Table S1. Variable and Fixed operating costs assumptions

Variable operating costs	**Value**	**Reference**
Materials		
Wood ($/dry ton)	80	[1]
Corncob ($/dry ton)[a]	80	
Lignin Price ($/ metric ton)[b]	120	
Ethanol ($/metric ton)	700	[2]
Natural gas ($/million Btu)	12	[3]
Formic acid cost ($/Metric ton)	1000	[2]
Process water ($/m^3)	0.07	[4]
Boiler feed water chemicals ($/kg)	3	[4]
Ash disposal, ($/metric ton)	20	[4]
Wastewater treatment ($/1000 m^3)	56	[4]
Fixed operating costs		
Labor costs (US$ million/year)	4.2	[4]
Benefits and general overhead	90% of labor costs	[4]
Maintenance	0.25% of fixed capital investment	[4]
Insurance and taxes	0.7% of fixed capital investment	[4]

[a] The corncob cost is assumed to be same as wood price for comparison purposes

[b] The annualized cost of lignin shown in Table S1 has been assessed by assuming that lignin can be sold as a boiler fuel

Table S2: Discounted cash flow analysis assumptions

Parameter	**Assumption**	**Reference**

Cost year analysis	2019	
Plant capacity (dry metric tons of feedstock per day)	2000	[1]
Plant life (years)	30	[1]
Operating days per year[a]	330	[1]
Discount rate	10%	[1]
Income tax rate	35%	[1]
Equity	40%	[1]
Loan interest	8%	[1]
Lona term (years)	10	[1]
Type of Depreciation	MACRS*	[4]
Depreciation period (years)	7	[4]
Plant salvage value	0	[4]
Construction period	3 (8% 1st yr., 61% 2nd yr., 31% 3rd yr.	[1]
Startup time (years)	0.25	[1]
Revenues during startup	50% of normal	[1]
Fixed costs during startup	100% of normal	[1]
Variable costs during startup	75% of normal	[1]

a Plant on stream factor was assumed at 0.9, which is equivalent to 330 operating days.

Table S3: Factors used to assess the total capital investment from total installed costs.

Total Installed Costs (TIC)		**Reference**
1. Prorateable expenses	10.0% of TIC	[5]
2. Field expenses	10.0% of TIC	[5]
3. Home office & construction fee	20.0% of TIC	[5]
4. Project contingency	10.0% of TIC	[5]
5. Other costs (start-up, permits, etc.)	10.0% of TIC	[5]
Total Indirect costs (TI)	=Sum of 1 to 5	
Fixed Capital Investment (FCI)	=TIC + TI	
Land	1% of FCI	[4]
Working Capital (WC)	5% of FCI	[5]
Total Capital Investment (TCI)	= FCI+ Land+ WC	

Table S4: The absolute change in minimum selling price values of C5 and C6 sugar production with formic acid pulping process for a change in the liquid to solid ratio, composition of cellulose and hemicellulose, and lignin price.

Liquid to solid ratio	Absolute MSP value ($/kg)
1	0.14
2	0.17
4	0.22
6	0.27
8	0.31

Composition of cellulose and hemicellulose (%)	Absolute MSP value ($/kg)
39.5	0.58
44.8	0.53
50.2	0.48
60.0	0.41
69.9	0.36
79.8	0.32

Lignin price ($/kg)	Absolute MSP value ($/kg)
0.12	0.33
0.20	0.32
0.25	0.31
0.3	0.30
0.35	0.29
0.40	0.28

Table S5: The absolute change in minimum selling price values of C5 and C6 sugar production with the combined autohydrolysis and Organosolv process for a change in the liquid to solid ratio, composition of cellulose and hemicellulose, and lignin price.

Liquid to solid ratio	Absolute MSP value ($/kg)
1.2	0.29
2.5	0.34
5	0.45
7.5	0.55

Composition of cellulose and hemicellulose (%)	Absolute MSP value ($/kg)
32.8	0.95
49.1	0.80
59.9	0.66
69.9	0.58
80.0	0.52

Lignin price ($/kg)	Absolute MSP value ($/kg)
0.12	0.66
0.15	0.62
0.2	0.6
0.25	0.58
0.3	0.56
0.35	0.53
0.4	0.51

Table S6: Operating conditions and Material balance of the combined autohydrolysis and Organosolv process

Equipment/	Operating conditions	Mass flow in	Mass flow out

Process		(kg/h)	(kg/h)
Autohydrolysis	Temperature (°C): 200 Pressure (barg): 17 Residence time (min): 42	Steam/Water: 647589 Wood: 83333	Hydrolysate: 730922
Evaporator	Heat Duty (MW): 8 Pressure (atm): 0.055	Hydrolysate: 730922	Top vapor (wastewater) flow rate: 277628 Bottom liquid and solid mixture flow rate: 453293 (Xylose and Xylo-oligomers 3.2 wt.%; Xylan 0.5 wt.%; Lignin 5.1 wt.%; Cellulose 8.5 wt.%)
Filtration	Temperature (°C): 40 Pressure (atm): 1	Mixture of cellulose and lignin, C5sugars, and water: 453293	Retentate: Cellulose and lignin solids: 130500 (of which 50 wt.% is moisture) Filtrate: C5 sugars (Xylose 1.4 wt.%; xylan 2.9 wt.%) and water (kg/h): 324793
Multiple Effect Evaporator	Temperature (°C): 40 Pressure (atm): 0.055	C5 sugars and water: 324793	Top vapor (wastewater) flow rate: 157977 Bottom liquid C5 sugar (10 wt.%) and water mixture flow rate: 166815
Organosolv reactor	Temperature (°C): 180 Pressure (barg): 32 Residence time (min): 120	Solids flow in: 130550 Ethanol and water flow: 492566	Hydrolysate: 623116
Evaporator	Heat duty (MW): 0 Pressure (bar): 4	Hydrolysate: 623116	Top vapor (ethanol and water) flow rate) : 227570 Bottom liquid and solid flow rate (kg/h): 395446
Filtration	Temperature (°C): 40 Pressure (atm): 1	Mixture of liquid and solid flow rate: 395446	Cellulose rich solids: 84966 (>90% cellulose) (50 wt.% moisture) Filtrate flow rate: 310480
Distillation	Temperature (°C): 40	Mixture of	Lignin rich bottom solids:

	Pressure (mbar): 1 Number of stages: 3	liquid and solid flow rate**:** 310480	19600 Top condensate flow (ethanol and water) rate: 290880

Table S7: Operating conditions and Material balance of the Formic acid pulping process

Equipment/ Process	Operating conditions	Mass flow in (kg/h)	Mass flow out (kg/h)
Formic acid pulping	Temperature (°C): 60 Pressure (barg): 17 Residence time (min): 150	Formic acid, 733330, HCl: 1666 Water: 98333 Corncob: 83333	Hydrolysate: 916663
Vacuum Evaporator	Temperature (°C): 60 Pressure (bar): 0.24 Heat duty (MW): 8	Hydrolysate: 916663	Top vapor (formic acid, water, HCl) flow rate: 44332 Bottom liquid and solid flow rate: 788998
Filtration	Temperature (°C): 40 Pressure (atm): 1	Mixture of cellulose (4.2 wt.%), lignin (1.72 wt.%), formic acid (87 wt.%), C5 sugars (3.5 wt.%), and water (3.58 wt.%): 788998	Cellulose 68420 (of which 50 wt.% is moisture) Filtrate: C5 sugars, formic acid, lignin, water (kg/h): 720578
Vacuum Evaporator	Temperature (°C): 60 Pressure (atm): 0.1	Total mass flow rate: 720578	Total vapor (formic acid (88 wt.%) and water (12 wt.%)) flow rate: 672912 Total bottom flow rate: 47666 (8.5 wt.% water; 63 wt.% C5 sugars; and 28.5 wt.% lignin)
Distillation	Temperature (°C): 101 Pressure (atm): 1 Number of stages: 15	Total mass flow rate: 672912	Total condensate (formic acid and water) flow rate: 638702 Total wastewater flow rate: 16966
Centrifuge	Temperature (°C): 25 Pressure (atm): 1 RPM: 1000	Water: 415410 C5 sugars: 17159:	Lignin as retentate: 28596 (50 wt.% moisture) Filtrate: 417557

		Lignin: 13584	
Multiple Effect Evaporator	Temperature (°C): 40 Pressure (atm): 0.055	C5 sugars and water: 432569	Top vapor (wastewater) flow rate: 260979 Bottom liquid C5 sugar (100 g/l) and water mixture flow rate: 171590

Reaction schemes employed in RSTOIC reactor model:

In Aspen, cellulose (glucan), hemicellulose (xylan), lignin, and extractives (medium chain fatty acids are selected as a model molecule) are defined as solid compounds. Acetate (used native Aspen component acetic acid) is defined as a conventional compound. The biomass stream is defined in Aspen with mass fractions of cellulose, hemicellulose, lignin, extractives, and acetates specified in the manuscript. While assessing the sensitivity of biomass composition to the minimum selling price, the mass fractions of cellulose and hemicelluloses are varied accordingly.

Autohydrolysis reactor

Xylan + water → Xylose (86% conversion of xylan to xylose)
Acetate → Acetic acid (100% conversion of acetate)

Organosolv reactor

After filtration, the stream predominantly containing cellulose and lignin solids is sent to an Organosolv reactor in which lignin is solubilized in ethanol

Lignin $\xrightarrow{ethanol + Water}$ soluble lignin (90% conversion of lignin) (Please note the soluble lignin is defined as a conventional compound in Aspen assuming the higher heating value of lignin and soluble lignin as same, which is 23, 906 BTU/kg[5])

Cellulose $\xrightarrow{ethanol + Water}$ Cellulose (Please note that the ethanol and water do not participate in the reaction and the mixture only acts as a solvent)

Formic acid pretreatment

Xylan + water $\xrightarrow{Formic\ acid}$ Xylose (40% conversion of xylan)

Xylan + water $\xrightarrow{Formic\ acid}$ Xylose oligomer (60% conversion of xylan) (Assumed the properties of xylose and xylose oligomer are the same)

Acetate $\xrightarrow{Formic\ acid}$ Acetic acid (100% conversion of acetate)

Lignin $\xrightarrow{Formic\ acid}$ soluble lignin (90% conversion of lignin)

(Formic acid acts as an acid catalyst and solvent and therefore do not participate in the reaction)

References

1. Jones, S. et al., 2013. Process Design and Economics for the Conversion of Lignocellulosic Biomass to Hydrocarbon Fuels, PNNL-23053
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4. Towler, G., Sinnott, R., C 2008. Chemical Engineering Design: Principles, Practice, and Economics of Plant and Process Design, Elsevier.
5. Schoen et al., 2011. Process Design and Economics for Biochemical Conversion of Lignocellulosic Biomass to Ethanol, NREL/TP-5100-47764.