c_p biomass$_{\text{as fed}}$ (assumed constant in the range 25-104°C) = 1.35 kJ/(kg*K);[8]
- c_p condensable hydrocarbons (assumed constant in the range 104-389°C) = 2.0 kJ/(kg*K);[8]
- c_p char (assumed constant in the range 104-389°C) = 1.8 kJ/(kg*K);[8]
- ΔE_{Therm} NCG + water (excluding H_2) between 104-389°C (E_{Therm}) = 1.48 MJ/kg biomass$_{\text{as fed}}$;[Aspen Plus]
- ΔE_{Therm} H_2 between 42-389°C = 5.03 MJ/kg;[Aspen Plus]

Assumptions:

- Reactor is adiabatic and in steady-state;
- Catalyst stays in the bed (any replacement catalyst is ignored);
- Incoming biomass is at 104°C (due to drying) and H_2 is at 42°C (due to compression);

The energy entering the reactor, for the reference condition of 25°C and excluding the chemical and thermal energy of the unreacted H_2, is:

E_{input}
$= E_{Chem.\ Biomass} + E_{Chem.\ H2React} + E_{Thermal\ Biomass} + E_{Thermal\ H2React}$
$= [\ 19.64 * 39.64\ ] + [\ 141.78 * 1.93\ ^{1)}\ ] + [\ 1.35*10^{-3} * (104 - 25) * 44.05\ ] + [\ 1.93 * 0.25\ ]$
= 1058 MW

The energy leaving the reactor, for the reference condition of 25°C and excluding the chemical energy of the unreacted H_2 and the thermal energy required to heat the unreacted H_2 from 25°C to 42°C, is:

E_{output}
$= E_{Chem.\ NCG} + E_{Chem.\ Char} + E_{Chem.\ Condensable\ hydrocarbons} + E_{Thermal\ NCG\ +\ aqua} + E_{Thermal\ Char} + E_{Thermal\ Liquid} + E_{Thermal\ H2unreact}$
$= [\ 10.1 * 2.73 + 55.52 * 1.54 + 51.9 * 2.76 + 50.32 * 1.69\ ] + [\ 23.76 * 5.74\ ] + [\ 43.6 * 10.83\ ] +$
$[\ 1.48 * 44.05\ ] + [\ 1.8*10^{-3} * (389 - 25) * 5.74\ ] + [\ 2.0*10^{-3} * (389 - 25) * 10.83\ ] + 5.03 * F_{H2Unreact}$
$= 1027 + 5.03 * F_{H2Unreact}$

The amount of unreacted H_2 is:
$F_{H2Unreact} = (1058 - 1027) / 5.03 = 6.17$ kg/s

As this is the H_2 flow leaving the reactor, the H_2 consumption in the catalytic hydropyrolyis reactor should be added, resulting in a total H_2 input flow of 8.10 kg/s, or a H_2/biomass ratio of **0.21 kg H_2/kg biomass$_{MAF}$**.

Summary

Thermal regulation requires the largest H_2 flow. The input H_2 flow value calculated for this option (**0.21 kg H_2/kg biomass$_{MAF}$**) is therefore used for the process simulations carried out in this research.

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1) The amount of H_2 reacting in a 3,425 t/d$_{dry}$ biomass catalytic hydropyrolysis system is 1.95 kg H_2/s. Of this, 1.93 kg H_2/s reacts in the catalytic hydropyrolysis reactor and 0.02 kg H_2/s reacts in the hydrodeoxygenation reactor.

Appendix C. Catalytic hydropyrolysis and hydrodeoxygenation reactor simulations

This section describes how experimental data published by GTI[1,3] were used for purposes of simulating the catalytic hydropyrolysis and hydrodeoxygenation reactors. Some small adjustments were made to the data to enable closing of mass balances in the process simulations.

Performance of the catalytic hydropyrolysis (HPyr) and the hydrodeoxygenation (HDO) reactors are based on results published by GTI, specifically run 8/23 and run 3/9 in references 1 and 3 and Table 8 in reference 1. 2) The data were adjusted in the following ways:

- The following numbers were adjusted to close mass balances.
  - O-content of the biomass was adjusted from 43.9 to 43.86 $\text{wt\%}_{\text{dry}}$.
  - H_2 consumption and product output are reported by GTI per unit $\text{biomass}_{\text{MAF}}$.[1,3] To close the simulated mass balance required making the assumption that the reported values were actually given per unit $\text{biomass}_{\text{as fed}}$.
  - Required H_2 as reactant in run 3/9 was changed from 46 gr H_2/kg $\text{biomass}_{\text{MAF}}$ to 47 gr H_2/kg $\text{biomass}_{\text{as fed}}$.
  - S-content in the liquid phase leaving the HDO was adjusted from 0.01 to 0.005 wt%.
  - O-content in the liquid phase leaving the HDO was set to 2.0 wt%. 3)
  - For both the 8/23 and 3/9 runs, elemental composition of the liquid phase is normalised to 1.
- It is assumed that all remaining atoms (C, H, N, O, S) are in the char;
- The HDO lowers the O-content of the liquid and converts unsaturated HC into saturated HC,[1,3] but detailed information on the performance of an HDO reactor in the context of a catalytic hydropyrolysis process has not been published. Our HDO simulations recognize that in a conventional HDO reactor the main reactions are hydrogenation and hydrodeoxygenation. We assume that the only unsaturated hydrocarbons leaving the HPyr reactor are ethylene, propylene and aromatics.4) It is assumed that ethylene and propylene undergo hydrogenation in the HDO reactor but that the aromatics are too stable to react. Regarding the oxygen content, it is assumed that hydrodeoxygenation reduces the O-content of the liquid phase to 1.0 wt%; 5)
- The operating pressure of the HPyr and HDO system are reported to be 22.4 bar. It is assumed that the 22.4 bar is the inlet pressure to the HPyr reactor and that no intermediate repressurization occurs;

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2) Run 8/23 in reference 1 and run 3/9 in reference 3 are believed to show data from the same experiment. Table 8 in reference 1 has mixed wood as feedstock, but it is unclear to which run the data belong. We assume that the data for mixed wood in Table 8 belongs to the same experiment as run 8/23. Data for runs 8/23 and 3/9 were selected because the runs use the same catalyst in the HPyr reactor and similar reactor temperatures. Run 8/23 reports mass balances across the coupled HPyr + HDO system, while run 3/9 reports the balance only across the HPyr. This enables an estimation of how the HDO reactor performs. No other pair of runs have conditions (e.g., catalyst type, feedstock type, HPyr temperature, etc.) as similar as the two selected runs.

3) The data in 8/23 and Table 8 do not match for this parameter.[1] For sulfur this can be corrected assuming rounding of 0.0052 to 0.01 wt%. For nitrogen, the N-content in the liquid phase has to be lowered from 0.06 to 0.03 wt% to match the N-content in the gasoline and diesel fractions reported in Table 8. The run 8/23 data are used and N-content in the gasoline and diesel fractions are adjusted accordingly. As the run 8/23 data do not give the O-content, only a maximum value, the data from Table 8 is used.

4) The H:C ratios in the liquid phase are 1.65 after the HPyr reactor and 1.61 after the HDO reactor. As these values are almost identical, it is assumed that almost no saturation of alkenes takes place in the HDO. Since an HDO reactor would react any alkenes, it is reasoned that the H_2 in the HPyr reactor already reacts with any formed alkenes resulting in almost no alkenes leaving the HPyr reactor.

5) In Table 8 of reference 1 the O-content of both gasoline and diesel is <1 wt%. It is therefore assumed that the HDO will reduce the O-content of the liquid phase from 2.0 to 1.0 wt% using H_2.

- The reported H:C ratios of the light hydrocarbon fraction (“gasoline”) and the heavy (“diesel”) fractions when produced from mixed wood are 1.70 and 1.30, respectively, for an overall H:C ratio of 1.60 for the liquid fraction. The elemental mass balance in our simulation will not close when using an overall H:C ratio of 1.60 (with $66\%_{weight}$ gasoline with an H:C ratio of 1.70, and $34\%_{weight}$ diesel with an H:C ratio of 1.30). The 1.30 value for the diesel fraction is low compared with values reported using lemna or algae as feedstock (1.64 and 1.79 respectively).[1,3] A value of 1.41 for diesel enables closure of our simulated mass balance, so we have adopted this value.

Input data

The input data used in the process simulations reported in the main text are displayed in the left-hand sections of the next few tables. The right column(s) are data from the literature.[1,3]

Table C1. Product yields (gr/kg $biomass_{dry}$).

	Used for Process Simulations		Literature data
Yield	HPyr	HDO	Run 8/23 [a)]
CO	69	69	69
CO_2	78	78	78
CH_4	39	39	39
C_2H_6	70	70	71
C_3H_8	43	43	43
Liquid	273	273	273
Char	145	N.A. [b)]	142 [b)]
Water [c)]	444	447	392
H_2 reacted	-49	-49	-49

a) The published experimental yield data for run 8/23 are for hydropyrolysis followed by hydrodeoxygenation of mixed wood and were originally reported as yields relative to mass of as-fed biomass. As noted earlier in this supplementary material, we assume the reported yields were actually relative to mass of dry biomass input.

b) The char is removed between the HPyr and HDO reactors in the simulation as well as in the experiments. However, to allow comparison of the experimental char yield with the simulation model, the char yield (after HPyr) of run 8/23 is reported in the table.

c) The higher water fraction in the simulation is due to a higher assumed moisture content of the as-fed biomass (10 wt% compared to 5.6 wt% in the literature).

Table C2. Elemental composition of liquid streams exiting reactors ($\%_{weight}$).

	Used for process simulation		Literature data
	HPyr	HDO	Run 8/23 [a)]
C	86.34	87.22	85.3
H	11.60	11.71	11.5
O	2.00	1.00	< 2.2
N	0.06	0.06	0.06
S	0.01	0.01	0.01

a) The data for run 8/23 are the published experimental data for hydropyrolysis followed by hydrodeoxygenation of mixed wood.

Table C3. Elemental compositions of the gasoline-like and diesel-like streams.

	Used for process simulation		Published data [1,3]	
	Gasoline	Diesel	Gasoline	Diesel
C (wt%)	86.6	88.4		
H (wt%)	12.4	10.4		
O (wt%)	1.0	1.0	< 1	< 1
N (ppm)	308	1207	162	634
S (ppm)	52	52	52	52
H:C (molar)	1.70	1.41	1.70	1.30

Appendix D. Stream table for process flow diagram for the Phyiscal case

This section contains the component flows, temperatures and pressures of the main mass flows in the **Physical** case.

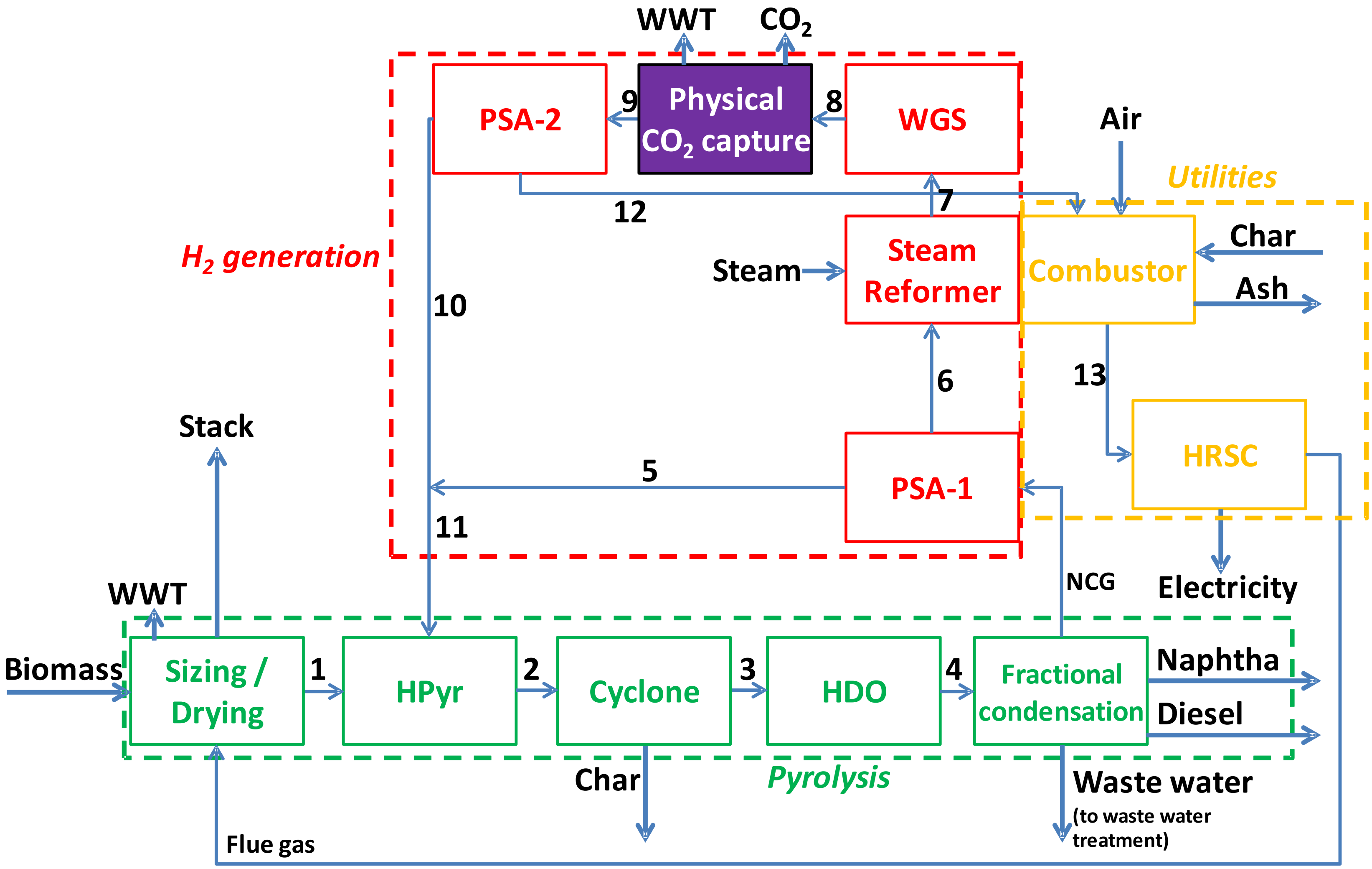

Figure D1. Mass balance schematic of the Physical case.

Table D1A. Mass flows, temperatures and pressures of the Physical case.

	Biomass	1	2	Char	3	4	Naphtha	Diesel	NCG	5
Temperature (°C)	15	104	389	389	389	392	15	15	35	35
Pressure (bar)	1.0	22.4	21.9	21.9	21.9	21.4	21.4	21.4	21.4	20.9
Mass flow (kg/hr)	119,048	92,593	109,620	12,067	97,553	97,553	14,878	7,665	37,789	10,995
Naphtha						14,878	14,878			
Diesel						7,665		7,665		
H_2			12,966		12,966	12,936			12,936	10,995
H_2O			36,807		36,807	37,071				
CO			5,738		5,738	5,738			5,738	
CO_2			6,533		6,533	6,533			6,533	
O_2										
N_2			39		39	39				
NH_3			47		47	47				
Ar										
C			62		62	62				
S			3		3	3				
CH_4			3,234		3,234	3,234			3,234	
C_2H_6			5,800		5,800	5,800			5,800	
C_3H_8			3,548		3,548	3,548			3,548	
SO_2										
Biomass	119,048	92,593								
Bio-oil			22,776		22,776					
Char			12,067	12,067						
Ash										

Table D1B. Mass flows, temperatures and pressures of the Physical case (continued).

	6	Steam	7	8	CO_2	9	10	11	12	Air
Temperature (°C)	35	233	950	300	35	35	35	41	500	15
Pressure (bar)	1.5	29.7	28.0	25.5	25.5	25.0	24.5	22.4	1.5	1.0
Mass flow (kg/hr)	26,793	36,708	63,501	63,501	36,487	27,014	6,032	17,027	11,179	451,303
Naphtha										
RDB										
H_2	1,940		5,733	7,096		7,096	6,032	17,027	1,064	
H_2O		36,708	22,123	9,945		9,945			141	2,789
CO	5,738		22,996	4,060		4,060			4,060	
CO_2	6,533		10,790	40,541	36,487	4,054			4,054	206
O_2										103,796
N_2										338,763
NH_3										
Ar										5,748
C										
S										
CH_4	3,234		1,859	1,859		1,859			1,859	
C_2H_6	5,800									
C_3H_8	3,548									
SO_2										
Biomass										
Bio-oil										
Char										
Ash										

Table D1C. Mass flows, temperatures and pressures of the Physical case (continued).

	Char	Ash	15	16	Stack	WWT*
Temperature (°C)	389	1,400	1,049	249	90	15
Pressure (bar)	21.9	1.0	1.0	1.0	1.0	1.0
Mass flow (kg/hr)	12,067	417	474,133	474,133	474,133	73,480
Naphtha						
RDB						
H_2						
H_2O			21,395	21,395	21,395	73,329
CO						
CO_2			43,200	43,200	43,200	
O_2			64,985	64,985	64,985	
N_2			338,764	338,764	338,764	39
NH_3						47
Ar			5,748	5,748	5,748	
C						62
S						3
CH_4						
C_2H_6						
C_3H_8						
SO_2			41	41	41	
Biomass						
Bio-oil						
Char	12,067					
Ash		417				

* WWT is the combined waste water streams of the biomass drying, fractional condenser and physical CO_2 capture blocks.

Appendix E. Energy and mass balances, capital costs, and levelized production costs

A total of eight cases were investigated in this study. The four cases highlighted in the main article are given in red. The design of the other four cases are described briefly in the main article. Energy balances are given in Table E1 and carbon balances are given in Table E2. The LCA GHG emissions of the biofuels are given in Table E3. Capital cost breakdowns are given in Table E4. Table E5 and Table E6 give production cost breakdowns with GHG valuations of 0 and 100 \$/t $CO_{2,eq}$, respectively.

Table E1. Energy balances. For each case, the biomass input rate is 3,425 t/d biomass$_{dry}$.

Energy balance	**Base case**	**Physical capture**	**Chemical capture**	**NG - Vent**	**NG - Physical**	**NG - Chemical**	**Reduced yield**	**Increased yield**
Input (MW LHV)								
Biomass (30 wt% moisture)	687	687	687	687	687	687	687	687
Natural gas	0	0	0	99	99	99	0	0
Output (MW LHV)								
Light HC	297	297	297	297	297	297	230	351
Heavy HC	149	149	149	149	149	149	115	176
Total HC	446	446	446	446	446	446	346	527
Electricity	55	48	13	46	39	34	89	26
Char				131	131	131		
Efficiency (LVH based)								
Liquid efficiency	65%	65%	65%	57%	57%	57%	50%	77%
Liquid + electricity eff.	73%	72%	67%	63%	62%	61%	63%	81%
Total efficiency	73%	72%	67%	79%	78%	78%	63%	81%
Bio intensity (GJ biomass/GJ liquid)	1.5	1.5	1.5	1.5	1.5	1.5	2.0	1.3

Table E2. Carbon balance of the conversion facility of the different case studies.

Carbon balance	**Base case**	**Physical capture**	**Chemical capture**	**NG - Vent**	**NG - Physical**	**NG - Chemical**	**Reduced yield**	**Increased yield**
Input (t C/hr)								
Biomass	71	71	71	71	71	71	71	71
Natural gas				5	5	5		
Output (t C/hr)								
Light HC	22	22	22	22	22	22	17	26
Heavy HC	12	12	12	12	12	12	9	14
Char				13	13	13		
Captured		17	34		17	27		
Emitted	37	20	4	30	13	3	45	31

Table E3 Breakdown of GHG emissions.

Net GHG emissions (kg CO_{2eq}/GJ_{LHV} liquid)	**Base case**	**Physical capture**	**Chemical capture**	**NG - Vent**	**NG - Physical**	**NG - Chemical**	**Reduced yield**	**Increased yield**
Photosynthesis	-162	-162	-162	-162	-162	-162	-209	-137
Biomass upstream	6	6	6	6	6	6	8	5
NG upstream				2	2	2		
Biofuel downstream	1	1	1	1	1	1	1	1
Biofuel combustion	77	77	77	77	77	77	77	77
Electricity credit	-22	-20	-5	-19	-16	-14	-47	-9
CCS downstream		0	0		0	0		
Emitted	85	46	9	68	29	7	132	60
Total	**-15**	**-51**	**-74**	**-27**	**-63**	**-83**	**-38**	**-3**
$GHGI_{2005}$	0.06	-0.29	-0.71	-0.07	-0.43	-0.65	0.06	0.06

Table E4. Scoping-study capital cost breakdowns.

Capital cost (M$)	**Base case**	**Physical capture**	**Chemical capture**	**NG - Vent**	**NG - Physical**	**NG - Chemical**	**Reduced yield**	**Increased yield**
Pre-treatment	80	80	80	79	79	79	80	80
Pyrolysis + HDO	116	116	116	116	116	116	116	116
H_2 generation	201	199	201	200	198	200	214	189
Product upgrading	63	63	63	62	62	62	63	63
HRSG + ST	125	125	105	115	116	115	155	99
CO_2 capture		146	372		146	319		
Total	584	729	936	572	717	891	628	547

Table E5. Production cost breakdowns when the GHG emissions valuation is 0 \$/t CO_{2eq}.

Prod. cost (\$/$GJ_{LHV\ liquid}$) at (0 \$/t CO_{2eq})	**Base case**	**Physical capture**	**Chemical capture**	**NG - Vent**	**NG - Physical**	**NG - Chemical**	**Reduced yield**	**Increased yield**
Capital charge (CCF = 2) [6]	8.7	10.8	13.9	8.5	10.6	13.2	12.0	6.9
O&M	2.1	2.6	3.3	2.0	2.6	3.3	2.9	1.6
Biomass	8.7	8.7	8.7	8.7	8.7	8.7	11.3	7.4
Natural gas				1.3	1.3	1.3		
Char disposal				0.7	0.7	0.7		
CO_2 trans. & injection		1.3	2.1		1.3	1.6		
GHG allowances								
Additional refining	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5
Electricity credit	-2.3	-2.0	-0.6	-2.0	-1.7	-1.5	-4.9	-1.0
Production cost	**21.6**	**25.9**	**31.9**	**23.9**	**28.2**	**31.8**	**25.8**	**19.5**
BEOP (\$/bbl)	90	112	144	102	124	143	112	78

Table E6. Production cost breakdowns when the GHG emissions valuation is 100 \$/t CO_{2eq}.

Prod. cost (\$/$GJ_{LHV\ liquid}$) at (100 \$/t CO_{2eq})	**Base case**	**Physical capture**	**Chemical capture**	**NG - Vent**	**NG - Physical**	**NG - Chemical**	**Reduced yield**	**Increased yield**
Capital charge (CCF = 2) [6]	8.7	10.8	13.9	8.5	10.6	13.2	12.0	6.9
O&M	2.1	2.6	3.3	2.0	2.6	3.3	2.9	1.6
Biomass	8.7	8.7	8.7	8.7	8.7	8.7	11.3	7.4
Natural gas				1.3	1.3	1.3		
Char disposal				0.7	0.7	0.7		
CO_2 trans. & injection		1.3	2.1		1.3	1.6		
GHG allowances	0.7	-3.2	-6.9	-0.8	-4.6	-6.9	0.9	0.6
Additional refining	4.5	4.5	4.5	4.5	4.5	4.5	4.5	4.5
Electricity credit	-4.6	-4.0	-1.1	-3.9	-3.3	-2.9	-9.6	-1.9
Production cost	**20.1**	**20.8**	**24.5**	**21.2**	**21.9**	**23.6**	**21.9**	**19.1**
BEOP (\$/bbl)	34	38	57	40	43	52	43	29

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[6] CCF stands for capital cost factor. See the main article for more information on this factor.

Appendix F. Biochar

Burying biochar is a carbon mitigation strategy if it results in long-term storage of the carbon in the soil. The ability of biochar to resist biotic degradation, through which carbon would return to the atmosphere, depends on the pyrolysis process by which it was created and on the soil and climate conditions where the biochar is buried. Mean residence time - the average time biochar remains in the soil after burying - has been estimated to be anywhere from 8 to over 13,900 years.[9-10] The large range in estimates is due largely to big uncertainties inherent in biochar studies, including those arising from differences in biochar production methods, in soil characteristics, and in climate. Further research is required to understand what the mean residence time of biochar produced via hydropyrolysis might be in different soil and climate regimes.

There are additional uncertainties regarding the impact of biochar on soil fertility, a main driver for biochar use today. Field studies have been performed mostly in the tropics, with only a few trials performed in temperate regions.[10-13] A meta-analysis of these field studies indicates that biochar tends to increase soil fertility, but negative effects on fertility were also found.[10]

Finally, the value of biochar as a soil productivity enhancer is highly uncertain today, both because of uncertainties as to how a given biochar will affect productivity of a given soil and because of the immaturity of biochar markets. Surveys by the International Biochar Initiative showed an average wholesale price of 2,740 $/t for pure biochar in 2013 and 2,060 $/t for pure biochar in 2014.[13-14] Two studies evaluating the economics of biochar assumed 200 $/t biochar as the price in a mature commercial market.[15-16]

Appendix G. Impact of yield

Catalytic hydropyrolysis results are reported in the literature for several different feedstocks, including mixed wood, maple wood, corn stover, bagasse and lemna.[1,3] The elemental compositions of corn stover, mixed wood and bagasse are given in Table G1. Results indicate that the biofuel yield varies with the feedstock, ranging from 0.21 kg biofuel/kg$_{dry}$ biomass for corn stover to 0.32 kg biofuel/kg$_{dry}$ biomass for bagasse and lemna (see Figure G1). The yield with mixed wood used in our process simulations falls between these feedstocks (0.27 kg biofuel/kg$_{dry}$ biomass).

Table G1. Elemental composition of mixed wood, bagasse and corn stover (wt%).[1,3]

	Corn Stover	Mixed Wood	Bagasse
C	40.2	49.7	43.1
H	5.0	5.8	5.0
O	35.7	43.9	35.3
N	1.0	0.11	0.34
S	0.05	0.03	0.10
Ash	18.1	0.5	16.2

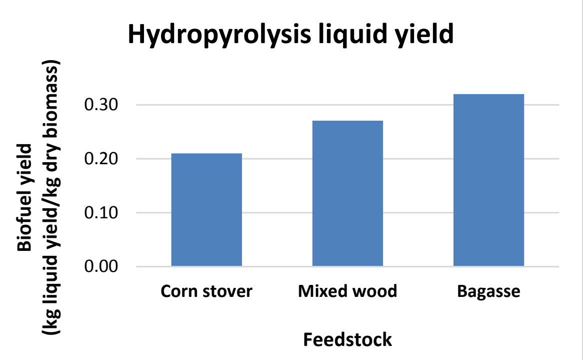

Figure G1. Effect biomass feedstock on biofuel yield. [1,3]

A change in biofuel yield also impacts the yields of char, water and non-condensable gases (NCG). Assessing the effect of a different biofuel yield on the performance of a hydropyrolysis facility requires that the yields of these other fractions are adjusted appropriately. For example, simply changing the yields might satisfy the overall mass balance, but will most likely not satisfy the elemental mass balance as 1) each fraction of the pyrolysis product has a different elemental composition; 2) the experimental yield data that might be used in a simulation are based on different feedstocks, each with its own elemental composition (see Table G1); and 3) the H_2 demand will vary with the feedstock. Therefore, the following algorithm was used to estimate the composition of each fraction for different biofuel yields:

1) Hydrocarbon yield was assumed to be 20% for the reduced yield case and 30% for the increased yield case. Hydrocarbons include C_1, C_2 and C_3 molecules as well as the biofuel itself;
2) All other yields were normalized proportionally - increased in the **Reduced** yield case and decreased in the **Increased** yield case - to satisfy the C-balance;
3) Water yield was adjusted to satisfy the O-balance;
4) H_2 consumed as reactant was adjusted to satisfy the H-balance;
5) The N-, and S-content of the biofuel were kept constant. The N- and S-balances were satisfied by adjusting their content in the ash fraction;

These modifications resulted in the following yields used in our process simulations:

Table G2. Yields after the HDO reactor (gr/kg $biomass_{dry}$).

	Reduced yield	**Base case**	**Increased yield**
CO	108	69	37
CO_2	123	78	42
CH_4	30	39	46
C_2H_6	54	70	82
C_3H_8	33	43	50
Liquid	212	273	323
Char [a)]	224	145	80
Water	355	447	515
H_2-consumption	-28	-49	-62

a) The char yield is the yield after the catalytic hydropyrolysis reactor.

Appendix H. Pyrolysis transport fuel properties

A comparison between specifications for petroleum-derived fuels and the published properties of catalytic hydropyrolysis oil (CHPO) is given in Table H1 and Table H2.

For the CHPO gasoline-like fraction (Table H1):

- Oxygen, olefin and aromatic content meet specifications;
- Final boiling point meets US specification and is only slightly above European specification;
- RON number is below specification;
- Sulfur is on the high side and does not meet European or US specifications;
- Due to lack of data (indicated with question marks in the table), other specifications cannot be compared.

For the CHPO diesel-like fraction (Table H2):

- Flash point and lubricity easily meet specifications;
- T90 distillation slightly exceeds specifications;
- Density is on the high side;
- Viscosity and S-content exceed specifications;
- Cetane number is far below specifications;
- Due to lack of data (indicated with question marks in the table), other specifications cannot be compared.

Table H1. Gasoline specifications. Last column is performance of catalytic hydropyrolysis oil.

	US	Euro-4	Euro-5	Cat. 4[a]	Cat. 5[a]	CHPO [b] [1]
RON, min		95 [17-18]	95 [18]	91 [19]	95 [19]	87 [1]
MON, min		85 [17-18]	85 [18]	82 [19]	85 [19]	?
(RON + MON) / 2, min	87 [18]					?
Vapor pressure (kPa)	54 – 103 [20]	≤ 60 [17-18]	≤ 70 [18]	45-105 [19]		?
Final boiling point (°C), max	225 [20]	210 [17]		195 [17]		220 [1]
Density (kg/m^3), 15°C			720-775 [18]	715-770 [19]	720-775 [19]	?
Oxygen (wt%), max	2.7 [c] [20]	2.7 [17]	3.7 [18]	2.7 [19]	2.7 [19]	<1.0 [1]
Sulfur (ppm), max	10-80 [d] [20]	50 / 10 [17]	10 [18]	5-10 [19]	10 [19]	52 [1]
Olefins (vol%), max		18 [17]	18 [18]	10 [19]	10 [19]	0.3 [1]
Aromatics (vol%), max	19-28 [18]	35 [17-18]	35 [18]	35 [19]	35 [19]	37 [1]
Benzene (vol%), max	0.62 (1.3) [e] [20]	1 [17-18]	1 [18]	1 [19]	1 [19]	?
Methanol (vol%), max	2.75 [f] [20]	3 [17-18]		0 [19]	0 [19]	?
Ethanol (vol%), max		5 [17]		10 [19]	10 [19]	?
C3+ alcohols (vol%), max				0.1 [17]		?
C5+ ethers (vol%), max		15 [17]				?
Other ethers (vol%), max		10 [17]				?
Unwashed gums (mg/100 ml), max				30 [19]	30 [19]	?
Washed gums (mg/100 ml), max	5 [18]		5 [18]	5 [19]	5 [19]	?
Oxidation stability (h), min	4 [20]			8 [19]	8 [19]	?

a) World-Wide Fuel Charter (WWFC) defined a generic set of guideline specifications to help refiners, motor manufactures and legislators form a consensus global opinion on likely future fuel specifications. Category 4 corresponds to markets with advanced requirements for emission control, e.g., US Tier 2, US Tier 3, US 2007 / 2010 Heavy Duty On-Highway, US Non-Road Tier 4, California LEV II, Euro 4, Euro 5, Euro 6, JP 2009 or equivalent emission standards. Category 5 corresponds to markets with highly advanced requirements for emission control and fuel efficiency, e.g., US 2017 light duty fuel economy, US heavy duty fuel economy, California LEV III or equivalent emission control and fuel efficiency standards in addition to Category 4-level emission control standards. The WWFC is a product of the joint efforts of the European Automobile Manufacturers Association (ACEA), the Alliance of Automobile Manufacturers (Alliance), the Engine Manufacturers Association (EMA), and the Japan Automobile Manufacturers Association (JAMA).

b) Data for the catalytic hydropyrolysis oil is taken from Table 5, Table 8 and Figure 17 in reference 1.

c) Gasoline fuel may contain no more than 2.0 wt% O. Gasoline containing aliphatic ethers and/or alcohols (excluding methanol) may contain no more than 2.7 wt% O.
d) Current sulfur levels must not exceed 80 ppm with an average content of 30 ppm. The average content will be lowered to 10 ppm starting in 2017.
e) Although gasoline may contain up to 1.30 vol% benzene, refiners must produce gasoline with an average maximum benzene content of 0.62 vol%.
f) Gasoline may contain up to 0.3 vol% methanol. This limit is increased to 2.75 vol% if an equal volume of butanol or higher molecular weight alcohol is present in the gasoline.

Table H2. Diesel specifications. Last column is performance of catalytic hydropyrolysis oil.

	US [a)]	Euro-4	Euro-5	Cat. 4 [b)]	Cat. 5 [b)]	CHPO [c)] [1,21]
Cetane number, min	40 [18,22]	51 [17]	51 [18]	55	55	25 [d)] [1]
Density (kg/m^3), 15°C		820-845 [17-18]	≥ 845 [18]	820-840	820-840	850 [21]
Viscosity (cSt), 40°C	1.9-4.1 [22]	2.0-4.5 [17-18]	2.0-4.5 [18]	2.0-4.0	2.0-4.0	7.6 [21]
Flash point (°C), min	52 [22]	55 [17-18]	55 [18]	55	55	156 [21]
Lubricity (µm), 60°, max	520 [22]	460 [17]		400	400	330 [21]
T90 distillation point (°C), max	338 [22]			320	320	341 [21]
T95 distillation point (°C), max		360 [17]]		340	340	?
Sulfur (ppm), max	15 [e)] [23]	10 [17-18]	10 [18]	10	10	9-52 [1,21]
Total aromatics (wt%), max	35 [22]			15	15	?
Polycyclic aromatics (wt%), max		11 [17-18]	8 [18]	2		?
Water (ppm), max	500 [f)] [22]	200 [17]		200	200	50 [21]

a) Data from ASTM D975-15a is for No. 2 grade diesel.
b) See note a) of Table H1.
c) Data for the catalytic hydropyrolysis oil is taken from Table 8 and Table 18 in reference 1 and from reference 21. The diesel cut is 280-370°C (535-700F).
d) The number reported in the literature is the cetane index. The cetane number also takes into account additives added to the fuel to improve performance. The cetane index for conventional diesel is usually slightly lower than the cetane number.
e) Set by the EPA via Title 40 CFR 80.520.
f) Specification is a maximum of 0.05 vol% water and sediment.

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