Supporting Information. Multistage torrefaction and *in situ* catalytic upgrading to hydrocarbon biofuels: analysis of life cycle energy use and greenhouse gas emissions

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S1. Direct Land-Use Change

Direct land-use change impacts are calculated using guidelines provided via the intergovernmental panel for climate change (IPCC) tier 1 methodology. This work assumes that only grasslands-land coverage is converted to SRWC plantations, as grasslands are considered an ideal candidate for conversion to SRWC plantations relative to other land-types (i.e. wetlands, forestlands, cropland, and developed land). For example, wetlands play multiple important ecological functions and are often located on protected lands, established forestland provide free "waste" forestry resources and due to high biomass concentration represent a significant carbon-sink, conversion of cropland for biofuel production may lead to increased competition between the use of land for food or fuel production, and conversion of developed land i.e. 'settlements' is often cost prohibitive. Thus, it is likely that grasslands would be targeted for conversion to SRWC plantations.

Large-scale geospatial crop modeling and databases, such as the biofuel ecophysiological traits and yields database, predict the highest yields of SRWCs poplar and willow are concentrated in the northeastern region of the U.S., which is characteristically a temperate (cold, wet) climate zone, and whose soil characteristics are primarily represented by high activity clays (HAC), and thus representative of nominal direct land-use change impacts. The soil organic carbon concentration for HACs in Temperate (cold, wet) climates regions is assumed to be 95 (Tonnes C ha^{-1} in 0-30 cm depth) based on data provided via the IPCC, further details are provided in Table S1.

Climate Region	HAC Soils	LAC Soils	Sandy Soils	Spodic Soils	Volcanic Soils	Wetland Soils
Boreal – Dry & Wet	68	N/A	10	117	20	146
Cold Temperate – Dry	50	33	34	N/A	20	87
Cold Temperate – Wet	95	85	71	115	130	87
Warm Temperate – Dry	38	24	19	N/A	70	88
Warm Temperate – Wet	88	63	34	N/A	80	88
Tropical – Dry	38	35	31	N/A	50	86
Tropical – Moist	65	47	39	N/A	70	86
Tropical –Wet	44	60	66	N/A	130	86
Tropical – Montane	88	63	34	N/A	80	86

Obtained from IPCC - Table 2.3: Default reference (under native vegetation) soil organic C stocks (SOC_{REF}) for Mineral Soils (Tonnes C ha^{-1} in 0-30 cm depth)

Table S1. Soil Organic Carbon Stocks (SOC_{REF}) for Mineral Soils (Tonnes C ha^{-1} in 0-30 cm depth)

In the IPCC methodology, the SOC concentrations of land-types (i.e. Grasslands, Croplands, Forestlands, etc.) are estimated via adjusting the reference SOC_{REF} for mineral soils, based on land-use (F_{LU}) and land management (F_{MG}) factors. Coefficients for F_{LU} and F_{MG} factors are provided in Table S2. A triangular distribution is utilized to randomly sample land management (F_{MG}) factors, with an upper bound of 1, most likely value of 0.95, and a minimum of 0.7.

Factor	Level	Climate Regime	IPCC default	Error (%)
[1]Land Use (F_{LU})	All	All	1	N/A

[2]Management (F_{MG})	Nominally managed (non-degraded)	All	1	N/A
[3]Management (F_{MG})	Moderately Degraded grassland	Temperate	0.95	13
[4]Management (F_{MG})	Severely Degraded	All	0.7	40

Obtained from IPCC - Table 6.2: Relative Stock Change Factors for Grassland Management

[1]All permanent grassland is assigned a land-use factor of 1

[2]Represents non-degraded and sustainably managed grassland, but without significant management improvements.

[3]Represents overgrazed or moderately degraded grassland, with somewhat reduced productivity (relative to the native or nominally managed grassland) and receiving no management inputs

[4]Implies major long-term loss of productivity and vegetation cover, due to severe mechanical damage to the vegetation and/or severe soil erosion

Table S2. Carbon Stock Factors For Grassland Management

The SOC for grasslands are estimated via the product of the SOC_{REF} (i.e. 95 Tonnes C ha^{-1}) and land-use and land-management factors, see Eqn 1.

(1) $$SOC = SOC_{REF} \times F_{LU} \times F_{MG}$$

In this work it is assumed that the SOC carbon concentrations for SRWC plantations can be represented via IPCC defined *Forestlands.* Due to uncertainty regards the SOC concentrations for forestlands, IPCC methodology suggest that the SOC_{REF} be used as a proxy to estimate the SOC for forestlands. Using this methodological framework, changes in SOC resulting from conversion of grassland to SRWC plantations are estimated via Eqn 2.

(2) $$\Delta SOC = SOC_{REF} \times (F_{Grasslands} \times F_{MG} - 1)$$

Estimates for the total above- and below- ground biomass (tonnes d.m. ha^{-1}) for grasslands are provided in Table S3.

IPCC Climate Zone	**Peak above-ground biomass** (tonnes d.m. ha^{-1})	**Total* above-ground and below-ground non-woody biomass** (tonnes d.m. ha^{-1})	**Error** (%)[1]
Boreal – Dry & Wet	1.7	8.5	75
Cold Temperate – Dry	1.7	6.5	75
Cold Temperate – Wet	2.4	13.6	75
Warm Temperate – Dry	1.6	6.1	75
Warm Temperate – Wet	2.7	13.5	75
Tropical – Dry	2.3	8.7	75
Tropical – Moist & Wet	6.2	16.1	75

[1]Represents a nominal estimate of error, equivalent to two times standard deviation, as a percentage of the mean.

Obtained from IPCC - Table 6.4: Default biomass stocks present on grassland, after conversion from other land use

Table S3. Above-ground and Below-ground Grassland Biomass Stocks

Total GHG emissions and/or reductions (Tonnes CO_2 ha^{-1}) from direct LUC are calculated based on the mass of CO_2 emitted via removal of above-ground and below-ground biomass due to conversion of grassland to SRWC plantations, and changes in the soil-organic carbon concentrations, and is provided in Eqn 3.

$$GHG\ Emissions = (Biomass_{Above+Below} \times \left(\frac{47\ kg\ C}{100\ kg\ d.m.}\right) + \Delta SOC) \times (\frac{44\ kg\ CO_2}{12\ kg\ C}) \quad (3)$$

Values for $Biomass_{Above+Below}$ are estimated via IPCC defined climate zone: Cold Temperate – Wet (tonnes d.m. ha^{-1}). A normal probability distribution is utilized to randomly sample from the total above-ground and below-ground biomass, based on reported standard deviation. Biomass is assumed to have an average carbon concentration of 0.47 kg C / kg Biomass-Dry Matter, consistent with IPCC guidelines. A conversion factor of 44/12 is utilized to convert from an elemental carbon to CO_2-basis. It is assumed that total dLUC impacts are normalized over the 20-year lifetime of the biorefinery[1].

S2. Cultivation and Harvesting: Woody Biomass

Process inventories for woody biomass production are randomly sampled via statistical bootstrapping and are developed based on harmonized field trials reported in ref[2], see Tables S4-S20. Direct GHG emissions due to land application of Urea (CH_4N_2O) as well as Lime ($CaCO_3$) are modeling assuming that all carbon is converted to carbon dioxide (CO_2).

Country	**Location**	**Species**	**Age** (yrs)	**Yield** (MT $ha^{-1}yr^{-1}$)
Spain	Granada	Poplar	3	13.7
Spain	Madrid	Poplar+Willow	2	13.5
Spain	Soria	Poplar	4	12
Spain	Zamora	Poplar	3	7.7
Italy	Bagni di Tivoli	Poplar	8	10
Spain	Girona	Poplar+Willow	2	15.5
Spain	Leon	Poplar	3	6.9
Spain	Navarra	Poplar	3	16
Italy	Pisa	Poplar	15	8
Italy	Pisa	Poplar	15	11.3
Italy	Cavallermaggiore	Poplar+Willow	9	5.5
Italy	Caramagna piemonte	Poplar/Willow	9	8.2
Italy	Lombriasco	Poplar/Willow	9	1.3
Italy	Casale Monferrato	Poplar/willow	9	9.5
Italy	Bigarello	Poplar	10	4.4
Italy	Ostiano	Poplar	10	16
Italy	Ostiano	Poplar	10	20
Slovakia	Malanta	Willow	13	14.3
Czech Rep.	Nová Olešná	Poplar/Willow	na	10.2
Czech Rep.	Bystřice	Poplar	16	3.2
Czech Rep.	Smilkov	Poplar	16	7.2
Czech Rep.	Rosice	Poplar	12	13.2
Germany	Arnsfeld	Poplar	14	5.6
Germany	Großschirma	Willow	3	10.1
Germany	Großschirma	Poplar	na	9.4
Germany	Krummenhennersdorf	Poplar/Willow	8	11.3

Belgium	Zwijnaarde	Poplar/Willow	4	3.5
Belgium	Boom	Poplar	16	5.2
Belgium	Lochristi	Poplar/Willow	2	4
Germany	Gersdorf	Willow	7	7.8
Germany	Zschadrass	Willow	5	14.7
Germany	Commichau	Poplar	6	9.1
Germany	Skäßchen	Poplar	15	2.9
Germany	Großthiemig	Poplar	na	7
Germany	Thammenhain	Poplar/Willow	15	7.1
Germany	Nochten	Poplar	15	2.8
Germany	Vetschau	Poplar	7	3.4
Germany	Methau I	Poplar/Willow	17	12.9
Germany	Methau II	Poplar	17	9.2
Germany	Köllitsch	Poplar/Willow	5	5.95
Netherlands	Lelystad	Willow	na	8
Germany	Kuhstorf	Poplar/Willow	na	7.7
Germany	Laage	Poplar	na	23.9
Ireland	Loughgall	Willow	21	11
Denmark	Vråvej	Willow	16	9.2
Estonia	Saare	Willow	12	9.1
Sweden	Hjulsta	Willow	15	9.5

*Adapted from ref[2]

Table S4. Reported Growth Rates for Woody Biomass

SRWC System 1 (Stand life: 15 yrs)	**Diesel Use** (L ha^{-1})	**Input Rate** (unit ha^{-1})	**Frequency** (# times over stand life)
Plowing	25.77	-	1
Harrowing	7.21	-	1
Disking	-	-	-
Mechanical Weeding	-	-	-
Chemical Weeding	7.5	4 l gly	6
Fertilizing (lime)	-	-	-
Fertilizing (N/P/K)	4.32	107 kg (N)	4
Planting	45.25	11,500 cuttings	1
Pest Control	-	-	-
Irrigation	-	-	-
Coppicing	30	-	1
Harvesting/Chipping	75	-	4
Stump Removal	38.70	-	1

*Based on site: Hjulsta

Table S5. Process Inventory for SRWC System 1

SRWC System 2 (Stand life: 21 yrs)	**Diesel Use** (L ha^{-1})	**Input Rate** (unit ha^{-1})	**Frequency** (# times over stand life)
Plowing	7	-	1

Harrowing	2.3	-	1
Disking	-	-	-
Mechanical Weeding	2.2	-	-
Chemical Weeding	1.2	2.25 kg gly	5
Fertilizing (lime)	2.3	3 MT	1
Fertilizing (N/P/K)	2.8	128/28/178 (kg)	5
Planting	2.8	15,000 cuttings	1
Pest Control	-	-	-
Irrigation	-	-	-
Coppicing	-	-	-
Harvesting/Chipping	74.85	-	7
Stump Removal	38.70	-	1

*Based on site : Loughgall

Table S6. Process Inventory for SRWC System 2

SRWC System 3 (Stand life: 2 yrs)	**Diesel Use** (L ha^{-1})	**Input Rate** (unit ha^{-1})	**Frequency** (# times over stand life)
Plowing	40	-	2
Harrowing	32	-	1
Disking	20	-	1
Mechanical Weeding	14	-	2
Chemical Weeding	10	5 l oxy	2
Fertilizing (lime)	-	-	-
Fertilizing (N/P/K)	-	-	-
Planting	16.3	10,000 cuttings	1
Pest Control	10.5	0.18 kg cyp	2
Irrigation	165.5	3397 m3	3
Coppicing	-	-	-
Harvesting/Chipping	34.0	-	2
Stump Removal	38.70	-	1

*Based on site: Girona

Table S7. Process Inventory for SRWC System 3

SRWC System 4 (Stand life: 4 yrs)	**Diesel Use** (L ha^{-1})	**Input Rate** (unit ha^{-1})	**Frequency** (# times over stand life)
Plowing	18	-	1
Harrowing	8	-	1
Disking	-	-	-
Mechanical Weeding	25	-	-
Chemical Weeding	4	4 l oxy, 4 l gly	4
Fertilizing (lime)	-	-	-
Fertilizing (N/P/K)	4	400 kg (12N/22P/22K) & 230 kg CAN (27%)	5

Planting	98	19,700 cuttings	1
Pest Control	-	-	-
Irrigation	-	1333 m3	4
Coppicing	48	-	1
Harvesting/Chipping	160	-	1
Stump Removal	38.70	-	1

*Based on site: Soria

Table S8. Process Inventory for SRWC System 4

SRWC System 5 (Stand life: 15 yrs)	**Diesel Use** (L ha^{-1})	**Input Rate** (unit ha^{-1})	**Frequency** (# times over stand life)
Plowing	45	-	1
Harrowing	30	-	1
Disking	30	-	1
Mechanical Weeding	19	-	2
Chemical Weeding	-	-	-
Fertilizing (lime)	-	-	-
Fertilizing (N/P/K)	18	30 kg N	4
Planting	30	7,142 cuttings	1
Pest Control	-	-	-
Irrigation	45	300 m3	3
Coppicing	-	-	-
Harvesting/Chipping	132	-	5
Stump Removal	38.70	-	1

*Based on site: Pisa

Table S9. Process Inventory for SRWC System 5

SRWC System 6 (Stand life: 8 yrs)	**Diesel Use** (L ha^{-1})	**Input Rate** (unit ha^{-1})	**Frequency** (# times over stand life)
Plowing	46.54	-	1
Harrowing	46.14	-	2
Disking	-	-	-
Mechanical Weeding	8.74	-	16
Chemical Weeding	2	2 l met & 1 l lu	12
Fertilizing (lime)	-	-	-
Fertilizing (N/P/K)	5.6	500 kg (8/24/24)	6
Planting	75.35	10,000 cuttings	1
Pest Control	-	-	-
Irrigation	-	-	-
Coppicing	-	-	-
Harvesting/Chipping	122.2	-	4
Stump Removal	38.70	-	1

*Based on site: Bagni di Tivoli

Table S10. Process Inventory for SRWC System 6

SRWC System 7 (Stand life: 16 yrs)	**Diesel Use** (L ha^{-1})	**Input Rate** (unit ha^{-1})	**Frequency** (# times over stand life)
Plowing	33.2	-	1
Harrowing	11.8	-	1
Disking	-	-	-
Mechanical Weeding	2.7	-	7
Chemical Weeding	2.8	3 kg gly; 9 kg oxa	6
Fertilizing (lime)	-	-	-
Fertilizing (N/P/K)	-	-	-
Planting	-	10,000 cuttings	1
Pest Control	-	-	-
Irrigation	-	-	-
Coppicing	-	-	-
Harvesting/Chipping	74.9	-	4
Stump Removal	38.70	-	1

*Based on site: Boom

Table S11. Process Inventory for SRWC System 7

SRWC System 8 (Stand life: 2 yrs)	**Diesel Use** (L ha^{-1})	**Input Rate** (unit ha^{-1})	**Frequency** (# times over stand life)
Plowing	16.66	-	1
Harrowing	13.51	-	1
Disking	11.4	-	1
Mechanical Weeding	8.36	-	5
Chemical Weeding	6.88	0.3 l Az, 2.5 l Ar, & 3.5 l gly	7
Fertilizing (lime)	-	-	-
Fertilizing (N/P/K)	-	-	-
Planting	21.04	8,000 cuttings	1
Pest Control	9.84	1 l tom & 1 l mat	1
Irrigation	-	-	-
Coppicing	-	-	-
Harvesting/Chipping	49.47	-	1
Stump Removal	38.70	-	1

*Based on site: Lochristi

Table S12. Process Inventory for SRWC System 8

SRWC System 9 (Stand life: 16 yrs)	**Diesel Use** (L ha^{-1})	**Input Rate** (unit ha^{-1})	**Frequency** (# times over stand life)
Plowing	46.5	-	1
Harrowing	6	-	1
Disking	4	-	1

Mechanical Weeding	2	-	5
Chemical Weeding	1.2	4 l sto	3
Fertilizing (lime)	1.9	-	1
Fertilizing (N/P/K)	1.9	120 kg (21/3/10)	7
Planting	4.2	12,000 cuttings	1
Pest Control	-	-	-
Irrigation	1	-	3
Coppicing	-	-	-
Harvesting/Chipping	14.0	-	7
Stump Removal	38.7	-	1

*Based on site: Vravej

Table S13. Process Inventory for SRWC System 9

SRWC System 10 (Stand life: 3 yrs)	**Diesel Use** (L ha^{-1})	**Input Rate** (unit ha^{-1})	**Frequency** (# times over stand life)
Plowing	21.7	-	1
Harrowing	17.6	-	1
Disking	10.2	-	1
Mechanical Weeding	5.1	-	2
Chemical Weeding	4.9	2 kg gly	4
Fertilizing (lime)	2.6	-	1
Fertilizing (N/P/K)	2.6	(90/8/60)	3
Planting	27.3	13,500 cuttings	1
Pest Control	1.2	0.42 kg del	3
Irrigation	1.2	300 m3	1
Coppicing	-	-	-
Harvesting/Chipping	27.4	-	4
Stump Removal	38.7	-	1

*Based on site: Großschirma

Table S14. Process Inventory for SRWC System 10

SRWC System 11 (Stand life: 10 yrs)	**Diesel Use** (L ha^{-1})	**Input Rate** (unit ha^{-1})	**Frequency** (# times over stand life)
Plowing	22.9	-	1
Harrowing	26.3	-	1
Disking	-	-	-
Mechanical Weeding	28.3	-	5
Chemical Weeding	3.7	4 l gly	5
Fertilizing (lime)	5.5	1 MT	1
Fertilizing (N/P/K)	3.8	80 kg Urea	4
Planting	22.7	5,560 cuttings	1
Pest Control	3.7	2 kg del	5
Irrigation	6.5	400 m3	5

Coppicing	-	-	-
Harvesting/Chipping	80.6	-	5
Stump Removal	39	-	1

*Based on site: Ostiano

Table S15. Process Inventory for SRWC System 11

SRWC System 12 (Stand life: 9 yrs)	**Diesel Use** (L ha^{-1})	**Input Rate** (unit ha^{-1})	**Frequency** (# times over stand life)
Plowing	27	-	2
Harrowing	24	-	1
Disking	22	-	1
Mechanical Weeding	13	-	6
Chemical Weeding	7	3 kg gly	6
Fertilizing (lime)	-	-	1
Fertilizing (N/P/K)	14	(30/44/83)	4
Planting	40	8,330 cuttings	1
Pest Control	-	-	-
Irrigation	-	1500 m3	4
Coppicing	-	-	-
Harvesting/Chipping	97	-	5
Stump Removal	39	-	1

*Based on site: Casale Monferrato

Table S16. Process Inventory for SRWC System 12

SRWC System 13 (Stand life: 3 yrs)	**Diesel Use** (L ha^{-1})	**Input Rate** (unit ha^{-1})	**Frequency** (# times over stand life)
Plowing	30	-	1
Harrowing	16	-	1
Disking	-	-	-
Mechanical Weeding	12	-	3
Chemical Weeding	8	4 l oxy	1
Fertilizing (lime)	-	-	-
Fertilizing (N/P/K)	8	450 kg (8/15/15)	1
Planting	17	13,333 cuttings	1
Pest Control	20	0.5 kg del	1
Irrigation	210	1333 m3	3
Coppicing	-	-	-
Harvesting/Chipping	36	-	1
Stump Removal	39	-	1

*Based on site: Leon

Table S17. Process Inventory for SRWC System 13

SRWC System 14 (Stand life: 3 yrs)	**Diesel Use** (L ha^{-1})	**Input Rate** (unit ha^{-1})	**Frequency** (# times over stand life)
Plowing	25.0	-	1
Harrowing	20	-	1
Disking	-	-	-
Mechanical Weeding	17	-	4
Chemical Weeding	6	3 l gly	3
Fertilizing (lime)	-	-	-
Fertilizing (N/P/K)	-	-	-
Planting	17	13,333 cuttings	1
Pest Control	-	-	-
Irrigation	-	1,667 m3	3
Coppicing	-	-	-
Harvesting/Chipping	37	-	1
Stump Removal	39	-	1

*Based on site: Granada

Table S18. Process Inventory for SRWC System 14

SRWC System 15 (Stand life: 3 yrs)	**Diesel Use** (L ha^{-1})	**Input Rate** (unit ha^{-1})	**Frequency** (# times over stand life)
Plowing	30	-	2
Harrowing	14	-	3
Disking	-	-	-
Mechanical Weeding	17	-	8
Chemical Weeding	3.6	4 l (oxy + gly)	4
Fertilizing (lime)	-	-	-
Fertilizing (N/P/K)	4.4	235 kg (15/15/15)	6
Planting	17	13,333 cuttings	1
Pest Control	3.6	1.5 l Ch1	5
Irrigation	-	1,890 m3	3
Coppicing	-	-	-
Harvesting/Chipping	36	-	1
Stump Removal	39	-	1

*Based on site: Zamora

Table S19. Process Inventory for SRWC System 15

Activities	**Diesel Use** (L ha^{-1})	**Input Rate** (unit ha^{-1})
Plowing	24	-
Flattening	18	-
Fertilizing	7	80 kg N
Fertilizing	7	100 kg P

Fertilizing	7	60 kg K
Fertilizing	11	1000 kg CaCo3
Chemical Weeding	7	1 l AZ 500
Chemical Weeding	7	1 l Kerb50
Chemical Weeding	7	1 l Basts
Mechanical Weeding	20	-
*Manual Weeding	-	65 h

Data is based on 1 ha land use, and an average production of 153,000 cuttings per ha. Adapted from ref[3]
*Impacts due to Labor are not considered in this work

Table S20. Process Inventory for Cuttings Production

Harvest efficiency, i.e. the fraction of dry matter yield that is harvested, is dependent on the harvesting technology. This work assumes a uniform distribution for harvesting efficiency with a lower bound of 77.4% and upper bound of 94.5%, see Table S21 for additional information.

Harvesting Technology	**Avg Efficiency** (%)	**Reference**
Self propelled cut-and-chip harvester	77.4	Ref[4]
Tractor-pulled stem harvester	94.5	Ref[4]

Table S21. Harvest Efficiency

Direct volatilization of N fertilizer to N_2O is randomly sampled via statistical bootstrapping, based on 59 field trials conducted on various agricultural lands[5-31], and is provided in Table S22.

N_2O Conversion Rate (%)	**Measurement Year(s)**	**Reference**
0.52	2005 and 2006	Halvorson et al. 2008
0.45	2005 and 2006	Halvorson et al. 2008
0.75	2005 and 2006	Halvorson et al. 2008
0.90	Prior to 2001	Bouwman et al. 2002
6.60	2004-2006	Chantigny et al. 2010
0.40	2004-2006	Chantigny et al. 2010
0.83	2007-2008	Halvorson et al. 2010
0.85	2007-2008	Halvorson et al. 2010
0.14	2007-2008	Halvorson et al. 2010
0.33	2007-2008	Halvorson et al. 2010
0.06	2007	Halvorson et al. 2010
0.09	2008	Halvorson et al. 2010
0.21	2007	Halvorson et al. 2010
0.26	2008	Halvorson et al. 2010
0.32	2007	Halvorson et al. 2010
0.09	2008	Halvorson et al. 2010
0.41	2007	Halvorson et al. 2010
0.26	2008	Halvorson et al. 2010

1.02	2000-2001	Wagner-Riddle et al. 2007
0.73	2003-2004	Wagner-Riddle et al. 2007
0.14	2008	Venterea et al. 2011
0.17	2009	Venterea et al. 2011
0.42	2010	Venterea et al. 2011
0.69	2002-2006	Del Grosso et al. 2008
0.63	2002-2006	Del Grosso et al. 2008
0.34	2009	Halvorson et al. 2011
0.51	2010	Halvorson et al. 2011
0.20	2007	Halvorson et al. 2010
0.16	2008	Halvorson et al. 2010
0.69	2009-2010	Halvorson and Del Grosso 2012
0.21	2009-2010	Halvorson and Del Grosso 2012
0.26	2009-2010	Halvorson and Del Grosso 2012
0.38	2009-2010	Halvorson and Del Grosso 2012
0.91	2009	Sistani et al. 2011
1.60	2009	Sistani et al. 2011
2.60	2009	Sistani et al. 2011
1.20	2009	Sistani et al. 2011
2.80	2009	Sistani et al. 2011
3.20	2009	Sistani et al. 2011
0.48	2010	Sistani et al. 2011
0.36	2010	Sistani et al. 2011
1.40	2010	Sistani et al. 2011
0.40	2010	Sistani et al. 2011
0.60	2010	Sistani et al. 2011
0.058	2010	Sistani et al. 2011
0.50	2005-2006	Haile-Mariam et al. 2008
0.30	2005-2006	Haile-Mariam et al. 2008
1.29	1979-1987	Eichner 1990
0.77	Unspecified	Skiba et al. 1996
2.1	Unspecified	Benckiser et al. 1996
0.39	Unspecified	Hutchinson et al. 1992
6.8	Unspecified	Williams et al. 1992
1.25	Unspecified	Mosier and Hutchinson. 1981
1.0	Unspecified	Qian et al. 1997
0.95	Unspecified	Vermoesen et al. 1996
5.00	Unspecified	Shepherd et al. 1991
1.25	Unspecified	Bounman et al. 1995
0.36	Unspecified	Mosier et al. 1986
1.20	Unspecified	Anderson et al. 1987

Table S22. Direct Nitrogen Volatilization Rates (%)

Indirect N volatilization was developed based on estimates of soil nitrogen leaching and run-off rates as well as conversion rates of soil N to N_2O as reported by the Intergovernmental Panel for Climate Change (IPCC)[32] and are provided in Table S23. A triangular distributions is utilized to estimate key parameters for indirect nitrogen volatilization rates, based on minimum, maximum and most likely values.

Parameters	Min	Max	Most Likely
Soil Nitrogen Volatilization Rate (%)	3%	30%	10%
Leaching and runoff rate of soil nitrogen (%)	10%	80%	30%
The conversion rate of leached and runoff nitrogen to N in N_2O (%)	0.05%	2.5%	0.75%

Table S23. Indirect Nitrogen Volatilization Rates (%)

S3. Short-Term Storage of Biomass

Regression equations are utilized to estimate dry matter loss as a function of storage time, based on experimental data provided in ref[33], see Table S24.

Storage Time (Days)	Dry Matter Loss (%)
2.1	0.5
3.4	0.8
7.7	1.9
35.7	6.3
51.7	8.3
63.2	9.6

Table S24. Dry Matter Loss (%) as a function of Storage Time

Linear regression provides a good fit to experimental data (R^2=0.99), the regression equation is provided in Eqn 4.

(4) $$Dry\ Matter\ Loss\ (\%) = 0.1498 \times Storage\ Time\ (days) + 0.4767$$

The emissions factors for storage off-gases (kg-off-gases kg-biomass^{-1}) during biomass storage are estimated using Eqn. 5

(5) $$EF_i = \frac{P \times Vg \times M_{wt} \times C_i \times Storage\ Time\ (days)}{R \times T \times M \times 10^9}$$

Where P is the pressure of the container (101,300 Pa), Vg is the volume of gas (0.00152 m^3), M_{wt} is the molecular weight (g mole^{-1}) of the off gases (CO: 28, CO_2: 44, and CH_4: 16), R is the ideal gas constant (8.31 J mol^{-1} K^{-1}), T is the temperature of the storage (293.15 K), M is the mass of the stored biomass on a dry basis (0.562 kg), and C_i is the volumetric concentration increase of the *ith* off-gas (ppmv 10^{-6} day^{-1}), based on experimental values reported in ref[34].

Parameter	Type	Unit	Value	Definition
P	Constant	Pa	101,300	Pressure of Storage Gas
Vg	Constant	m^3	0.00152	Volume of Gas
M_{wt}	Constant	g $mole^{-1}$	CO:28, CO_2:44, CH_4:16	Molecular Weight of Off-gasses
R	Constant	J mol^{-1} K^{-1}	8.31	Ideal Gas Constant
T	Constant	Kelvin	293.15	Temperature
M	Constant	kg-dry biomass	0.562	Mass of stored Biomass
C_i	Constant	ppmv day^{-1}	CO:59.5, CO_2:190.1, CH_4:3.82	Off Gas Concentration Increase
Storage Time	Variable	Days	30 to 60	Storage Period

Table S25. Parameters used in calculating emissions factors for storage off-gases

PPM concentrations for storage off-gases for the 11th day were reverse calculated via Eqn 5 and emissions factors reported in ref[34]. It is assumed that the off-gas concentration of CO, CO_2, and CH_4 increase linearly with time when biomass is stored at 20 ^{O}C[34]. The increase in off-gas concentration (PPMV increase per day) is estimated via dividing the experimental concentration PPM at the 11th day by the storage time (days). For example, the rate of CO_2 PPM per day is assumed to be 654.2 PPM/11 Days = 190.1 PPM day^{-1}. The concentration rate is used to extrapolate total off-gas concentration for a nominal storage period.

Storage Off-Gases	Concentration (PPM after 11 days)	Concentration Increase (C_i) (PPM increase per day)
CO	654.2	59.5
CO_2	2090.7	190.1
*CH_4	42	3.82

*Due to data limitations PPM for CH4 could not be calculated direct, and was estimated via graphical interpretation. Results from ref [34], indicate that the 11-day PPM for CH4 at a storage temperature of 20OC lies between 40 and 45 PPM. In this work it is assumed that the 11-day CH4 concentration is 42 PPM.

Table S26. Storage Off-Gas Concentration and Concentration Rate

For example, the mass of CO_2 emitted over an 11-day storage on a dry basis is estimated to be

$$Emissions\ Factor\ CO_2 = \frac{(101{,}300)\times(0.00152)\times(44)\times(190.1)\times(11)}{(8.31)\times(293.15)\times(0.562)\times 10^9} = 1.03\times10^{-5}\frac{kg\ CO_2}{kg\ Dry\ Matter}$$

The emissions factor on a wet basis is estimated to be $9.09\text{x}10^{-6}$ (i.e. 9.09 mg CO_2/kg-biomass) equivalent to the results reported in ref[34].

$$CO_2 = \frac{(101{,}300)\times(0.00152)\times(44)\times(190.1)\times(11)}{(8.31)\times(293.15)\times(0.64)\times 10^9} = 9.09\times10^{-6}\frac{kg\ CO_2}{kg\ Biomass\ (wet)}$$

A uniform distribution was assumed for short-term storage, with a minimum of 30 days and a maximum of 60 days.

S4. Transportation of Stored Biomass to Refinery Gate

Transportation distance from farm-to-refinery was modeled via a triangular distribution assuming one-way transport via lorries and is outlined in Table S28. A minimum one-way transportation distance of 50 km, most likely value of 100 km, and maximum of 150 km were selected, and capture a broad range of values reported via prior published literature[1, 35, 36].

Transport Distance: Farm to Refinery	***References***
50 miles (~80 km)	Jones et al. 2013[1]
100 km (to BTL) or 50 km (to CHP)	Roedl et al. 2010[35]
60 miles (~96 km)	Zhang et al. 2013[36]

BTL: Biomass to Liquid; CHP: Combined Heat and Power

Table S27. Literature Survey: Transportation of Biomass from Farm to Refinery

Parameters	**Transport Distance: Farm to Refinery**
Min	50 km
Max	150 km
Most Likely	100 km

Table S28. Triangular Distribution: Transportation of Biomass from Farm to Refinery

S5. Pretreatment: Grinding And Chopping

The specific energy requirement for grinding/chopping of woody biomass is represented via the following formula[37]:

(6) $$E = aX^{-b}$$

Where E is the specific energy requirement (kJ/kg-dry biomass) and X is the aperture size in millimeters (mm). It assumed that woody biomass is chopped/ground to a particle size of 3mm[38], and all grinding/chopping energy is provided via electricity. Regression coefficients were taken from Miao et al.[37] and are provided in Table S29.

Feedstock	**Regression Coefficient (a)**	**Regression Coefficient (b)**	**Specific Energy Consumption** (kJ/kg-dry biomass)
Air-dry Willow	2408	-1.103	716.8

Table S29. Key Parameters for Grinding and Chopping of Woody Biomass

S6. Experimental Setup, Model Compound Methodology, and Laboratory Scale Results

Feedstock: Red oak sawdust was used as a starting material for single stage fast pyrolysis and stage 1 experiments. For stage 2, the solid product (solid residue) obtained from stage 1 was used as the feedstock, while for stage 3 (or fast pyrolysis), the solid residue produced from stage 2 was the starting material.

Apparatus: A CDS Analytical Pyroprobe 5250T apparatus (milligrams scale unit) was used to obtain the composition of organic compounds for each stage in the case of multi-stage scenario as well as for the single stage fast pyrolysis case (see Figure S1). Samples were prepared by loading 0.60-0.80 mg of biomass into a fire polished quartz tube with a filler rod and quartz wool above the rod to prevent the biomass from falling out of the bottom (see Figure S2).

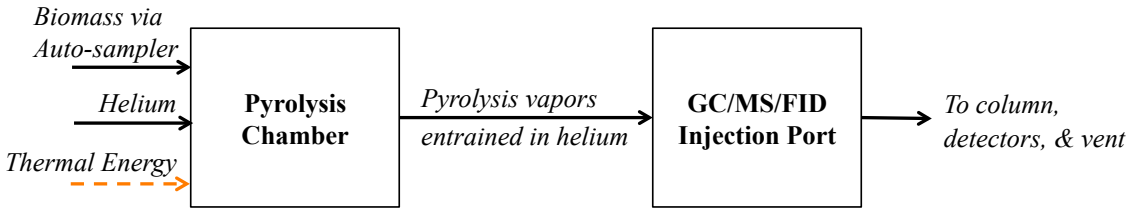

Figure S1. Pyroprobe Schematic

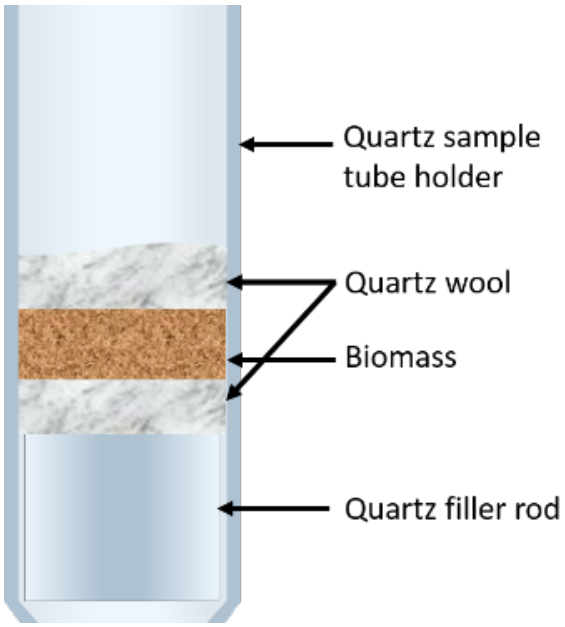

Figure S2. Quartz Sample Tube Diagram

Reactions were carried out in a helium carrier gas at one atmosphere and 94 ml/min total flow, and all experiments utilized a 1000°C / second temperature ramp. Evolved vapors were transported via transfer lines heated to 300°C into a Shimadzu QP-2010+ GC/MS-FID system with a 60m long semi-polar RTX-1701 column (250µm diameter, 0.25µm film thickness) for the identification and quantification of organic compounds[39]. Over 100 individual compounds are identified and quantified. These compounds are aggregated into groups, which have common

upgrading chemical functionalities, and are listed in Table S30. Each of the groups is assigned a model compound based on the most prevalent and/or chemically representative compound within the group. For example, large non-furanic anhydrosugar compounds are represented by levoglucosan; the group of methoxy phenols (phenols with at least one methoxy group attached to the ring) is represented by guaiacol, a major compound in that group.

Compound Identified by GC	Model compound
Acetic acid	*Acetic Acid*
2-Propenal Acetaldehyde Propanal-2-one Butanal 1-Penten-3-one 2,3-Butanedione 3-Pentanone 2-Butanone Hydroxyacetaldehyde 2-Butenal (cis or trans) c2-Hydroxypropanal Hydroxypropanone 2-Propenoic acid methyl ester 1-Hydroxy-2-butanone 3-Hydroxypropanal 2-Hydroxy-3-oxobutanal 1-Acetyloxypropane-2-one 2-Hydroxy-butanedial Butanedial 2,3-Dihydroxyhex-1-ene-4-one	*Acetol*
Furan 2-Methylfuran 2,5-dimethylfuran 2-Acetylfuran 2,3-Dihydro Furan (2H)-Furan-3-one	*Furan*
2-Furaldehyde 2-Furfuryl alcohol 5-Methyl-2-furaldehyde (5H)-Furan-2-one Dihydro-methyl-furanone 2-Hydroxy-1-methyl-1-cyclopentene-3-one Methyl-butyraldehyde derivative gamma-Lactone derivative gamma-Butyrolactone 5-Hydroxymethyl-2-furaldehyde 4-Cyclopentene-1,3-dione 2-Furoic acid methyl ester OH-methyl-dihydropyranone 4-Hydroxy-5,6-dihydro-(2H)-pyran-2-one 3-Hydroxy-2-methyl-pyran-4-one	*Furfural*

Methyl-dihydro-(2H)-pyran-2-one	
2-Cyclopenten-1-one, 2-methyl-	
Cyclopentanone	
Levoglucosan	
1,4:3,6-Dianhydro-glucopyranose	
1,6-Anhydro-beta-D-mannopyranose	*Levoglucosan*
1,5-Anhydro-beta-D-xylofuranose	
Anhydrosugar: unknown	
Toluene	
Phenol	
Styrene	
Benzene, ethyl-	
Benzene, 1,2-dimethyl-	*Toluene*
Benzaldehyde	
Anisole	
1,2,4-Trimethoxybenzene	
Benzylalcohol	
o-Cresol	
m-cresol	
Catechol	
Acetophenone	
Phenol, 4-vinyl-	
Phenol, 2,6-dimethyl-	
Phenol, 2-ethyl-	*Cresol*
Benzaldehyde, 4-hydroxy-	
Catechol, 3-methyl-	
Phenol, 4-allyl-	
Phenol, 4-propenyl-	
Anisole, 2,4-/2,5-dimethyl-	
Phenol, 2-propyl-	
Guaiacol	
Guaiacol, 3-methyl-	
Guaiacol, 4-vinyl-	
Guaiacol, 3-ethyl	
Vanillin	
Syringol	
Eugenol	
Isoeugenol	
Guaiacol, 4-propyl-	
Homovanillin	*Guaiacol*
Acetoguaiacone	
Syringol, 4-methyl-	
Vanillic acid	
Guaiacol, 4-(oxy-allyl)-	
Coniferaldehyde	
Syringol, 4-vinyl-	
Guaiacyl acetone	
Propioguaiacone	
Coniferyl alcohol	
Syringol, 3-ethyl-	

Dihydroconiferyl alcohol
Syringaldehyde
Syringol, 4-allyl-
Propioguaiacone, alpha-oxy-
Syringol, 4-propenyl-
Syringol, 4-propyl-
Homosyringaldehyde
Acetosyringone
Syringol, 4-(oxy-allyl)-
Sinapaldehyde
Syringyl acetone
Propiosyringone
Sinapyl alcohol
Propiosyringone, alpha-oxy-

Table S30. Model compound aggregation scheme based on identified compounds in the Pyroprobe chromatogram

The total area of the identified compounds accounts for typically ~85% of the total chromatogram area. The remainder of the chromatogram area is in numerous very small peaks distributed throughout the chromatogram, isomeric or chemically similar compounds to those positively identified. The remaining chromatogram area is attributed proportionally to the compound groups. The resulting volatile organic product yields (reported as the mass fraction of the original dry oak biomass) are reported in Table S31, as well as the final biochar resulting from the third stage (i.e. pyrolysis) treatment in the Pyroprobe based on tube weight following the third stage thermal treatment.

	Multistage Torrefaction and Pyrolysis (Mass Fraction %)				**Single Stage Pyrolysis (Mass Fraction %)**
Product	1st Stage	2nd Stage	Pyrolysis (3rd stage)	Total	Total
H_2O	9.20	6.80	0.00	16.00	13.20
Acetic Acid	5.21	1.79	0.39	7.38	8.47
Acetol	2.34	1.80	1.29	5.43	9.24
Furan	0.01	0.14	0.09	0.23	0.28
Furfural	3.99	3.81	0.54	8.33	5.01
Levoglucosan	0.00	6.89	3.48	10.37	18.44
Toluene	0.00	0.64	0.23	0.87	0.37
Guaiacol	2.51	2.26	1.25	6.01	5.86
Cresol	0.03	0.80	0.28	1.12	1.17
Biochar	-	-	10.50	10.50	9.01

Table S31. Model compound characterization of bio-oil produced via three-stage torrefaction and Pyrolysis system, and base-case single stage pyrolysis system. Results are presented as the mass fraction of total input ash-free dry biomass, and are based on volatile organic product yields obtained from the Pyroprobe.

In order to accurately measure non-condensable gases and water in the volatilized product, a larger-scale micropyrolysis unit was used. The micropyrolyzer consists of a gram scale reactor

and utilizes a twin-screw loss-in-weight feeding auger to load the biomass into the reactor. The unit is divided into three sections, viz., feeding section, reaction section and collection section. The entire feeding unit (comprising hopper, twin-screw auger and motor) rests on a 120 kg capacity scale which continuously measures mass of the feeding unit and an automated controls system maintains a constant mass flow-rate. In the reaction section, a stainless steel reactor was placed inside an electrical furnace, which acts as a heat source and heats the reactor to the desired temperature. The reactor was heated to the desired temperature before the biomass was introduced into it. A thermocouple was inserted inside the reactor from the bottom to directly measure the biomass temperature. Two streams of nitrogen gas, one to the bottom of the reactor and another one to the end of the feeding tube (but above the furnace), were used as fluidizing and sweep gas (or carrier gas). The nitrogen gas with a flow rate of 550 ml/min was pre-heated by flowing through stainless steel tubing coiled around the reactor before flowing into the reactor from the bottom. This pre-heated gas sweeps (or carries) the vapors produced inside the reactor to the sequential ice water and liquid nitrogen condensers (or traps) where the vapors were condensed and the liquid was collected for further analyses. The nitrogen flow at the end of feeding tube prevents any vapors produced inside the reactor from entering and subsequently condensing in the feeding channel. A cyclone separator was positioned in series between the reactor and the condensers to ensure the solid residue was not carried into the condensers along with the effluent gas. The effluent gas (carrier gas + non-condensable gases) exiting the liquid nitrogen condenser flows through the wet test meter before it is vented in order to measure the volume of non-condensable gases. Total liquid product includes the liquid collected in both the condensers.

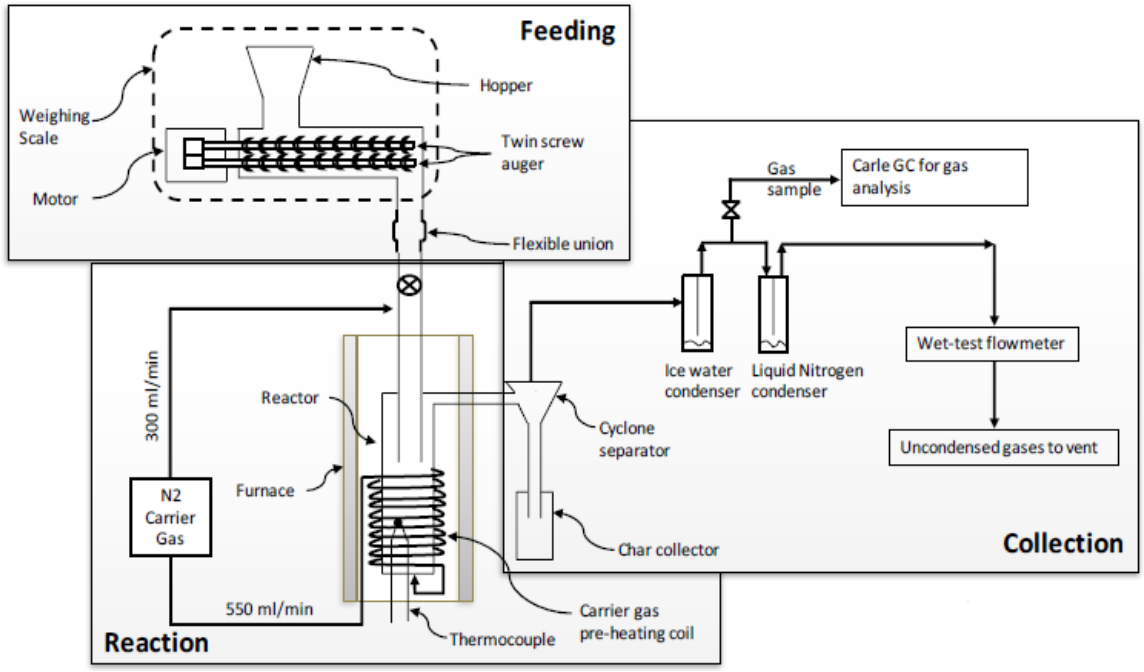

Figure S3. Bench Scale Reactor System

Water content analysis (reported as liquid weight percent) was carried out using a METTLER-TOLEDO V20 Volumetric Karl Fischer Titration Unit. Typically, 0.01-0.1mg (depending on the water content in the liquid sample; larger amount in the case of lower water content) of liquid sample was injected into the titration cell using a syringe and the result was displayed as weight

percent (wt. %) of the injected amount. It is assumed that the yield of water (grams of water/g of raw oak) obtained from micro-pyrolyzer for each stage is similar to that obtained from the pyroprobe.

During the pyrolysis and torrefaction experiments carried out in the micropyrolysis system, the non-condensable gases were quantitatively analyzed using a CARLE® Series 400 Analytical Gas Chromatograph (AGC) equipped with a dual thermal conductivity detector. The gas was sampled after the ice water condenser using a 20 ml syringe at different reaction times and injected into the AGC. Effluent gas flowrate was measured using the wet test meter. PeakSimple Chromatography Software from SRI Instruments was used to integrate the chromatogram peaks. After obtaining the peak area, the calibration curves were used to estimate the concentration (mole %) of non-condensable gases in the injected samples. The mass of non-condensable gases is calculated based on the effluent gas flowrate and assuming STP conditions (one mole of an ideal gas at STP occupies 22.4 liters). GC measurements of volatile products from the Pyroprobe are coupled with estimates of H_2O and non-condensable gases content obtained via the micro-pyrolyzer; the resulting product distributions for each stage are shown in Table 32.

	Multistage Torrefaction and Pyrolysis (Mass Fraction %)				**Single Stage Pyrolysis** (Mass Fraction %)
Product	1st Stage	2nd Stage	Pyrolysis	Total	Total
H_2O	9.20	6.80	0.00	16.00	13.20
Acetic Acid	5.21	1.79	0.39	7.38	8.47
Acetol	2.34	1.80	1.29	5.43	9.24
Furan	0.01	0.14	0.09	0.23	0.28
Furfural	3.99	3.81	0.54	8.33	5.01
Levoglucosan	0.00	6.89	3.48	10.37	18.44
Toluene	0.00	0.64	0.23	0.87	0.37
Guaiacol	2.51	2.26	1.25	6.01	5.86
Cresol	0.03	0.80	0.28	1.12	1.17
Oligomers	-	-	-	6.56	4.66
Bio-Oil (Wet Basis)	23.29	24.92	7.53	55.74	62.04
Gases	7.20	8.50	11.50	27.20	24.30
Biochar			10.50	10.50	9.01
Total	30.49	33.42	29.53	100.00	100.00

Table S32. Model compound characterization of bio-oil produced via three-stage torrefaction and Pyrolysis system, and base-case single stage pyrolysis system. Results are presented as the mass fraction of total input ash-free dry biomass, and are constructed based on coupling the volatile composition obtained from the Pyroprobe with analysis of NCG and water formation obtained from the micropyrolysis unit.

The oligomers content was calculated by difference and is defined in Eqn. 7

$$(7) \qquad \left(\begin{matrix}Mass\ fraction\\ oligomers\end{matrix}\right) = 1 - \left(\begin{matrix}mass\ fraction\\ biochar\end{matrix}\right) - \left(\begin{matrix}mass\ fraction\\ noncondensable\\ gases\end{matrix}\right) - \left(\begin{matrix}mass\ fraction\\ water\end{matrix}\right) - \left(\begin{matrix}mass\ fraction\\ GC-quantified\\ volatiles\end{matrix}\right)$$

In this study, the oligomeric content was assumed to be upgradable and was distributed evenly among all the liquid products, resulting in the product distribution given below in Table S33. The

data provided in Table S33 provides the analytical basis and underlying framework for the ASPEN model.

	Multistage Torrefaction and Pyrolysis (Mass Fraction %)				**Single Stage Pyrolysis** (Mass Fraction %)
Product	1st Stage	2nd Stage	Pyrolysis	Total	Total
H_2O	9.20	6.80	0.00	16.00	13.20
Acetic Acid	6.06	2.09	0.45	8.60	9.28
Acetol	2.73	2.10	1.50	6.33	10.12
Furan	0.01	0.16	0.10	0.27	0.31
Furfural	4.65	4.43	0.63	9.71	5.49
Levoglucosan	0.00	8.02	4.05	12.08	20.20
Toluene	0.00	0.75	0.26	1.01	0.40
Guaiacol	2.93	2.63	1.45	7.01	6.42
Cresol	0.04	0.93	0.33	1.30	1.29
Bio-Oil (Wet Basis)	25.61	27.91	8.78	62.30	66.69
Gases	7.20	8.50	11.50	27.20	24.30
Biochar	0.00	0.00	10.50	10.50	9.01
Total	32.81	36.41	30.78	100.00	100.00

Table S33. Model compound characterization of bio-oil derived via a three-stage torrefaction and pyrolysis design, and comparison with single-stage fast pyrolysis (500 ^{O}C). Results are presented as the mass fraction (%) of total input ash-free dry biomass.

S7. Woody Biomass, Torrefied Biomass, and Biochar Composition

Composition of woody and torrefied biomass, was based on experimental data for oak feedstock, obtained via the University of Oklahoma, see Table S34. The carbon and hydrogen content in the solid products as well as the raw oak was measured using a CE-440 Elemental Analyzer, purchased from Exeter Analytical, Inc. Oxygen content was obtained by difference based on the assumption that the amount of other elements (S, Mg, Ca, K, N, etc.) in the raw biomass as well as the solid products is negligible. Biochar produced via multistage and base-case single stage pyrolysis system is assumed to have the same elemental composition. Further, it is assumed that the elemental composition of solid product obtained from micro-pyrolyzer for each stage is similar to that obtained from pyroprobe.

	Elemental Composition (%)				**Proximate Analysis** (%)			
Parameters (Ash Free Dry Basis)	C	H	O	Total	Moisture Content	Ash Content	Volatile Matter	Fixed Carbon
Oak[1,2]	46.9	6.0	47.1	100	0	0	83.9	16.1
1st Stage Torrefied Oak[1,*]	53.9	5.4	40.7	100	0	0	83.9	16.1
2nd Stage Torrefied Oak[1,*]	62.9	4.8	32.3	100	0	0	83.9	16.1
Biochar[3]	86.1	3.4	10.4	100	0	0	32	68

[1]Element composition of Oak and torrefied biomass was based on experimental trials conducted at the University of Oklahoma (Personal Communication).
[2]The Volatile Mater and Fixed Carbon for woody-biomass were obtained via the Phyllis2 Database

*Due to data limitations the Volatile Matter and Fixed Carbon for torrefied biomass was assumed to be equivalent to oak biomass.
[3]Biochar elemental composition and proximate analysis is based on values reported from ref[40]. Elemental composition of biochar was adjusted from their original value(s) to conserve total elemental balance (i.e. so that C, H, and O % sum to 100%).

Table S34. Biomass and Biochar Composition

S8. Estimation of Biomass And Biochar/Ash Higher Heating Value

The higher heating values (HHV) for oak biochar/ash for multistage and fast pyrolysis systems are estimated to be 30.8 and 30.2 MJ/kg, respectively, see Table S35. The HHVs are constructed based on correlations provided in Channiwala and Parikh[41], see Eqn 8.

(8) $HHV\ (\frac{MJ}{kg}) = 0.3491 * [C\%] + 1.1783 * [H\%] + 0.105 * [S\%] - 0.1034 * [O\%] - 0.0151 * [N\%] - 0.0211 * [A\%]$

Where C%, H%, O%, N%, S%, A% represent the carbon, hydrogen, oxygen, nitrogen, sulfur, and ash content respectively, expressed in mass percentages on a dry basis.

Parameter	C	H	O	Ash	HHV (MJ/kg)
Fast Pyrolysis - Biochar/Ash Dry Basis (kg/hr)	6376.4	254.2	772.4	1141.7	-
Elemental Fraction (%)	74.6	3.0	9.0	13.4	30.2
Multistage Torrefaction/Pyrolysis - Biochar/Ash Dry Basis (kg/hr)	7434.4	296.3	900.5	1141.7	-
Elemental Fraction (%)	76.1	3.0	9.2	11.7	30.8

Table S35. Estimation of Biochar/Ash Higher Heating Value

S9. Catalytic Upgrading Strategies

Process yields for catalytic upgrading strategies (ketonization, alkylation, hydrogenation, hydrodeoxygenation) were modeled using equilibrium design blocks in AspenPlus. Specific reaction stoichiometry considered for each of the strategies is described below.

Ketonization: In ketonization two carboxylic acids react to form a ketone, producing carbon dioxide and water as by-products in the reaction, see Eqn 9.

(9) $$R_1COOH + R_2COOH \rightarrow R_1COR_2 + CO_2 + H_2O$$

Using Eqn 9, all possible ketones that can be produced via ketonization of carboxylic acids are provided in Table S36.

KET#	Carboxylic Acid	Carboxylic Acid	Ketone	Product 1	Product 2

KET1	CH_2O_2	CH_2O_2	CH_2O	H_2O	CO_2
KET2	CH_2O_2	$C_2H_4O_2$	C_2H_4O	H_2O	CO_2
KET3	CH_2O_2	$C_3H_4O_3$	$C_3H_4O_2$	H_2O	CO_2
KET4	CH_2O_2	$C_4H_4O_4$	$C_4H_4O_3$	H_2O	CO_2
KET5	CH_2O_2	$C_4H_6O_4$	$C_4H_6O_3$	H_2O	CO_2
KET6	CH_2O_2	$C_6H_{12}O_7$	$C_6H_{12}O_6$	H_2O	CO_2
KET7	$C_2H_4O_2$	$C_2H_4O_2$	C_3H_6O	H_2O	CO_2
KET8	$C_2H_4O_2$	$C_3H_4O_3$	$C_4H_6O_2$	H_2O	CO_2
KET9	$C_2H_4O_2$	$C_4H_4O_4$	$C_5H_6O_3$	H_2O	CO_2
KET10	$C_2H_4O_2$	$C_4H_6O_4$	$C_5H_8O_3$	H_2O	CO_2
KET11	$C_2H_4O_2$	$C_6H_{12}O_7$	$C_7H_{14}O_6$	H_2O	CO_2
KET12	$C_3H_4O_3$	$C_3H_4O_3$	$C_5H_6O_3$	H_2O	CO_2
KET13	$C_3H_4O_3$	$C_4H_4O_4$	$C_6H_6O_4$	H_2O	CO_2
KET14	$C_3H_4O_3$	$C_4H_6O_4$	$C_6H_8O_4$	H_2O	CO_2
KET15	$C_3H_4O_3$	$C_6H_{12}O_7$	$C_8H_{14}O_7$	H_2O	CO_2
KET16	$C_4H_4O_4$	$C_4H_4O_4$	$C_7H_6O_5$	H_2O	CO_2
KET17	$C_4H_4O_4$	$C_4H_6O_4$	$C_7H_8O_5$	H_2O	CO_2
KET18	$C_4H_4O_4$	$C_6H_{12}O_7$	$C_9H_{14}O_8$	H_2O	CO_2
KET19	$C_4H_6O_4$	$C_4H_6O_4$	$C_7H_{10}O_5$	H_2O	CO_2
KET20	$C_4H_6O_4$	$C_6H_{12}O_7$	$C_9H_{16}O_8$	H_2O	CO_2
KET21	$C_6H_{12}O_7$	$C_6H_{12}O_7$	$C_{11}H_{22}O_{11}$	H_2O	CO_2

Table S36. Ketonization - Products

Alkylation: during alkylation, an alkylating agent is utilized to upgrade furanic and phenolic compounds, producing a higher carbon chain alkylate as well as H_2O, see Eqn 10. Alkylates formed via alkylation of different reagents and alkylating agents is provided in Table S37.

(10) $$C_aH_bO_c + C_dH_eO_f \rightarrow C_{a+d}H_{b+e-2}O_{c+f-1} + H_2O$$

	Reagent	Alkylating Agent	Alkylate	Reagent			Alkylating Agent			Alkylate		
				C	H	O	C	H	O	C	H	O
Alkylation #1	Furan	Ethylene Glycol	ALK1 (C6H8O2)	4	4	1	2	6	2	6	8	2
	Furan	Propylene Glycol	ALK2 (C7H10O2)	4	4	1	3	8	2	7	10	2
	Furan	Isopropanol	ALK3 (C7H10O1)	4	4	1	3	8	1	7	10	1
	Furan	Butylene Glycol	ALK4 (C8H12O2)	4	4	1	4	10	2	8	12	2
	Methylfuran	Ethylene Glycol	ALK5 (C7H10O2)	5	6	1	2	6	2	7	10	2
	Methylfuran	Propylene Glycol	ALK6 (C8H12O2)	5	6	1	3	8	2	8	12	2
	Methylfuran	Isopropanol	ALK7 (C8H12O1)	5	6	1	3	8	1	8	12	1
	Methylfuran	Butylene Glycol	ALK8 (C9H14O2)	5	6	1	4	10	2	9	14	2
	Guaiacol	Ethylene Glycol	ALK9 (C9H12O3)	7	8	2	2	6	2	9	12	3

Alkylation #2	Guaiacol	Propylene Glycol	ALK10 (C10H14O3)	7	8	2	3	8	2	10	14	3
	Guaiacol	Isopropanol	ALK11 (C10H14O2)	7	8	2	3	8	1	10	14	2
	Guaiacol	Butylene Glycol	ALK12 (C11H16O3)	7	8	2	4	10	2	11	16	3
	Cresol	Ethylene Glycol	ALK13 (C9H12O2)	7	8	1	2	6	2	9	12	2
	Cresol	Propylene Glycol	ALK14 (C10H14O2)	7	8	1	3	8	2	10	14	2
	Cresol	Isopropanol	ALK15 (C10H14O1)	7	8	1	3	8	1	10	14	1
	Cresol	Butylene Glycol	ALK16 (C11H16O2)	7	8	1	4	10	2	11	16	2
	Toluene	Ethylene Glycol	ALK17 (C9H12O1)	7	8	0	2	6	2	9	12	1
	Toluene	Propylene Glycol	ALK18 (C10H14O1)	7	8	0	3	8	2	10	14	1
	Toluene	Isopropanol	ALK19 (C10H14)	7	8	0	3	8	1	10	14	0
	Toluene	Butylene Glycol	ALK20 (C11H16O1)	7	8	0	4	10	2	11	16	1
	ALK1 (C6H8O2)	Ethylene Glycol	2ALK1 (C8H12O3)	6	8	2	2	6	2	8	12	3
	LK1 (C6H8O2)	Propylene Glycol	2ALK2 (C9H14O3)	6	8	2	3	8	2	9	14	3
	ALK1 (C6H8O2)	Isopropanol	2ALK3 (C9H14O2)	6	8	2	3	8	1	9	14	2
	ALK1 (C6H8O2)	Butylene Glycol	2ALK4 (C10H16O3)	6	8	2	4	10	2	10	16	3
	ALK2 (C7H10O2)	Ethylene Glycol	2ALK5 (C9H14O3)	7	10	2	2	6	2	9	14	3
	ALK2 (C7H10O2)	Propylene Glycol	2ALK6 (C10H16O3)	7	10	2	3	8	2	10	16	3
	ALK2 (C7H10O2)	Isopropanol	2ALK7 (C10H16O2)	7	10	2	3	8	1	10	16	2
	ALK2 (C7H10O2)	Butylene Glycol	2ALK8 (C11H18O3)	7	10	2	4	10	2	11	18	3
	ALK3 (C7H10O1)	Ethylene Glycol	2ALK9 (C9H14O2)	7	10	1	2	6	2	9	14	2
	ALK3 (C7H10O1)	Propylene Glycol	2ALK10 (C10H16O2)	7	10	1	3	8	2	10	16	2
	ALK3 (C7H10O1)	Isopropanol	2ALK11 (C10H16O1)	7	10	1	3	8	1	10	16	1
	ALK3 (C7H10O1)	Butylene Glycol	2ALK12 (C11H18O2)	7	10	1	4	10	2	11	18	2
	ALK4 (C8H12O2)	Ethylene Glycol	2ALK13 (C10H16O3)	8	12	2	2	6	2	10	16	3
	ALK4 (C8H12O2)	Propylene Glycol	2ALK14 (C11H18O3)	8	12	2	3	8	2	11	18	3
	ALK4 (C8H12O2)	Isopropanol	2ALK15 (C11H18O2)	8	12	2	3	8	1	11	18	2
	ALK4 (C8H12O2)	Butylene Glycol	2ALK16 (C12H20O3)	8	12	2	4	10	2	12	20	3
	ALK5 (C7H10O2)	Ethylene Glycol	2ALK17 (C9H14O3)	7	10	2	2	6	2	9	14	3

ALK5 (C7H10O2)	Propylene Glycol	2ALK18 (C10H16O3)	7	10	2	3	8	2	10	16	3		
ALK5 (C7H10O2)	Isopropanol	2ALK19 (C10H16O2)	7	10	2	3	8	1	10	16	2		
ALK5 (C7H10O2)	Butylene Glycol	2ALK20 (C11H18O3)	7	10	2	4	10	2	11	18	3		
ALK6 (C8H12O2)	Ethylene Glycol	2ALK21 (C10H16O3)	8	12	2	2	6	2	10	16	3		
ALK6 (C8H12O2)	Propylene Glycol	2ALK22 (C11H18O3)	8	12	2	3	8	2	11	18	3		
ALK6 (C8H12O2)	Isopropanol	2ALK23 (C11H18O2)	8	12	2	3	8	1	11	18	2		
ALK6 (C8H12O2)	Butylene Glycol	2ALK24 (C12H20O3)	8	12	2	4	10	2	12	20	3		
ALK7 (C8H12O1)	Ethylene Glycol	2ALK25 (C10H16O2)	8	12	1	2	6	2	10	16	2		
ALK7 (C8H12O1)	Propylene Glycol	2ALK26 (C11H18O2)	8	12	1	3	8	2	11	18	2		
ALK7 (C8H12O1)	Isopropanol	2ALK27 (C11H18O1)	8	12	1	3	8	1	11	18	1		
ALK7 (C8H12O1)	Butylene Glycol	2ALK28 (C12H20O2)	8	12	1	4	10	2	12	20	2		
ALK8 (C9H14O2)	Ethylene Glycol	2ALK29 (C11H18O3)	9	14	2	2	6	2	11	18	3		
ALK8 (C9H14O2)	Propylene Glycol	2ALK30 (C12H20O3)	9	14	2	3	8	2	12	20	3		
ALK8 (C9H14O2)	Isopropanol	2ALK31 (C12H20O2)	9	14	2	3	8	1	12	20	2		
ALK8 (C9H14O2)	Butylene Glycol	2ALK32 (C13H22O3)	9	14	2	4	10	2	13	22	3		
ALK9 (C9H12O3)	Ethylene Glycol	2ALK33 (C11H16O4)	9	12	3	2	6	2	11	16	4		
ALK9 (C9H12O3)	Propylene Glycol	2ALK34 (C12H18O4)	9	12	3	3	8	2	12	18	4		
ALK9 (C9H12O3)	Isopropanol	2ALK35 (C12H18O3)	9	12	3	3	8	1	12	18	3		
ALK9 (C9H12O3)	Butylene Glycol	2ALK36 (C13H20O4)	9	12	3	4	10	2	13	20	4		
ALK0 (C10H14O3)	Ethylene Glycol	2ALK37 (C12H18O4)	10	14	3	2	6	2	12	18	4		
ALK10 (C10H14O3)	Propylene Glycol	2ALK38 (C13H20O4)	10	14	3	3	8	2	13	20	4		
ALK10 (C10H14O3)	Isopropanol	2ALK39 (C13H20O3)	10	14	3	3	8	1	13	20	3		
ALK10 (C10H14O3)	Butylene Glycol	2ALK40 (C14H22O4)	10	14	3	4	10	2	14	22	4		
ALK11 (C10H14O2)	Ethylene Glycol	2ALK41 (C12H18O3)	10	14	2	2	6	2	12	18	3		
ALK11 (C10H14O2)	Propylene Glycol	2ALK42 (C13H20O3)	10	14	2	3	8	2	13	20	3		
ALK11 (C10H14O2)	Isopropanol	2ALK43 (C13H20O2)	10	14	2	3	8	1	13	20	2		
ALK11 (C10H14O2)	Butylene Glycol	2ALK44 (C14H22O3)	10	14	2	4	10	2	14	22	3		
ALK12 (C11H16O3)	Ethylene Glycol	2ALK45 (C13H20O4)	11	16	3	2	6	2	13	20	4		

ALK12 (C11H16O3)	Propylene Glycol	2ALK46 (C14H22O4)	11	16	3	3	8	2	14	22	4
ALK12 (C11H16O3)	Isopropanol	2ALK47 (C14H22O3)	11	16	3	3	8	1	14	22	3
ALK12 (C11H16O3)	Butylene Glycol	2ALK48 (C15H24O4)	11	16	3	4	10	2	15	24	4
ALK13 (C9H12O2)	Ethylene Glycol	2ALK49 (C11H16O3)	9	12	2	2	6	2	11	16	3
ALK13 (C9H12O2)	Propylene Glycol	2ALK50 (C12H18O3)	9	12	2	3	8	2	12	18	3
AlLK13 (C9H12O2)	Isopropanol	2ALK51 (C12H18O2)	9	12	2	3	8	1	12	18	2
ALK13 (C9H12O2)	Butylene Glycol	2ALK52 (C13H20O3)	9	12	2	4	10	2	13	20	3
ALK14 (C10H14O2)	Ethylene Glycol	2ALK53 (C12H18O3)	10	14	2	2	6	2	12	18	3
ALK14 (C10H14O2)	Propylene Glycol	2ALK54 (C13H20O3)	10	14	2	3	8	2	13	20	3
ALK14 (C10H14O2)	Isopropanol	2ALK55 (C13H20O2)	10	14	2	3	8	1	13	20	2
ALK14 (C10H14O2)	Butylene Glycol	2ALK56 (C14H22O3)	10	14	2	4	10	2	14	22	3
ALK15 (C10H14O1)	Ethylene Glycol	2ALK57 (C12H18O2)	10	14	1	2	6	2	12	18	2
ALK15 (C10H14O1)	Propylene Glycol	2ALK58 (C13H20O2)	10	14	1	3	8	2	13	20	2
ALK15 (C10H14O1)	Isopropanol	2ALK59 (C13H20O1)	10	14	1	3	8	1	13	20	1
ALK15 (C10H14O1)	Butylene Glycol	2ALK60 (C14H22O2)	10	14	1	4	10	2	14	22	2
ALK16 (C11H16O2)	Ethylene Glycol	2ALK61 (C13H20O3)	11	16	2	2	6	2	13	20	3
ALK16 (C11H16O2)	Propylene Glycol	2ALK62 (C14H22O3)	11	16	2	3	8	2	14	22	3
ALK16 (C11H16O2)	Isopropanol	2ALK63 (C14H22O2)	11	16	2	3	8	1	14	22	2
ALK16 (C11H16O2)	Butylene Glycol	2ALK64 (C15H24O3)	11	16	2	4	10	2	15	24	3
ALK17 (C9H12O1)	Ethylene Glycol	2ALK65 (C11H16O2)	9	12	1	2	6	2	11	16	2
ALK17 (C9H12O1)	Propylene Glycol	2ALK66 (C12H18O2)	9	12	1	3	8	2	12	18	2
ALK17 (C9H12O1)	Isopropanol	2ALK67 (C12H18O1)	9	12	1	3	8	1	12	18	1
ALK17 (C9H12O1)	Butylene Glycol	2ALK68 (C13H20O2)	9	12	1	4	10	2	13	20	2
ALK18 (C10H14O1)	Ethylene Glycol	2ALK69 (C12H18O2)	10	14	1	2	6	2	12	18	2
ALK18 (C10H14O1)	Propylene Glycol	2ALK70 (C13H20O2)	10	14	1	3	8	2	13	20	2
ALK18 (C10H14O1)	Isopropanol	2ALK71 (C13H20O1)	10	14	1	3	8	1	13	20	1
ALK18 (C10H14O1)	Butylene Glycol	2ALK72 (C14H22O2)	10	14	1	4	10	2	14	22	2
ALK19 (C10H14)	Ethylene Glycol	2ALK73 (C12H18O1)	10	14	0	2	6	2	12	18	1

	ALK19 (C10H14)	Propylene Glycol	2ALK74 (C13H20O1)	10	14	0	3	8	2	13	20	1
	ALK19 (C10H14)	Isopropanol	2ALK75 (C13H20)	10	14	0	3	8	1	13	20	0
	ALK19 (C10H14)	Butylene Glycol	2ALK76 (C14H22O1)	10	14	0	4	10	2	14	22	1
	ALK20 (C11H16O1)	Ethylene Glycol	2ALK77 (C13H20O2)	11	16	1	2	6	2	13	20	2
	ALK20 (C11H16O1)	Propylene Glycol	2ALK78 (C14H22O2)	11	16	1	3	8	2	14	22	2
	ALK20 (C11H16O1)	Isopropanol	2ALK79 (C14H22O1)	11	16	1	3	8	1	14	22	1
	ALK20 (C11H16O1)	Butylene Glycol	2ALK80 (C15H24O2)	11	16	1	4	10	2	15	24	2

Table S37. Alkylation - Products

Hydrolysis and Oxidation

During hydrolysis and oxidation bio-oil compounds are converted to carboxylic acids via the use of an oxidizing agent, see Eqns 11 to 14.

(11) $C_3H_6O_2 + 2H_2O_2 \rightarrow C_3H_4O_3 + 3H_2O$

(12) $C_4H_4O + 3H_2O_2 \rightarrow C_4H_4O_4 + 3H_2O$

(13) $C_5H_4O_2 + 2H_2O_2 \rightarrow C_4H_6O_4 + CH_2O_2$

(14) $C_6H_{10}O_5 + H_2O_2 \rightarrow C_6H_{12}O_7$

Hydrogenation

Hydrogenation utilizes mild hydro-processing conditions to convert bio-oils compounds to stable intermediates, see Eqns 15 to 19.

(15) $C_2H_4O_2 + 3H_2 \rightarrow C_2H_6 + 2H_2O$

(16) $C_3H_6O_2 + H_2 \rightarrow C_3H_8O_2$

(17) $C_3H_6O + H_2 \rightarrow C_3H_8O$

(18) $C_5H_4O_2 + 2H_2 \rightarrow C_5H_6O_1 + H_2O$

(19) $2C_6H_{10}O_5 + 8H_2 \rightarrow C_2H_6O_2 + 2C_3H_8O_2 + C_4H_{10}O_2 + 2H_2O$

Hydrodeoxygenation

Hydrodeoxygenation utilizes severe hydroprocessing conditions to remove oxygen from bio-oil compounds, producing water as a byproduct. A generalized form of the reaction is defined in Eqn 20. The set of all possible reactions considered in HDO are provided in Table S38.

(20) $$C_aH_bO_c + (\frac{d-b+2c}{2})H_2 \rightarrow C_aH_d + cH_2O$$

HDO Reactions	Reaction Stoichiometry
Acetic Acid + Hydrogen = Ethane + Water	C2H4O2 + 3H2 = C2H6 + 2H2O
Formic Acid + Hydrogen = Methane + H2O	CH2O2+3H2 = CH4+2H2O
Pyruvic Acid + Hydrogen = Propane + H2O	C3H4O3 + 5H2 = C3H8+3H2O
Maleic Acid + Hydrogen = Butane + H2O	C4H4O4 + 7H2 = C4H10 + 4H2O
Succinic Acid + Hydrogen = Butane + H2O	C4H6O4 + 6H2 = C4H10 + 4H2O
Glucionic Acid + Hydrogen = Hexane + H2O	C6H12O7 + 8H2 = C6H14 + 7H2O
Acetone + Hydrogen = Propane + Water	C3H6O + 2H2 = C3H8 + H2O
Isopropanol + Hydrogen = Propane + Water	C3H8O+H2=C3H8+H2O
Ethylene Glycol + Hydrogen = Ethane + Water	C2H6O2 + 2H2 = C2H6 + 2H2O
Propylene Glycol + Hydrogen = Ethane + Water	C3H8O2+ 2H2 = C3H8 + 2H2O
Butylene Glycol + Hydrogen = Ethane + Water	C4H10O2 + 2H2 = C4H10 + 2H2O
Acetol + Hydrogen = Propane + Water	C3H6O2 + 3H2 = C3H8 + 2H2O
Furan + Hydrogen = Butane + Water	C4H4O + 4H2 = C4H10 + H2O
Furfural + Hydrogen = Pentane + Water	C5H4O2 + 6H2 = C5H12 + 2H2O
Methylfuran + Hydrogen = Pentane + Water	C5H6O + 4H2 = C5H12 + H2O
Levoglucosan + Hydrogen = Ethane + Propane + Butane + Water	2C6H10O5 + 10H2 = C2H6 + 2C3H8 + C4H10 + 10H2O
Guaiacol + Hydrogen = Cresol + Water	C7H8O2 +H2 = C7H8O + H2O
Cresol + Hydrogen = Toluene + Water	C7H8O +H2 = C7H8 + H2O
Ket1 + Hydrogen = Methane + Water	C1H2O1 + 2H2 = CH4 + H2O
Ket2 + Hydrogen = Ethane + Water	C2H4O1 + 2H2 = C2H6 + H2O
Ket3 + Hydrogen = Propane + Water	C3H4O2+ 4H2 = C3H8 + 2H2O
Ket4 + Hydrogen = Butane + Water	C4H4O3+ 6H2 = C4H10 +3 H2O
Ket5 + Hydrogen = Butane + Water	C4H6O3+ 5H2 = C4H10 + 3H2O
Ket6 + Hydrogen = Hexane + Water	C6H12O6+ 7H2 = C6H14 + 6H2O
Ket8 + Hydrogen = Butane + Water	C4H6O2+ 4H2 = C4H10 + 2H2O
Ket9 + Hydrogen = Pentane + Water	C5H6O3+ 6H2 = C5H12 + 3H2O
Ket10 + Hydrogen = Pentane + Water	C5H8O3+ 5H2 = C5H12 + 3H2O
Ket11 + Hydrogen = Heptane + Water	C7H14O6+ 7H2 = C7H16 + 6H2O
Ket12 + Hydrogen = Pentane + Water	C5H6O3+ 6H2 = C5H12 + 3H2O
Ket13 + Hydrogen = Hexane + Water	C6H6O4+ 8H2 = C6H14 + 4H2O
Ket14 + Hydrogen = Hexane + Water	C6H8O4+ 7H2 = C6H14 + 4H2O
Ket15 + Hydrogen = Octane + Water	C8H14O7+ 9H2 = C8H18 + 7H2O
Ket16 + Hydrogen = Heptane + Water	C7H6O5+ 10H2 = C7H16 + 5H2O
Ket17 + Hydrogen = Heptane + Water	C7H8O5+ 9H2 = C7H16 + 5H2O
Ket18 + Hydrogen = Nonane + Water	C9H14O8+ 11H2 = C9H20 + 8H2O
Ket19 + Hydrogen = Heptane + Water	C7H10O5+ 8H2 = C7H16 + 5H2O
Ket20 + Hydrogen = Nonane + Water	C9H16O8+ 10H2 = C9H20 + 8H2O
Ket21 + Hydrogen = Undecane + Water	C11H22O11+ 12H2 = C11H24 + 11H2O
1ALK1 + Hydrogen = Hexane + Water	C6H8O2 + 5H2 = C6H14 + 2H2O
1ALK2 + Hydrogen = Heptane + Water	C7H10O2+ 5H2 = C7H16 + 2H2O
1ALK3 + Hydrogen = Heptane + Water	C7H10O1+ 4H2 =C7H16 + H2O
1ALK4 + Hydrogen = Octane + Water	C8H12O2+ 5H2 = C8H18 + 2H2O
1ALK5 + Hydrogen = Heptane + Water	C7H10O2+ 5H2 = C7H16 + 2H2O
1ALK6 + Hydrogen = Octane + Water	C8H12O2+ 5H2 = C8H18 + 2H2O

1ALK7 + Hydrogen = Octane + Water	C8H12O1+ 4H2 = C8H18 + H2O
1ALK8 + Hydrogen = Nonane + Water	C9H14O2+ 5H2 = C9H20 + 2H2O
1ALK9 + Hydrogen = HDO1 + Water	C9H12O3+ 2H2 = C9H12O + 2H2O
1ALK10 + Hydrogen = HDO2 + Water	C10H14O3+ 2H2 = C10H14O + 2H2O
1ALK11 + Hydrogen = HDO3 + Water	C10H14O2+ H2 = C10H14O + H2O
1ALK12 + Hydrogen = HDO4 + Water	C11H16O3+ 2H2 = C11H16O + 2H2O
1ALK13 + Hydrogen = HDO5 + Water	C9H12O2+ 2H2 = C9H12 + 2H2O
1ALK14 + Hydrogen = HDO6 + Water	C10H14O2+ 2H2 = C10H14 + 2H2O
1ALK15 + Hydrogen = HDO7 + Water	C10H14O1+ H2 = C10H14 + H2O
1ALK16 + Hydrogen = HDO8 + Water	C11H16O2+ 2H2 = C11H16 + 2H2O
1ALK17 + Hydrogen = HDO9 + Water	C9H12O1+ H2 = C9H12 + H2O
1ALK18 + Hydrogen = HDO10 + Water	C10H14O1+ H2 = C10H14 + H2O
1ALK19 + Hydrogen = HDO11 + Water	C10H14 + H2 = C10H14 + H2O
1ALK20 + Hydrogen = HDO12 + Water	C11H16O1+ H2 = C11H16 + H2O
2ALK1 + Hydrogen = Octane + Water	C8H12O3 + 6H2 = C8H18 + 3H2O
2ALK2 + Hydrogen = Nonane + Water	C9H14O3 + 6 H2 = C9H20 + 3H2O
2ALK3 + Hydrogen = Nonane + Water	C9H14O2 + 5H2 = C9H20 + 2H2O
2ALK4 + Hydrogen = Decane + Water	C10H16O3 + 6H2 = C10H22 + 3H2O
2ALK5 + Hydrogen = Decane + Water	C10H16O3 + 6H2 = C10H22 + 3H2O
2ALK6 + Hydrogen = Decane + Water	C10H16O2 + 5H2 = C10H22 + 2H2O
2ALK7 + Hydrogen = Undecane + Water	C11H18O3 + 6H2 = C11H24 + 3H2O
2ALK8 + Hydrogen = Decane + Water	C10H16O1 + 4H2 = C10H22 + H2O
2ALK9 + Hydrogen = Undecane + Water	C11H18O2 + 5H2 = C11H24 + 2H2O
2ALK10 + Hydrogen = Dodecane + Water	C12H20O3 + 6H2 = C12H26 + 3H2O
2ALK11 + Hydrogen = Nonane + Water	C9H14O3 + 6H2 = C9H20 + 3H2O
2ALK12 + Hydrogen = Decane + Water	C10H16O3 + 6H2 = C10H22 + 3H2O
2ALK13 + Hydrogen = Decane + Water	C10H16O2 + 5H2 = C10H22 + 2H2O
2ALK14 + Hydrogen = Undecane + Water	C11H18O3 + 6H2 = C11H24 + 3H2O
2ALK15 + Hydrogen = Undecane + Water	C11H18O3 + 6H2 = C11H24 + 3H2O
2ALK16 + Hydrogen = Undecane + Water	C11H18O2 + 5H2 = C11H24 + 2H2O
2ALK17 + Hydrogen = Dodecane + Water	C12H20O3 + 6H2 = C12H26 + 3H2O
2ALK18 + Hydrogen = Undecane + Water	C11H18O1 + 4H2 = C11H24 + H2O
2ALK19 + Hydrogen = Dodecane + Water	C12H20O2 + 5H2 = C12H26 + 2H2O
2ALK20 + Hydrogen = Tridecane + Water	C13H22O3 + 6H2 = C13H28 + 3H2O
2ALK21 + Hydrogen = HDO13 + Water	C11H16O4 + 3H2 = C11H16O + 3H2O
2ALK22 + Hydrogen = HDO14 + Water	C12H18O4 + 3H2 = C12H18O + 3H2O
2ALK23 + Hydrogen = HDO15 + Water	C12H18O3 + 2H2 = C12H18O + 2H2O
2ALK24 + Hydrogen = HDO16 + Water	C13H20O4 + 3H2 = C13H20O + 3H2O
2ALK25 + Hydrogen = HDO17 + Water	C13H20O4 + 3H2 = C13H20O + 3H2O
2ALK26 + Hydrogen = HDO18 + Water	C13H20O3 + 2H2 = C13H20O + 2H2O
2ALK27 + Hydrogen = HDO19 + Water	C14H22O4 + 3H2 =C14H22O + 3H2O
2ALK28 + Hydrogen = HDO20 + Water	C13H20O2 + H2 = C13H20O + H2O
2ALK29 + Hydrogen = HDO21 + Water	C14H22O3 + 2H2 = C14H22O + 2H2O
2ALK30 + Hydrogen = HDO22 + Water	C15H24O4 + 3H2 = C15H24O + 3H2O
2ALK31 + Hydrogen = HDO23 + Water	C11H16O3 + 3H2 = C11H16 + 3H2O
2ALK32 + Hydrogen = HDO24 + Water	C12H18O3 + 3H2 = C12H18 + 3H2O
2ALK33 + Hydrogen = HDO25 + Water	C12H18O2 + 2H2 = C12H18 + 2H2O
2ALK34 + Hydrogen = HDO26 + Water	C13H20O3 + 3H2 = C13H20 + 3H2O
2ALK35 + Hydrogen = HDO27 + Water	C13H20O3 + 3H2 = C13H20 + 3H2O
2ALK36 + Hydrogen = HDO28 + Water	C13H20O2 + 2H2 = C13H20 + 2H2O
2ALK37 + Hydrogen = HDO29 + Water	C14H22O3 + 3H2 = C14H22 + 3H2O

2ALK38 + Hydrogen = HDO30 + Water	C13H20O1 + H2 = C13H20 + H2O
2ALK39 + Hydrogen = HDO31 + Water	C14H22O2 + 2H2 = C14H22 + 2H2O
2ALK40 + Hydrogen = HDO32 + Water	C15H24O3 + 3H2 = C15H24 + 3H2O
2ALK41 + Hydrogen = HDO33 + Water	C11H16O2 + 2H2 = C11H16 + 2H2O
2ALK42 + Hydrogen = HDO34 + Water	C12H18O2 + 2H2 = C12H18 + 2H2O
2ALK43 + Hydrogen = HDO35 + Water	C12H18O1 + H2 = C12H18 + H2O
2ALK44 + Hydrogen = HDO36 + Water	C13H20O2 + 2H2 = C13H20 + 2H2O
2ALK45 + Hydrogen = HDO37 + Water	C13H20O2 + 2H2 = C13H20 + 2H2O
2ALK46 + Hydrogen = HDO38 + Water	C13H20O1 + H2 = C13H20 + H2O
2ALK47 + Hydrogen = HDO39 + Water	C14H22O2 + 2H2 = C14H22 + 2H2O
2ALK48 + Hydrogen = HDO40 + Water	C13H20O0 + 0H2 = C13H20 + 0H2O
2ALK49 + Hydrogen = HDO41 + Water	C14H22O1 + H2 = C14H22 + H2O
2ALK50 + Hydrogen = HDO42 + Water	C15H24O2 + 2H2 = C15H24 + 2H2O

*1ALK19 and 2ALK48 are unaffected by HDO as the oxygen content of these compounds is null.

Table S38. Hydrodeoygenation - Products

Several multistage design cases, consisting of different catalytic strategies for upgrading fractionated bio-oil are considered. A detailed summary of the multistage systems is provided below:

Multistage System 1 upgrades bio-oil fractions independently, targeting promising conversion pathways based on the composition of each stream. In this configuration, stage 1 bio-oil undergoes ketonization (180 ^{O}C, 27 atm) to convert carboxylic acids (acetic acid) to ketones (acetone) and byproducts (CO_2, H_2O). Mild hydrogenation (100 ^{O}C, 27 atm) is performed to convert acetol to propylene glycol, acetone to isopropanol, and furfural to 2-methylfuran, producing water as a secondary product in the reaction. Post hydrogenation, stage 1 bio-oil is sent to an alkylation reactor (125 ^{O}C, 27 atm) in which alcohols act as alkylating agents to upgrade furanics (furan and 2-methylfuran) and aromatics (guaiacol, cresol, toluene) producing alkylates as well as water as a secondary product in the reaction. Stage 2 bio-oil undergoes an initial hydrolysis and oxidation (80 ^{O}C, 1 atm) step, using hydrogen-peroxide as an oxidizing agent to convert levoglucosan to glucionic acid, furfural to succinic and formic acid, furan to maleic acid, and acetol to pyruvic acid. Stage 2 bio-oil is sent to a ketonization reactor (360 ^{0}C, 27 atm), which converts carboxylic acids into ketones ranging from C1-C11 in carbon chain length, producing H_2O and CO_2 as byproducts. Stage 3 bio-oil is hydrogenated (100 ^{0}C, 27 atm), decomposing levoglucosan into alcohols (Ethylene Glycol, Propylene Glycol, Butylene Glycol), and converting acetic acid to ethane, acetol to propylene glycol, furfural to 2-methylfuran, producing water as a byproduct in the reaction. Stage 3 bio-oil is subsequently sent to an alkylation reactor (125 ^{0}C, 27 atm) in which alcohols act as alkylating agents to upgrade furanics (furan and 2-methylfuran) and aromatics (guaiaicol, cresol, toluene) producing alkylates as well as byproduct H_2O. All streams are hydrodeoxygenated (400 ^{0}C, 55 atm) for removal of oxygen from bio-oil compounds, forming H_2O in the reaction.

Multistage System 2 employs an integrated strategy, upgrading stage 1 & 2 bio-oil concurrently. In this design, hydrolysis and oxidation (80 ^{0}C, 1 atm) using H_2O_2 as an oxidizing agent, is utilized to convert light oxygenates, furanics, and anhydrosugars present in stage 1 & 2 bio-oil, into a host of carboxylic acids including formic acid, acetic acid, pyruvic acid, maleic acid, succinic acid, and glucionic acid, yielding water and carbon dioxide as byproducts. Integrated stage 1 & 2 bio-oil is sent to a ketonization reactor (360 ^{0}C, 27 atm) to produce ketones ranging from C1-C11 in carbon number, forming byproduct CO_2 and H_2O. Aromatics (guaiacol, cresol, toluene) and light ketones are separated from the integrated stage 1 & 2 bio-oil stream, and

coupled with stage 3 bio-oil. Partial hydrogenation (100 ^{0}C, 27 atm) of coupled stage 3 bio-oil is utilized to convert levoglucosan into alcohols, acetone to isopropanol, acetic acid to ethane, acetol to propylene glycol, and furfural to 2-methylfuran, producing H_2O during the reaction. Coupled stage 3 bio-oil is subsequently sent to an alkylation reactor (125 ^{0}C, 27 atm) in which alcohols (Ethylene Glycol, Propylene Glycol, Isopropanol, and Butylene Glycol) act as alkylating agents to upgrade furanics (furan and 2-methylfuran) and aromatics (guaiacol, cresol, toluene) producing alkylates as well as byproduct H_2O. All streams are hydrodeoxygenated (400^{0}C, 55 atm) for removal of oxygen from bio-oil compounds, forming H_2O in the reaction.

Multistage System 3 adopts an integrated minimalist approach, utilizing a minimal number of design blocks to upgrade bio-oil. In this design, integrated stage 1 & 2 bio-oil streams undergo ketonization (180 ^{0}C, 27 atm) to convert acetic acid into acetone, producing CO_2 and H_2O as byproducts in the reaction. Post-ketonization, integrated stage 1 & 2 bio-oil are coupled with stage 3 bio-oil and subsequently hydrogenated (100 ^{0}C, 27 atm). Hydroprocessing converts levoglucosan into alcohols, acetone to isopropanol, acetic acid to ethane, acetol to propylene glycol, and furfural to 2-methylfuran, producing H_2O during the reaction. Bio-oil is subsequently sent to an alkylation reactor (125 ^{0}C, 27 atm) in which alcohols (Ethylene Glycol, Propylene Glycol, Isopropanol, and Butylene Glycol) act as alkylating agents to upgrade furanics (furan and 2-methylfuran) and aromatics (guaiacol, cresol, toluene) producing alkylates as well as byproduct H_2O. All streams are hydrodeoxygenated (400^{0}C, 55 atm) to remove oxygen from bio-oil compounds, forming H_2O in the reaction.

S10. Biorefinery Utilities

Net heating and cooling duties for the evaluated design cases were constructed based on pinch analysis, assuming a dTmin of 10^{O}C. The hot and cold composite curves for each of the examined design cases are provided in Figures S4 through S7 shown below.

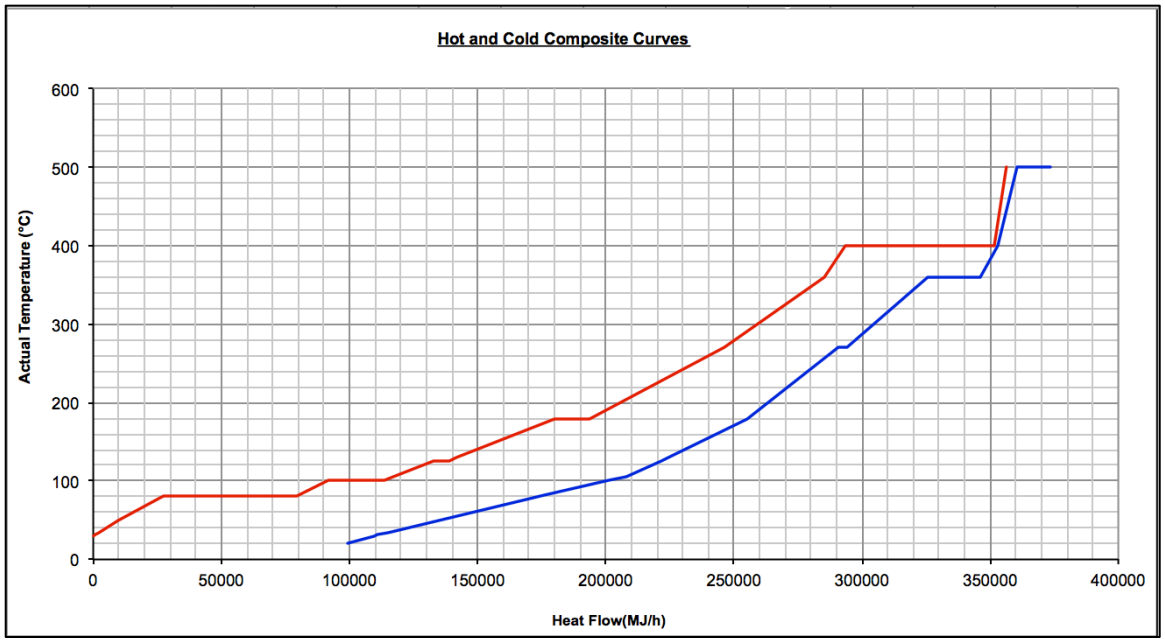

Figure S4. Multistage System 1: Hot and Cold Composite Curves

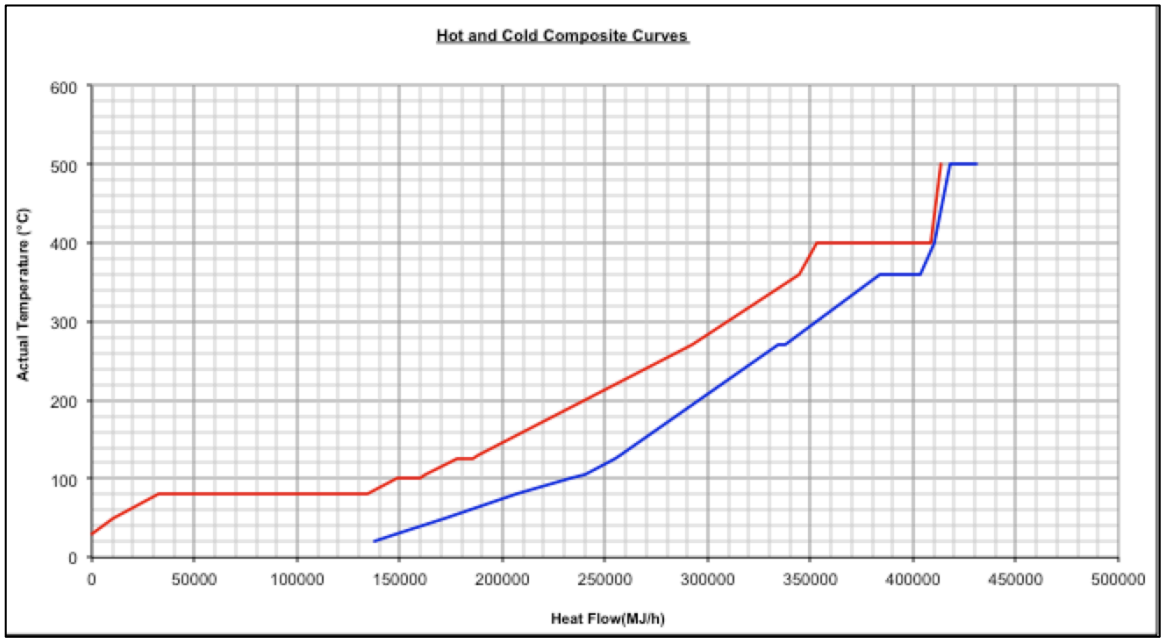

Figure S5. Multistage System 2: Hot and Cold Composite Curves

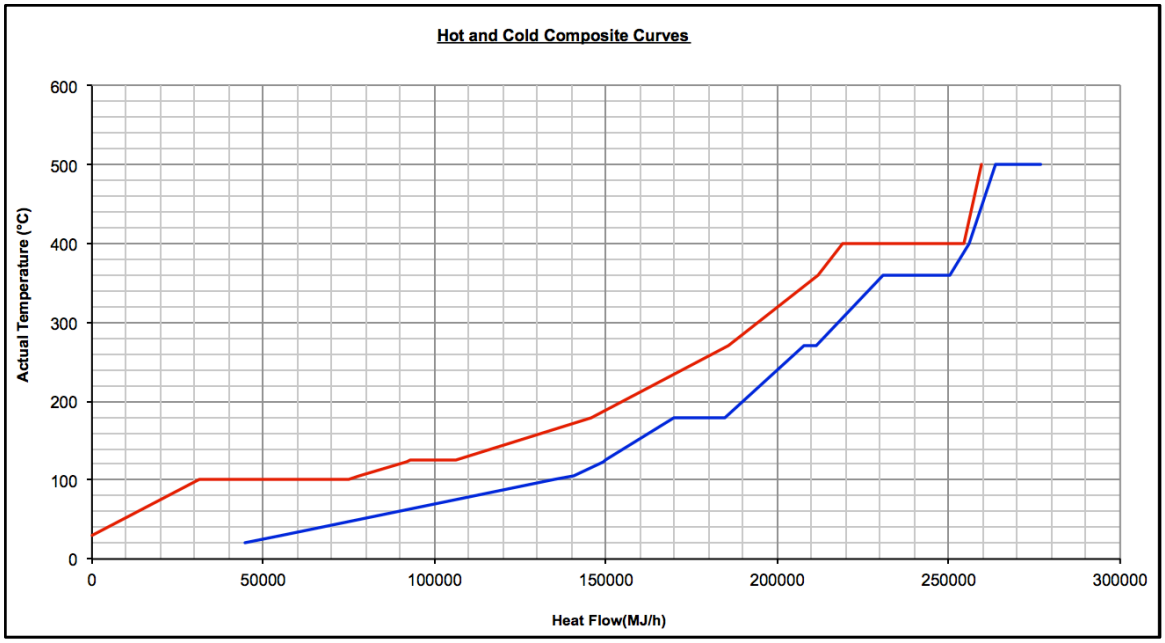

Figure S6. Multistage System 3: Hot and Cold Composite Curves

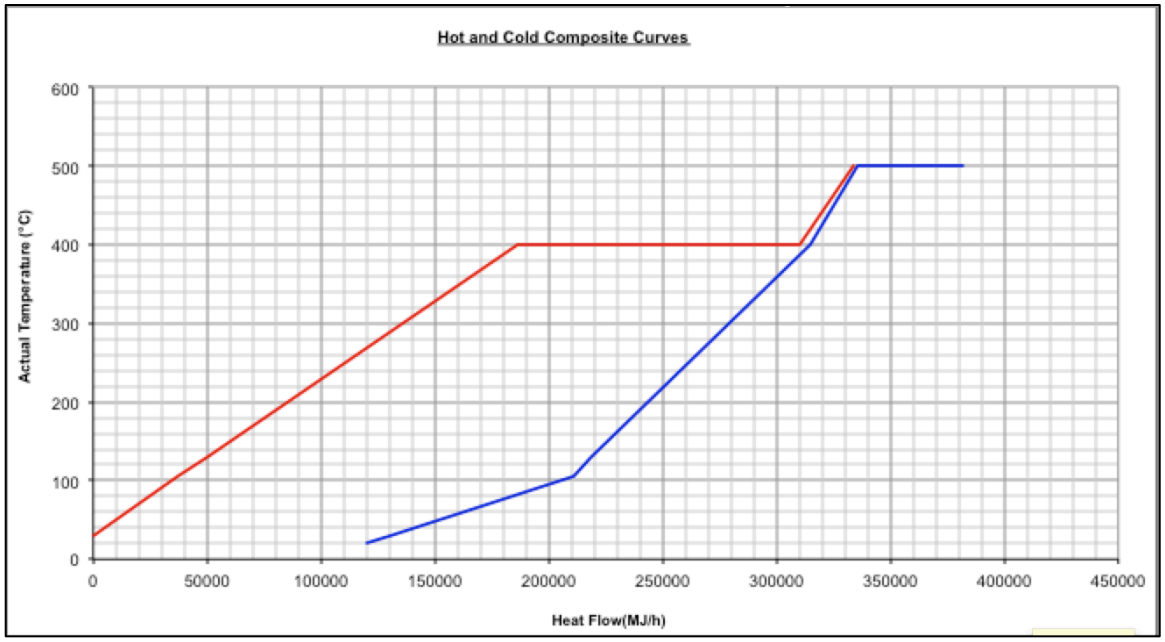

Figure S7. Single Stage Fast Pyrolysis and HDO: Hot and Cold Composite Curves

Electricity consumption for net cooling duty was estimated via the work required for pumping cooling water. The mass flow of cooling water (m) was estimated based on the specific heat capacity (C_p) of water (4180 J/kg-water), nominal temperature differential (10 ^{O}C), and net cooling duty (MJ/hr), defined in Eqn 21.

(21) $$mC_p\Delta T = Net\ Cooling\ Duty$$

The total pressure drop across the cooling water loop is estimated to be 38.7 psi (266.7 kPa), constructed based on 15 psi (pipe head losses) + 5 psi (exchanger losses) + 10 psi (control valve loss) + 8.7 psi of static head assuming water must be pumped to the top of the cooling tower an average height of 20 ft, Power required for cooling water pumps with a volumetric flow rate V, and an overall efficiency of 75% is provided in Eqn 22.

(22) $$Pump\ Power\ \left(\frac{MJ}{Hr}\right) = \frac{1}{\varepsilon}V\Delta P = \frac{1}{0.75} * \left(\frac{V}{10^6}\right)(266.7)$$

Process utilities for all examined design cases are provided in Table S39.

Parameter	Unit	Fast Pyrolysis HDO	Multistage Torrefaction & Pyrolysis		
			System 1	*System 2*	*System 3*
Pretreatment	Electricity (MJ/hr)	59733	59733	59733	59733
Compressors	Electricity (MJ/hr)	6095	2792	2980	1856
Pumps	Electricity (MJ/hr)	339	488	415	391
Cooling Utility	Electricity (MJ/hr)	1019	843	1173	381
*Heating Duty	Heat Input (MJ/hr)	48170	17372	17319	17198
*Cooling Duty	Heat Removed (MJ/hr)	119829	99068	137895	44830

*Based on Optimal Heat Exchange Network

Table S39. Biorefinery Utilities

S11. Transportation of Biofuel from Refinery Gate to Pump

Transportation of biomass-based diesel from the refinery-to-pump is based on the 2016 GREET model[42]. It is assumed that biomass-based diesel is transported from refinery to bulk terminal assuming a transportation mix of 8% by barge, 29% by rail, 63% by heavy duty truck (on a mass basis) and a corresponding average transportation distance of 520 miles, 800 miles, and 50 miles respectively. Biomass-based diesel is subsequently transported from bulk terminal to refueling station via heavy-duty trucks assuming a one-way transportation distance of 30 miles.

	Transportation Mix (% Mass Basis)	**Transport Distance: Refinery to Bulk Terminal** (Miles)
Heavy Truck	8 %	50 Miles
Rail	29 %	800 Miles
Barge	63 %	520 Miles

*Constructed based on data for pyrolysis diesel fuel pathways in the GREET 2016 Model[42].

Table S40. Transportation of Biofuel Diesel from Refinery to Bulk Terminal

	Transportation Mix (% Mass Basis)	**Transport Distance: Bulk Terminal to Refueling Station** (Miles)
Heavy Truck	100 %	30 Miles
Rail	-	-
Barge	-	-

*Constructed based on data for pyrolysis diesel fuel pathways in the GREET 2016 Model[42].

Table S41. Transportation of Biofuel from Bulk Terminal to Refueling Station

S12. Life Cycle Data Acquisition

Table S42 provides an overview of life cycle data sources and life cycle impact assessment (LCIA) methods used in this study

Material or Process Description	**Unit**	**Database**	**Method**	**C.I.**	**N**
Urea, as N (RER) | production | Alloc Def U	kg	Ecoinvent	IPCC 2013 GWP 100a V1.01	95%	10,000
Urea, as N (RER) | production | Alloc Def U	kg	Ecoinvent	Cumulative Energy Demand V 1.09	95%	10,000
Nitrogen fertilizer, as N (RER) | calcium ammonium nitrate production | Alloc, Def U	kg	Ecoinvent	IPCC 2013 GWP 100a V1.01	95%	10,000
Nitrogen fertilizer, as N (RER) | calcium ammonium nitrate production | Alloc, Def U	kg	Ecoinvent	Cumulative Energy Demand V 1.09	95%	10,000
Phosphate fertilizer, as P2O5 (RER) | triple superphosphate production | Alloc Def U	kg	Ecoinvent	IPCC 2013 GWP 100a V1.01	95%	10,000
Phosphate fertilizer, as P2O5 (RER) | triple superphosphate production | Alloc Def U	kg	Ecoinvent	Cumulative Energy Demand V 1.09	95%	10,000
Potassium Sulfate, as K2O (RER) | potassium sulfate production | Alloc Def, U	kg	Ecoinvent	IPCC 2013 GWP 100a V1.01	95%	10,000
Potassium Sulfate, as K2O (RER) | potassium	kg	Ecoinvent	Cumulative Energy Demand V 1.09	95%	10,000

sulfate production | Alloc Def, U					
Lime Fertilizer, at regional storehouse/RER Mass	kg	Agri-footprint	IPCC 2013 GWP 100a V1.01	N/A	N/A
Lime Fertilizer, at regional storehouse/RER Mass	kg	Agri-footprint	Cumulative Energy Demand V 1.09	N/A	N/A
Ground Calcium Carbonate (GCC) – Dry, uncoated, at plant, RER S	kg	Ecoinvent	IPCC 2013 GWP 100a V1.01	N/A	N/A
Ground Calcium Carbonate (GCC) – Dry, uncoated, at plant, RER S	kg	Ecoinvent	Cumulative Energy Demand V 1.09	N/A	N/A
Irrigation (US) | Processing | Alloc Def, U	kg	Ecoinvent	IPCC 2013 GWP 100a V1.01	N/A	N/A
Irrigation (US) | Processing | Alloc Def, U	kg	Ecoinvent	Cumulative Energy Demand V 1.09	N/A	N/A
Glyphosate (RER) | production | Alloc Def U	kg	Ecoinvent	IPCC 2013 GWP 100a V1.01	95%	10,000
Glyphosate (RER) | production | Alloc Def U	kg	Ecoinvent	Cumulative Energy Demand V 1.09	95%	10,000
Metolachlor (RER) | production | Alloc Def U	kg	Ecoinvent	IPCC 2013 GWP 100a V1.01	95%	10,000
Metolachlor (RER) | production | Alloc Def U	kg	Ecoinvent	Cumulative Energy Demand V 1.09	95%	10,000
Pesticide, unspecified (RER) | production | Alloc Def, U	kg	Ecoinvent	IPCC 2013 GWP 100a V1.01	95%	10,000
Pesticide, unspecified (RER) | production | Alloc Def, U	kg	Ecoinvent	Cumulative Energy Demand V 1.09	95%	10,000
Diesel (RoW) market for | Alloc Def U	Kg	Ecoinvent	IPCC 2013 GWP 100a V1.01	95%	10,000
Diesel (RoW) market for | Alloc Def U	kg	Ecoinvent	Cumulative Energy Demand V 1.09	95%	10,000
Transport, freight, lorry > 32 metric tons, EURO5 (ROW) | Alloc Def U	tkm	Ecoinvent	IPCC 2013 GWP 100a V1.01	95%	10,000
Transport, freight, lorry > 32 metric tons, EURO5 (ROW) | Alloc Def U	tkm	Ecoinvent	Cumulative Energy Demand V 1.09	95%	10,000
Electricity, High Voltage U.S. | Production Mix | Alloc, Def U	MJ	Ecoinvent	IPCC 2013 GWP 100a V1.01	95%	10,000
Electricity, High Voltage U.S. | Production Mix | Alloc, Def U	MJ	Ecoinvent	Cumulative Energy Demand V 1.09	95%	10,000
Zeolite, powder (RER) | Production | Alloc Def U	kg	Ecoinvent	IPCC 2013 GWP 100a V1.01	N/A	N/A
Zeolite, powder (RER) | Production | Alloc Def U	kg	Ecoinvent	Cumulative Energy Demand V 1.09	N/A	N/A
Hydrogen (reformer) E	kg	Industry data 2.0	IPCC 2013 GWP 100a V1.01	N/A	N/A
Hydrogen (reformer) E	kg	Industry data 2.0	Cumulative Energy Demand V 1.09	N/A	N/A
Heat, natural gas, at industrial furnace >100 kW/RER U	MJ	Ecoinvent	IPCC 2013 GWP 100a V1.01	95%	10,000
Heat, natural gas, at industrial furnace >100 kW/RER U	MJ	Ecoinvent	Cumulative Energy Demand V 1.09	95%	10,000
Hydrogen peroxide, without water, in 50% solution state (RER) | hydrogen peroxide production, product in 50% solution state | Alloc Def, U	kg	Ecoinvent	IPCC 2013 GWP 100a V1.01	95%	10,000
Hydrogen peroxide, without water, in 50% solution state (RER) | hydrogen peroxide production, product in 50% solution state | Alloc Def, U	Kg	Ecoinvent	Cumulative Energy Demand V 1.09	95%	10,000
Transport, freight, inland waterways, barge (RER) |processing| Alloc Def, U	tkm	Ecoinvent	IPCC 2013 GWP 100a V1.01	95%	10,000
Transport, freight, inland waterways, barge (RER) |processing| Alloc Def, U	tkm	Ecoinvent	Cumulative Energy Demand V 1.09	95%	10,000
Transport, freight train (US)| diesel| Alloc Def, U	tkm	Ecoinvent	IPCC 2013 GWP 100a V1.01	95%	10,000
Transport, freight train (US)| diesel| Alloc Def, U	tkm	Ecoinvent	Cumulative Energy Demand V 1.09	95%	10,000

Table S42. Life Cycle Data Sources

S13. Overview Of Key Parameters And Distributions

Parameter	Unit	Distribution	Mean	St. Dev.	Min	Max	Most Likely	Point Est.
Direct Land Use Change								
SOC_{REF}	Tonnes C ha^{-1}	Point Est.	-	-	-	-	-	95
F_{LU}	Unitless	Point Est.	-	-	-	-	-	1
F_{MG}	Unitless	Triangular	-	-	0.7	1	0.95	-
Above and Below Ground Biomass	Tonnes d.m ha^{-1}	Normal	13.6	5.1	-	-	-	-
Biomass Carbon Content	% C	Point Est.						47%
Cuttings Production								
N-Fertilizer application	kg N $Cutting^{-1}$	Point Est.	-	-	-	-	-	5.2E-04
P-Fertilizer application	kg P $Cutting^{-1}$	Point Est.	-	-	-	-	-	6.5E-04

K-Fertilizer application	kg K Cutting^{-1}	Point Est.	-	-	-	-	-	3.9E-04
$CaCO_3$ application	kg $CaCO_3$ Cutting^{-1}	Point Est.	-	-	-	-	-	6.5E-03
Herbicide Application	L Herbicide Cutting^{-1}	Point Est.	-	-	-	-	-	2.0E-05
Diesel Use	L Diesel Cutting^{-1}	Point Est.	-	-	-	-	-	7.5E-04
Woody Biomass Production								
Woody Biomass Growth Rates	Tonnes d.m ha^{-1}	Bootstrapping	-	-	-	-	-	-
SRWC Stand Life	Years	Bootstrapping	-	-	-	-	-	-
Cuttings	Cuttings ha^{-1}	Bootstrapping	-	-	-	-	-	-
N Fertilizer application	kg ha^{-1}	Bootstrapping	-	-	-	-	-	-
P Fertilizer application	kg ha^{-1}	Bootstrapping	-	-	-	-	-	-
K Fertilizer application	kg ha^{-1}	Bootstrapping	-	-	-	-	-	-
Lime Fertilizer application	kg ha^{-1}	Bootstrapping	-	-	-	-	-	-
Herbicide application	kg ha^{-1}	Bootstrapping	-	-	-	-	-	-
Irrigation application	m^3 ha^{-1}	Bootstrapping	-	-	-	-	-	-
Frequency - Plowing	Unitless	Bootstrapping	-	-	-	-	-	-
Frequency - Harrowing	Unitless	Bootstrapping	-	-	-	-	-	-
Frequency - Disking	Unitless	Bootstrapping	-	-	-	-	-	-
Frequency – Mechanical Weeding	Unitless	Bootstrapping	-	-	-	-	-	-
Frequency – Chemical Weeding	Unitless	Bootstrapping	-	-	-	-	-	-
Frequency – Fertilizing (Lime)	Unitless	Bootstrapping	-	-	-	-	-	-
Frequency – Fertilizing (N/P/K)	Unitless	Bootstrapping	-	-	-	-	-	-
Frequency – Planting	Unitless	Bootstrapping	-	-	-	-	-	-
Frequency – Pest Control	Unitless	Bootstrapping	-	-	-	-	-	-
Frequency – Irrigation	Unitless	Bootstrapping	-	-	-	-	-	-
Frequency – Coppicing	Unitless	Bootstrapping	-	-	-	-	-	-
Frequency – Harvesting/Chipping	Unitless	Bootstrapping	-	-	-	-	-	-
Frequency – Stump Removal	Unitless	Bootstrapping	-	-	-	-	-	-
Diesel Use - Plowing	L-Diesel ha^{-1}	Bootstrapping	-	-	-	-	-	-
Diesel Use - Harrowing	L-Diesel ha^{-1}	Bootstrapping	-	-	-	-	-	-
Diesel Use - Disking	L-Diesel ha^{-1}	Bootstrapping	-	-	-	-	-	-
Diesel Use – Mechanical Weeding	L-Diesel ha^{-1}	Bootstrapping	-	-	-	-	-	-
Diesel Use – Chemical Weeding	L-Diesel ha^{-1}	Bootstrapping	-	-	-	-	-	-
Diesel Use – Fertilizer (Lime)	L-Diesel ha^{-1}	Bootstrapping	-	-	-	-	-	-
Diesel Use – Fertilizer (N/P/K)	L-Diesel ha^{-1}	Bootstrapping	-	-	-	-	-	-
Diesel Use – Planting	L-Diesel ha^{-1}	Bootstrapping	-	-	-	-	-	-
Diesel Use – Pest Control	L-Diesel ha^{-1}	Bootstrapping	-	-	-	-	-	-
Diesel Use – Irrigation	L-Diesel ha^{-1}	Bootstrapping	-	-	-	-	-	-
Diesel Use – Coppicing	L-Diesel ha^{-1}	Bootstrapping	-	-	-	-	-	-
Diesel Use – Harvesting/Chipping	L-Diesel ha^{-1}	Bootstrapping	-	-	-	-	-	-
Diesel Use – Stump Removal	L-Diesel ha^{-1}	Bootstrapping	-	-	-	-	-	-
Direct N_2O Emissions	(% N volatilized)	Bootstrapping	-	-	-	-	-	-
Indirect N_2O	Soil N Vol. Rate (%)	Triangular	-	-	3%	30%	10%	-
Indirect N_2O	Runoff rate (%)	Triangular	-	-	10%	80%	30%	-
Indirect N_2O	Conv. Rate (%)	Triangular	-	-	0.05%	2.5%	0.75%	-
Harvest Efficiency	(%)	Uniform	-	-	77.4%	94.5%	-	-
Moisture Content Biomass (Pre-Storage)	(%)	Point Est.	-	-	-	-	-	50
Storage Period	Days	Uniform	-	-	30	60	-	-
Moisture Content Biomass (Post-Storage)	(%)	Point Est.	-	-	-	-	-	25
Local Transport								
Transport Biomass (Farm-to-Refinery)	Km	Triangular	-	-	50	150	100	-
Fuel Conversion & Upgrading								
Weight Hourly Space Velocity	Hr^{-1}	Point Est.	-	-	-	-	-	0.2
Catalyst Lifetime	Days	Uniform	-	-	60	365	-	-
Fuel Transport and Distribution								
Transport Biofuel (Refinery-to-Bulk Terminal) via Barge	Miles	Point Est.	-	-	-	-	-	520
Transport Biofuel (Refinery-to-Bulk Terminal) via Rail	Miles	Point Est.	-	-	-	-	-	800
Transport Biofuel (Refinery-to-Bulk Terminal) via Heavy Duty Truck	Miles	Point Est.	-	-	-	-	-	50
Transportation Mix (Barge)	%	Point Est.	-	-	-	-	-	8%
Transportation Mix (Rail)	%	Point Est.	-	-	-	-	-	29%

Transportation Mix (Heavy Duty Truck)	%	Point Est.	-	-	-	-	-	63%
Transport Biofuel (Bulk Terminal-to-Refueling station)	Miles	Point Est.	-	-	-	-	-	30
Coproduct and Scenario Analyiss								
CHP – Heat Conv. Efficiency	(%)	Triangular	-	-	44%	48%	52%	-
CHP – Electrical Conv. Efficiency	(%)	Triangular			20%	35%	25%	
Biochar Carbon Loss	(% C emitted to atm.)	Uniform	-	-	0%	20%	-	-
Transport Biochar (Refinery-to-Farm) via Heavy Duty Truck	Km	Triangular	-	-	50	150	100	-
Diesel Use - Biochar land application	L Diesel ha^{-1}	Triangular	-	-	0.9	4.7	2	-

Table S43. Overview of key parameters and probability distributions

S14. Calculation of EROI and Life Cycle GHG Emissions

Parameter	Symbol	Units	Notes
Biofuel Energy	$E_{biofuel}$	MJ	$(LHV_{biofuel})*(Mass_{biofuel})$
Coproduct Electricity	C_{Elec}	MJ	Based on CHP Electrical conversion efficiency. $C_{Elec} = C_{Elec,Exp} + C_{Elec,Recycle}$
Electricity Export	$C_{Elec,Exp}$	MJ	If Coproduct Electricity (C_{Elec}) exceeds Process Electricity Requirements (P_{Elec}), surplus electricity is exported offsite and displaces the U.S. average electricity mix. Electricity Export $(C_{elec,Exp}) = (C_{Elec}-P_{Elec})$.
Electricity Recycle	$C_{Elec,Recycle}$	MJ	Coproduct electricity that is used onsite to meet process electricity utility, $C_{Elec,Recycle} \leq P_{Elec}$
Coproduct Heat	C_{Heat}	MJ	Based on CHP Heat conversion efficiency. Only usable heat is considered (i.e. $C_{Heat,Recycle} \leq P_{Heat}$).
Process Electricity	P_{Elec}	MJ	Based on Elec. Utility from ASPEN simulation
Process Heat	P_{Heat}	MJ	Based on Heat Duty from ASPEN simulation
Primary Energy Impact Factor - Electricity	$IF_{PE,Elec}$	MJ Primary Fossil Energy/MJ-Electricity	Based on data obtained from life cycle databases
Primary Energy Impact Factor - Heat	$IF_{PE,Heat}$	MJ Primary Fossil Energy/MJ-Heat	Based on data obtained from life cycle databases
Global Warming Potential Impact Factor - Electricity	$IF_{GHG,Elec}$	kg CO_2e./MJ-Electricity	Based on data obtained from life cycle databases
Global Warming Potential Impact Factor - Heat	$IF_{GHG,Heat}$	kg CO_2e./MJ-Heat	Based on data obtained from life cycle databases
Primary fossil energy for all other material, energy, and emissions flows	PE_{Misc}	MJ Primary Fossil Energy	Primary Fossil Energy consumption for all material and energy flows (excluding process heating, electrical utility, and biofuel transport)
Life Cycle GHG emissions for all other material, energy, and emissions flows	GHG_{Misc}	kg CO_2e	Life cycle GHG emissions for all material, energy, and emissions flows (excluding process heating, electrical utility, and biofuel transport)
GHG sequestration from Biochar	GHG_{Char}	kg CO_2e	Based on carbon content (C%) of biochar, as well as fraction of carbon remitted to atm. as CO_2
Life Cycle GHG emissions from Biofuel Transport	$GHG_{Fuel\ Transport}$	kg CO_2e	Life cycle GHG emissions for transporting biofuel to regional fuel facility
Primary Energy	$PE_{Fuel\ Transport}$	MJ Primary Fossil	Primary Energy Consumption for transporting

Consumption from Biofuel Transport	Energy	biofuel to regional fuel facility

Table S44. Key Parameters in the calculation of EROI and Life Cycle GHG Emissions

(23) $EROI_{Disp} = \frac{E_{biofuel}}{[(PE_{Misc})+IF_{PE,Heat}*(P_{Heat}-C_{Heat})+IF_{PE,Elec}*(P_{Elec}-C_{Elec,Recycle})]-[IF_{PE,Elec}*(C_{Elec,Exp})]+PE_{Fuel\,Transport}]}$

(24) $EROI_{Energy\ Alloc} = \frac{E_{biofuel}}{[(PE_{Misc})+IF_{PE,Heat}*(P_{Heat}-C_{Heat})+IF_{PE,Elec}*(P_{Elec}-C_{Elec,Recycle})]*\left[\frac{E_{biofuel}}{E_{biofuel}+C_{Elec,Exp}}\right]+PE_{Fuel\,Transport}}$

(25) $GHG_{Disp,SA} = \frac{[(GHG_{Misc})+IF_{GHG,Heat}*(P_{Heat}-C_{Heat})+IF_{GHG,Elec}*(P_{Elec}-C_{Elec,Recycle})-GHG_{Char}]-[IF_{GHG,Elec}*(C_{Elec,Exp})]+GHG_{Fuel\,Trasport}}{E_{biofuel}}$

(26) $GHG_{Disp,CHP} = \frac{[(GHG_{Misc})+IF_{GHG,Heat}*(P_{Heat}-C_{Heat})+IF_{GHG,Elec}*(P_{Elec}-C_{Elec,Recycle})]-[IF_{GHG,Elec}*(C_{Elec,Exp})]+GHG_{Fuel\,Trasport}}{E_{biofuel}}$

(27) $GHG_{Energy\ Alloc,SA} = \frac{[(GHG_{Misc})+IF_{GHG,Heat}*(P_{Heat}-C_{Heat})+IF_{GHG,Elec}*(P_{Elec}-C_{Elec,Recycle})-GHG_{Char}]*\left[\frac{E_{biofuel}}{E_{biofuel}+C_{Elec,Exp}}\right]+GHG_{Fuel\,Trasport}}{E_{biofuel}}$

(28) $GHG_{Energy\ Alloc,CHP} = \frac{[(GHG_{Misc})+IF_{GHG,Heat}*(P_{Heat}-C_{Heat})+IF_{GHG,Elec}*(P_{Elec}-C_{Elec,Recycle})]*\left[\frac{E_{biofuel}}{E_{biofuel}+C_{Elec,Exp}}\right]+GHG_{Fuel\,Trasport}}{E_{biofuel}}$

SA: Biochar soil amendment pathways; **CHP:** Biochar-CHP pathways

The 10th, 50th, and 90th percentiles for EROI and life cycle GHG emission for renewable fuels produced via Fast Pyrolysis HDO and Multistage Systems are provided in Tables S45 and S46 respectively.

LCA Scheme	Biochar Coproduct Scenario	Fast Pyrolysis HDO	Multistage System 1	Multistage System 2	Multistage System 3
Displacement	Soil Amendment	-	1.66 (1.20,2.10)	1.32 (0.98,1.64)	2.07 (1.48,2.65)
Energy Allocation	Soil Amendment	0.96 (0.67,1.25)	1.66 (1.20,2.10)	1.32 (0.98,1.64)	2.07 (1.48,2.65)
Displacement	Combined Heat & Power	-	2.90 (1.73,4.95)	2.14 (1.36,3.38)	3.76 (2.17,6.51)
Energy Allocation	Combined Heat & Power	1.11 (0.78,1.45)	1.95 (1.38,2.53)	1.50 (1.11,1.88)	2.89 (1.89,4.07)

Results for EROI are tabulated as X (Y,Z) where X=50th Percentile, Y=10th Percentile, Z=90th Percentile

Table S45. Median EROI (MJ-Fuel/MJ-Primary Fossil Energy) for base-case Fast Pyrolysis HDO and Multistage Systems

LCA Scheme	Biochar Coproduct Scenario	Fast Pyrolysis HDO	Multistage System 1	Multistage System 2	Multistage System 3
Displacement	Soil Amendment	-	20 (11,40)	27 (16,49)	17 (10,35)
Energy Allocation	Soil Amendment	52 (35,89)	20 (11,40)	27 (16,49)	17 (10,35)
Displacement	Combined Heat & Power	-	30 (20,50)	38 (26,60)	38 (26,60)
Energy Allocation	Combined Heat & Power	87 (71,120)	42 (35,61)	53 (44,73)	53 (44,73)

Results for Life cycle GHG emissions are tabulated as X (Y,Z) where X=50th Percentile, Y=10th Percentile, Z=90th Percentile

Table S46. Median Life cycle GHG emissions (gCO_2e/MJ-Fuel) for base-case Fast Pyrolysis HDO and Multistage Systems

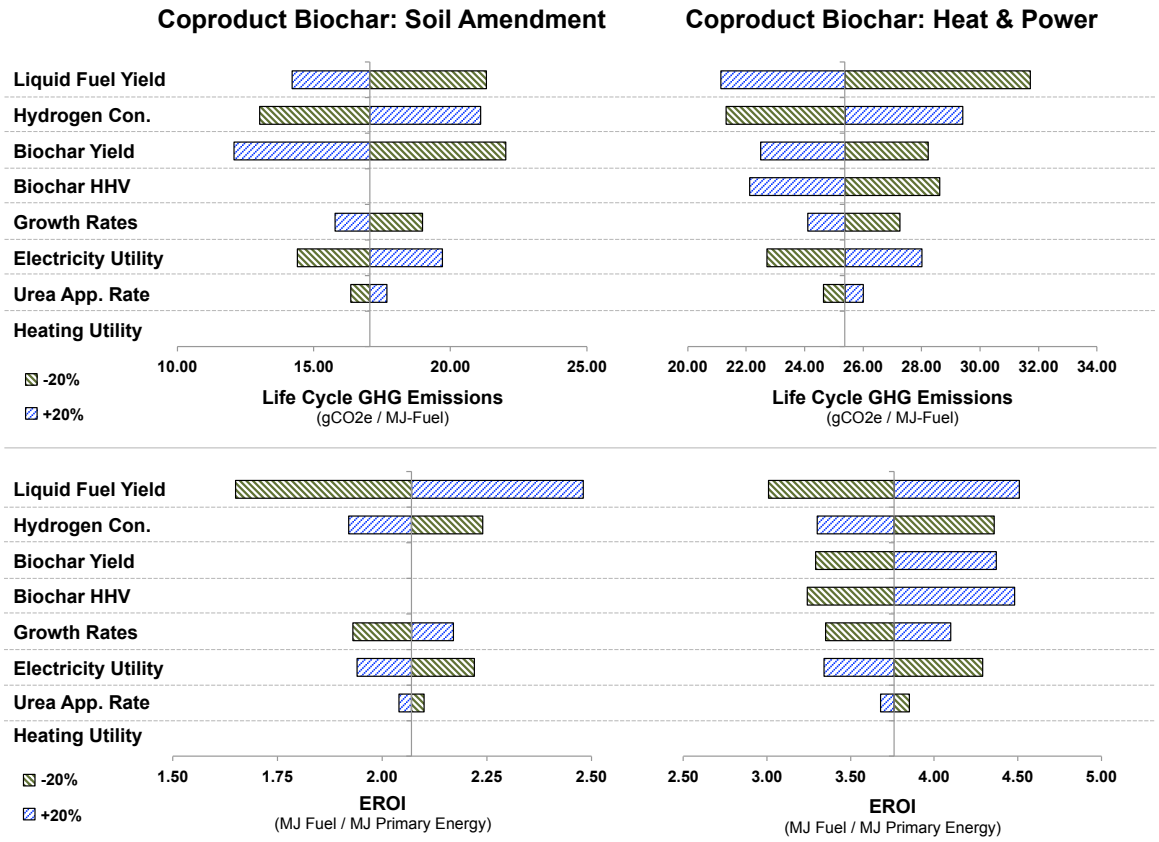

Figure S8. Sensitivity Analysis: Multistage Design Case #3. Tornado plots for median EROI and life-cycle GHG emissions using displacement method are presented.

S15. References

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S16. ASPEN Stream Tables

ASPEN stream summaries for renewable fuel produced via fast pyrolysis and HDO as well as multistage systems are provided in the accompanying excel file, and provide an overview of the material/energy flows, physical properties, and conditions of each of the streams in the ASPEN simulation. An overview of the process designs is provided in Figures S9 to S12.

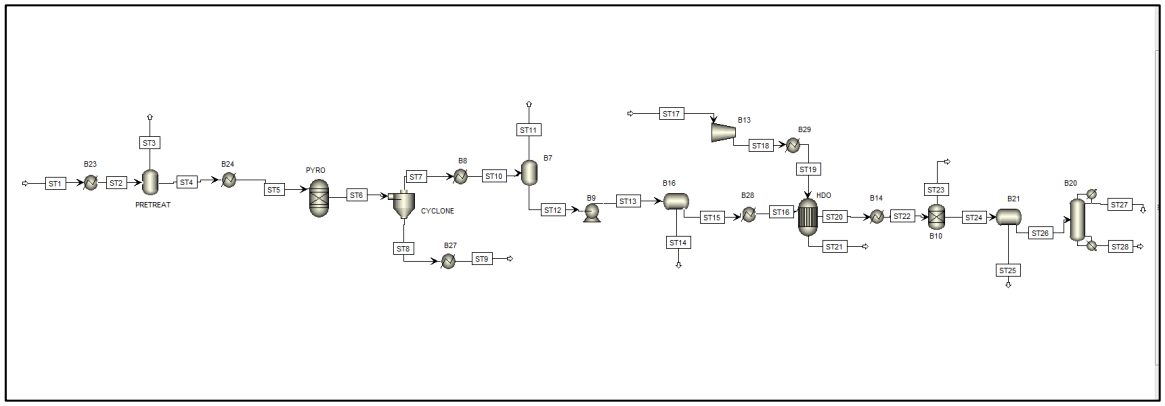

Fig S9. Single Stage Fast Pyrolysis and HDO

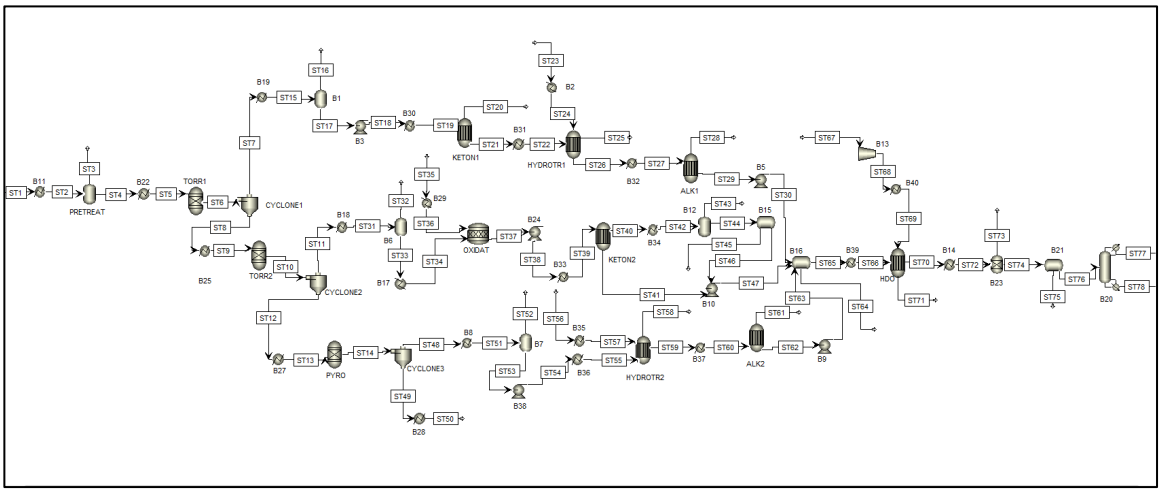

Fig S10. Multistage System 1

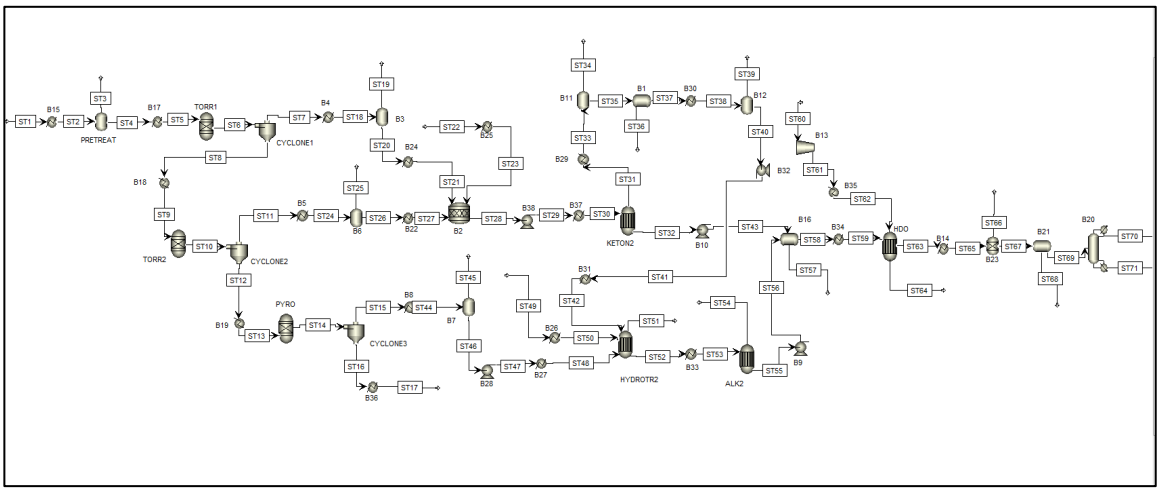

Fig S11. Multistage System 2

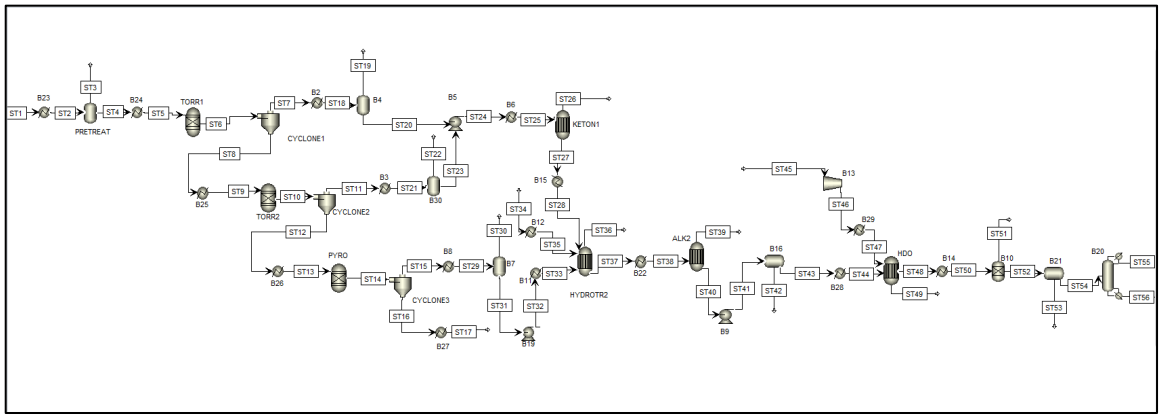

Fig S12. Multistage System 3