Electronic Supplementary Information (ESI)

Life cycle assessment and techno-economic analysis of the utilization of bio-oil components for the production of three chemicals

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1.1 Methodology for estimation of the total-capital investment

Table S1 Methodology for total-capital investment for nth plant

Item	Percent of TDEC
Total purchased equipment-delivered cost	100%
Purchased equipment installation	39%
Instrumentation and controls (installed)	13%
Piping (installed)	31%
Electrical systems (installed)	10%
Buildings (including services)	29%
Yard improvements	10%
Service facilities (installed)	55%
Total installed cost (TIC)	287%
Land (if purchase is required)	6%
Engineering and supervision	32%
Construction expenses	34%
Total direct and indirect plant costs (TDIC)	359%
Contractor's fee (CF)	5% of TDIC
Contingency (CO)	10% of TDIC
Fixed-capital investment (FCI)	TDIC+CF+CO
Working capital	15% of FCI
Total capital investment	475%

The total installed equipment cost is part of the total capital investment. The total capital investment for all processes consists of fixed-capital investment for physical equipment and facilities in the plant plus working capital which must be available to pay salaries, keep raw materials and products on hand, and handle other special items requiring a direct cash outlay. This method for estimating the total-capital investment is based on the percentage of delivered-equipment cost. Namely, the determination of the delivered-equipment cost is required firstly. The other items included in the fixed-capital investment are estimated as percentages of the delivered-equipment cost , and the working capital amounts to 15 percent of the fixed-capital investment.[1] The items included in the total-capital investment and the corresponding ratio factors based on delivered equipment cost are listed in Table S1. Unit process principles are used to determine the equipment specifications,[1, 2] and then the delivered-equipment cost of each piece of the process equipments can be estimated from appropriate manufacturers' bulletins, published cost data, empirical rules[1-3] or e-commerce websites (such as Alibaba) as listed in Table S2.

Table S2 The delivered-equipment cost of each piece of the process equipments

Equipments	Specification	Delivered-equipment cost
Sub 1		
Chopper	50 kw/ton	$44,137
Biomass Chopping Screen	60 ton/day	$3,286
Grinding Hammer Mill	50 kw/ton	$44,137
Biomass Grinding Screen	60 ton/day	$3,359
Belt Press	5.5 kw	$19,425
Bale Moving Forklift*4	1.25 ton/h	$14,021
Concrete Storage Slab	30 m*29 m*3.5 m	$87,631
Discharge Conveyor	0.75 kw/ton	$9,785
Bale Transport Conveyor	90 w/ton	$77,845
Bale Unwrapping Conveyor	5.5 kw	$29,210
Continuous Spray Rotary Drum	2.2 kw, 2.5 ton/h	$185,089
Rotary Dryer	2.2 kw	$99,519
Biomass Feeding Bin	Φ1.5*4.3 m	$6,047
Screw Feeder	0.75 kw/ton	$23,733
Pyrolysis Fluid Bed	Φ1.2 m*2 m	$122,099
Non-condensible Gas Blower	90 kw	$31,357
Pyrolysis Vapor Cyclones*2	3600 m^3 of gas per hour	$184,316
Bio-oil Condenser*2	600 m^2 of heat transfer area	$291,722
Electro-Static Precipitator	30 kw	$42,705
Condenser Water Pump*3	90 kw	$62,527
Ice making machine	53 /kw, 592 kg of ice per hour	$20,000
Condenser Oil Pump	5 kw	$6,952
Cooling Tower	Φ 8.8m*6.5m	$438,898
Wash Percolater	4 m^3	$31,459
Solids Combustor	Φ0.3 m*0.8 m	$35,680
Combustor Cyclones	3360 m^3 of gas per hour	$161,343
Combustion Gas Blower	85 kw	$9,084
Sub 2		
Settling Tank	3 m^3	$35,965
Filter, vacuum rotary drum	3 kw, 600 kg of filtrate /(m^2.h)	$185,089
Vacuum pump	10 kw	$28,655
Settling Tank	3 m^3	$35,965
Filter, vacuum rotary drum	3 kw, 600 kg of filtrate /(m^2.h)	$185,089
Vacuum pump	10 kw	$28,655
Mixer	10 kw, 3m^3	$73,805
Vacuum freeze dryer	130 kw, 1.2 ton water per hour	$365,261
Mixer	10 kw, 3 m^3	$73,805
Filter, vacuum rotary drum	3 kw, 600 kg of filtrate /(m^2.h)	$185,089
Evaporation crystallizer	1000 kg of acetic ether per	$452,879
Settling Tank	3 m^3	$35,965

Filter, vacuum rotary drum	3 kw, 600 kg of filtrate /(m^2.h)	$185,089
Vacuum pump	10 kw	$28,655
Sub 3		
Mixer*2	10 kw, 3 m^3	$147,610
Sub 4		
Evaporator	600 kg of water per hour	$349,285
Mixer	10 kw, 3 m^3	$73,805
Evaporator	600 kg of water per hour	$349,285
Mixer*4	3 kw, 0.8 m^3	$104,268
Filter, vacuum rotary drum*4	3 kw, 75 kg of filtrate /(m^2.h)	$212,611
Vacuum pump*4	10 kw	$114,620
Evaporator*2	50 kg of methanol per hour	$190,110

1.2 Methodology for estimation of the operating cost and direct production cost

Table S3 Variable costs employed in the estimation of the direct production costs (Source: www.alibaba.com and refs). [4-6]

Item	Value
Cotton straw	$83/metric ton
Fertilizer	$400/metric ton
Transport	$0.71/(ton.mile)
Sulfuric acid 98 wt.%	$300/metric ton
Process water	$1.0/metric ton
Activated carbon	$1500/metric ton
Calcium hydroxide	$110/metric ton
Hydrochloric acid 32 wt.%	$190/metric ton
Ethyl acetate	$1200/metric ton
Calcium oxide	$160/metric ton
Methanol	$700/metric ton
Sodium hydroxide	$500/metric ton
Phenol	$1300/metric ton
Formaldehyde 37 wt.%	$400/metric ton
Cooling water from river	$0.15/metric ton
Average hourly wage	$21/h
Electricity	$0.061/kwh
Steam (6 bar)	$20/metric ton
Solids disposal cost	$22.23/metric
Waste water disposal cost	$1.30/metric ton

The operating cost is divided into three classifications as follows: (1) direct production costs, which mainly involve expenditures for raw materials, direct operating labor, supervisory and clerical labor directly connected to the manufacturing operation, utilities, plant maintenance and repairs. Some variable cost parameters, such as the prices of cotton straw, phenol, and utilities, average hourly wage and water treatment cost, are listed on the Table S3; (2) fixed charges, essentially include expenses directly associated with depreciation, property taxes, insurance. Some assumptions for the estimation of fixed charges, such as depreciation period, type of depreciation and property tax rate, are listed on the Table S4; (3) plant-overhead costs, which are used for medical services, warehouses, safety services, warehouses and so on. The estimation of fixed charges and plant-overhead costs can be based on the method of 'Percentage of total-capital investment'.[7] However the estimation of direct production costs is slightly complex. Chemical engineering principles, such as material balance and energy balance, and the methodology proposed by Overcash et.al are used for calculation of the expenditures for raw materials and utilities.[8] The method of estimating labor requirements is based on adding up the various principal processing steps on the flow sheet and plant capacity, and the cost for direct supervisory and clerical labor averages about 15 percent of the cost for operating labor.[1] The method for estimation of the expenditures for plant maintenance and repairs is the same as that for estimation of fixed charges.

Table S4 Assumptions for the estimation of the fixed charges

Item	Value/method
Equipment depreciation period	20 years
Building depreciation period	40 years
Amortization period	5 years
Type of depreciation or amortization	Straight-line
Property tax rate	2% of FCI
Insurance rate	1% of FCI

1.3 Methodology for estimation of cash flow and IRR

Table S5 Assumptions or parameters for the calculation of IRR

Item	Value
Service life	20 years
Construction period	1 years
Income tax rate	39%
Annual capacity in the first year	30%
Annual capacity in the second year	50%
Annual capacity in the third year	80%
Salvage value at end of service life	Working capital+land+salvage value of buildings
Levoglucosan	15$/kg
Renewable phenol resin	2800$/metric ton
Road de-icer	700$/metric ton

The 20-year facility IRR is calculated on the basis of a cash flow sheet in order to perform a profitability evaluation.[1] The determination or estimation of the market prices for the three chemicals is important for calculation of IRR. Levoglucosan is advertised for sale at $1500/kg and $20~90/kg on the carbosynth's Web site and the Alibaba Web site, respectively.[9, 10] The purity of the levoglucosan sold at the carbosynth's Web site is 3% higher than that of the levoglucosan produced via the process. Moreover, from an economic perspective, mass production will lower the cost. Therefore, the price of the levoglucosan produced via the process is set at $15/kg in this analysis. The phenolic resins from America are priced around $4000/ton (¥25.5/kg) on the Guidechem Web site.[11] Considering that about 50wt% of the phenol used in the renewable phenol resin produced via the process is replaced and the phenolic resin is not as good as those phenolic resins based on petrochemical synthesis in quality and performance, the renewable phenol resin was valued at $2800/ton. Food grade calcium acetate is priced at about $1200/ton on the Alibaba Web site.[12] The deicer produced via the process is, at best, an industrial grade mixture of calcium salts. Hence the mixture is pegged at $700/ton. Some necessary parameters for the calculation of the cash flow sheet, such as construction period, income tax rate and product prices, are showed in Table S5.

Moreover, the cash flow sheet also involves so-called general expenses. The general expenses, including research and development, administrative, distribution, marketing expenses etc, are estimated at about 4% of the operating costs per year.[8] The cash flow sheet is listed in Table S6.

Table S6 The cash flow sheet

Year	Annual capacity	Cash flow
0	0	-$26,240,599
1	30%	-$12,199,189
2	50%	$2,381,781
3	80%	$13,413,186
4	100%	$15,232,873
5	100%	$15,232,873
6	100%	$20,350,000
7	100%	$20,350,000
8	100%	$20,350,000
9	100%	$20,350,000
10	100%	$20,350,000
11	100%	$20,350,000
12	100%	$20,350,000
13	100%	$20,350,000
14	100%	$20,350,000
15	100%	$20,350,000
16	100%	$20,350,000

17	100%	\$20,350,000
18	100%	\$20,350,000
19	100%	\$20,350,000
20	100%	\$26,701,958

1.4 The average delivery distance

Since the biorefinery plant is located at the center of a square rural area, where cotton straw is uniformly distributed, the distance traveled by a truck delivering the cotton straw is uncertain and should be a random variable. Therefore, the average transportation distance to this plant, namely the random variable expectation, will be supposed to be the actual distance traveled by trucks delivering all the cotton straw. A formula of computation of the average delivery distance was given by Brown et al, but the deduced method and details of this formula was not provided.[13] We give a following deduced method and steps of this formula.

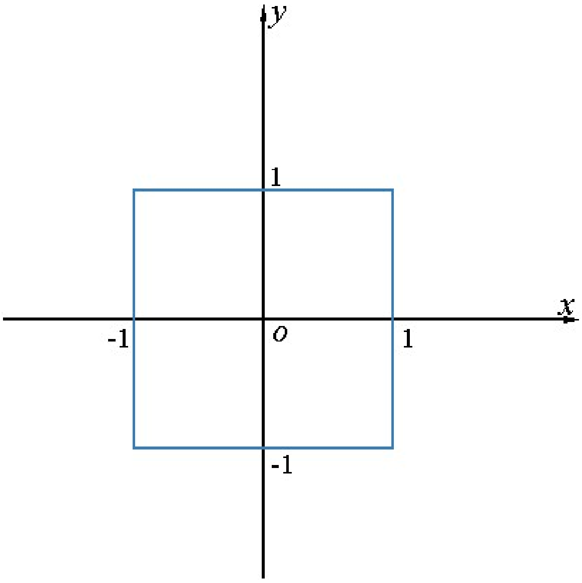

Fig. S1 A square with a side of length 2

Firstly, if F is the feedstock delivered annually to the plant, Y is the annual yield of cotton straw and f is the fraction of the acreage around the plant devoted to feedstock production, the square rural area should has a side of length $(F/(Y*f))^{0.5}$. Suppose that the average distance from a random point in the square to the center of the square is r_{ave} if the horizontal and vertical ordinate of the point all follow U (-1, 1).

Secondly, a square with a side of length 2 is considered as depicted in Fig. S1.

The average distance from a random point in the square to the center of the square (I) can be calculated as following if the horizontal and vertical ordinate of the point all follow U (-1, 1):

$$I = \int_{-1}^{1}\int_{-1}^{1}\sqrt{x^2+y^2} * \frac{1}{2} * \frac{1}{2} dxdy = \int_{0}^{1}\int_{0}^{1}\sqrt{x^2+y^2}\,dxdy$$

$$Let:\ x = r\cos\varphi, \mathrm{y} = \sin\varphi$$

$$So:$$

$$I = \int_{0}^{\frac{\pi}{4}} d\varphi \int_{0}^{\sec\varphi} r^2 dr + \int_{\frac{\pi}{4}}^{\frac{\pi}{2}} d\varphi \int_{0}^{\csc\varphi} r^2 dr$$

$$I = \frac{1}{3}(\sqrt{2} + Ln(1+\sqrt{2}))$$

Finally, the two squares are similar.

$$Q\frac{r_{ave}}{I}=\frac{\sqrt{\frac{F}{Yf}}}{2}$$

$$\therefore r_{ave}=\frac{1}{6}\sqrt{\frac{F}{Yf}}(\sqrt{2}+Ln(1+\sqrt{2}))$$

A ‘tortuosity factor’ τ is defined as the ratio of actual distance to the straight-line distance from the plant. Therefore, the average delivery distance, which is expressed as r_{square} in this following formula, should be:

$$r_{square}=\frac{1}{6}\tau\sqrt{\frac{F}{Yf}}(\sqrt{2}+Ln(1+\sqrt{2}))$$

In this study, F, Y, f and τ are assumed to be 18000 ton/year, 5 ton/acre per year, 60% and 1.5, respectively. Therefore, the average delivery distance is 1.76 miles.

2 Investment and production cost

2.1 The investment

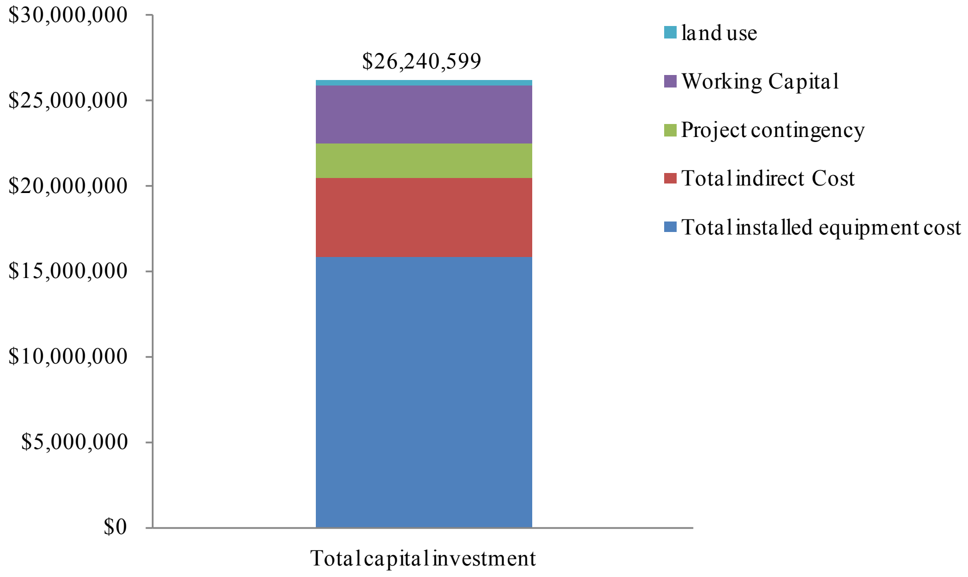

Fig. S2 Total capital investment of the process

As showed in Fig. S2, which represents total capital investment as the summation of total installed equipment cost, total indirect cost, project contingency, working capital cost, and land use, the total capital investment for the biorefinery process amounts to \$26.2 million, while the total installed equipment cost of the whole process is \$15.7 million. Such a scale of investment is one order smaller than the investment scale of biofuel plants.[5, 14, 15] However, Chemicals have normally higher added value than fuels. And this allows chemical plants can be operated with smaller scale of economies than fuel plants when the two kinds of plants have the same profit margin. Since the biorefinery process consists of four sub-processes, it is important to know the percentage of the total installed equipment cost for each sub-process.

Fig. S3 shows the relative weightings (percentage) of the four sub-processes represented in the total installed equipment cost of the whole process. Bio-oil preparation and separation (sub 1), extraction of levoglucosan (sub 2) and preparation of deicer (sub 4) separately contribute 38%, 34% and 25% of the total installed equipment cost, respectively. The really amazing thing about this figure is that production of renewable phenol resin (sub 3) is the smallest (only 3%) contributor to the total installed equipment cost. The reason is that the production of renewable phenol resin requires a minimum number of unit operations or equipments in comparison with other three sub-processes. From an economic point of view, the sub-process 4, the preparation of deicer, seemingly is not feasible or cost-effective because the total installed cost for the sub-process 4 accounts for 25% of the total but the selling price (\$700/ton) and the production rate (37kg/h) of the deicer are all comparatively low. On the other hand, it can be expected that the extraction of levoglucosan and the production of renewable phenol resin are all cost-effective because levoglucosan is a high added-value product and the production of renewable phenol resin needs relatively small equipment investment.

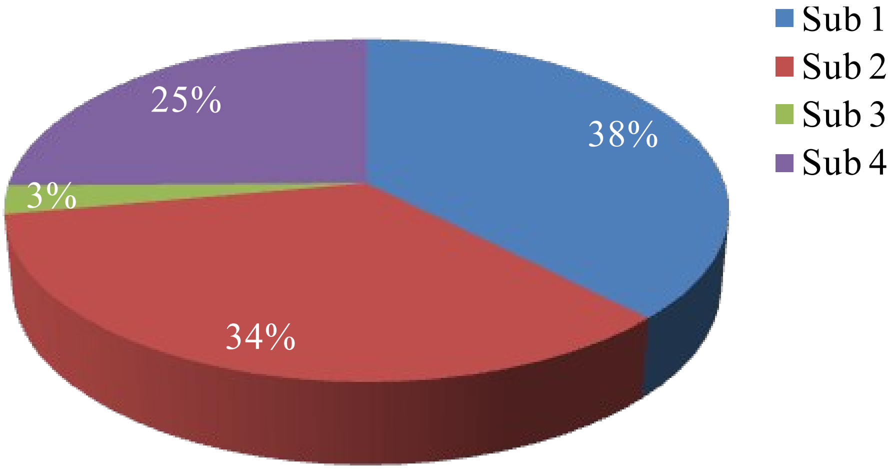

Fig. S3 The percentage of the total installed equipment cost for each sub-process

2.2 The production cost

Determination of the necessary capital investment is only one part of a complete cost estimate. Another equally important part is the estimation of costs for operating the plant or process. Fig. S4 shows the annual direct production costs for cotton straw to levoglucosan, renewable phenol resin and deicer. Similar to Fig. S3, the direct production cost of the whole process is breakdown to each sub-process area in Fig. S4.

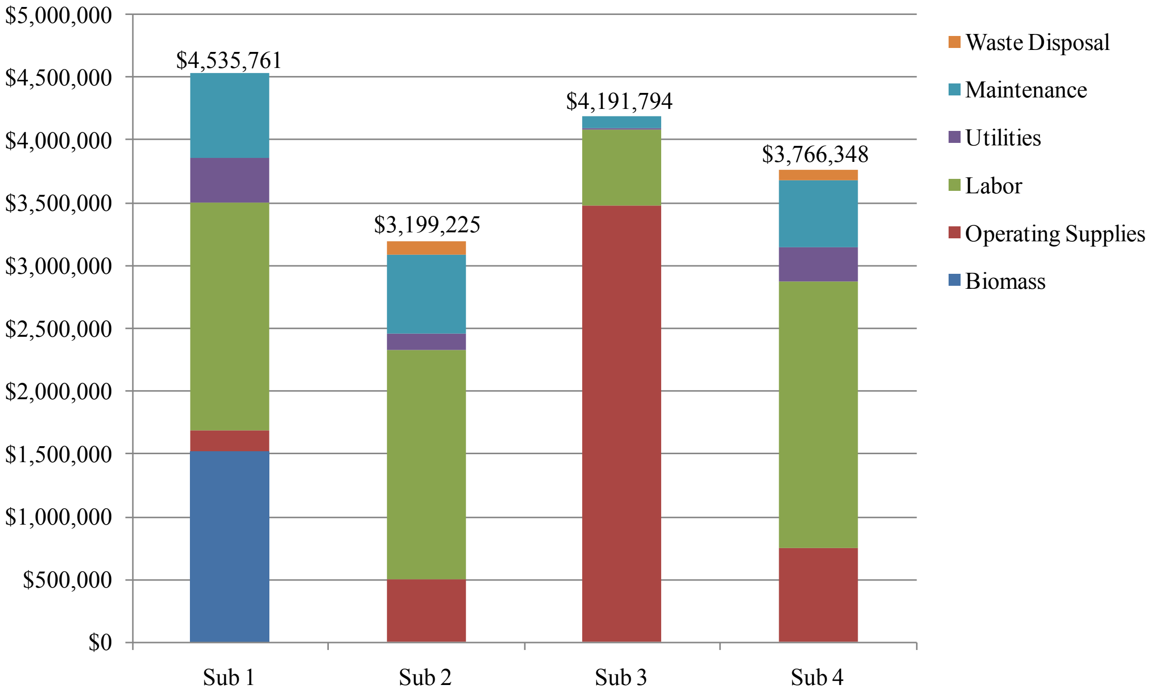

Fig. S4 The annual direct production costs

The direct production costs of the four sub-processes vary from around $3.2 million/year to $4.5 million/year, and total up to $15.7 million/year. There is not much difference between the annual direct production cost of sub 4 (preparation of deicer) and the annual direct production cost of sub 2 (extraction of levoglucosan) or sub 3 (production of renewable phenol resin). However, in consideration of the yearly outputs and product prices of the three chemicals, it can be also inferred that sub 4 (preparation of deicer) is not cost-effective. The labor costs of sub 1 (bio-oil preparation and separation), 2 (extraction of levoglucosan) and 4 (preparation of deicer) are the largest contributors to the annual direct production costs of the three sub-processes, respectively. This is because each of the three sub-processes contains quite a number of unit operations or equipments, which require a number of operating labor and a certain amount of direct supervisory and clerical labor for operation. On the basis of the same reason, the maintenance costs of the three sub-processes account for the certain proportion of the annual direct production costs of the three sub-processes. The operating supplies of sub 3 (production of renewable phenol resin) comprise the vast majority of the annual direct production cost of this sub-process because a substantial number of phenol and formaldehyde are used in the sub-process. Direct production cost is only part of operating cost. The operating cost includes all expenses directly connected with the manufacturing operation or the physical equipment of a process plant itself. However, unlike direct production cost, operating cost is not appropriate for being breakdown to process area because it includes plant-overhead costs, which are reserved for hospital and medical services, safety services, salvage services and warehouse facilities, etc.

As shown in Fig. S5, the operating cost of the whole process is around $22.2 million/year. The annual direct production cost, fixed charge and plant-overhead cost of the whole process account for about 71%, 12% and 17% of the operating cost, respectively. These percents are basically similar to other techno-economic analyses of some biorefinery processes via fast paralysis.[5, 6] However, the labor cost of the whole process occupies about 29% of the operating cost; In comparison with production of biofuels,[5, 6, 15] this percent is remarkably higher. There could be three reasons to explain this. Firstly, production of chemicals usually needs more purification steps or equipments than production of fuels. Secondly, not one chemical but three chemicals are produced in this birefinery process. Finally, mass production of biofuels usually is a continuous process, while the production of the three chemicals contains some batch steps. These reasons could result in more labor requirement in this birefinery process.

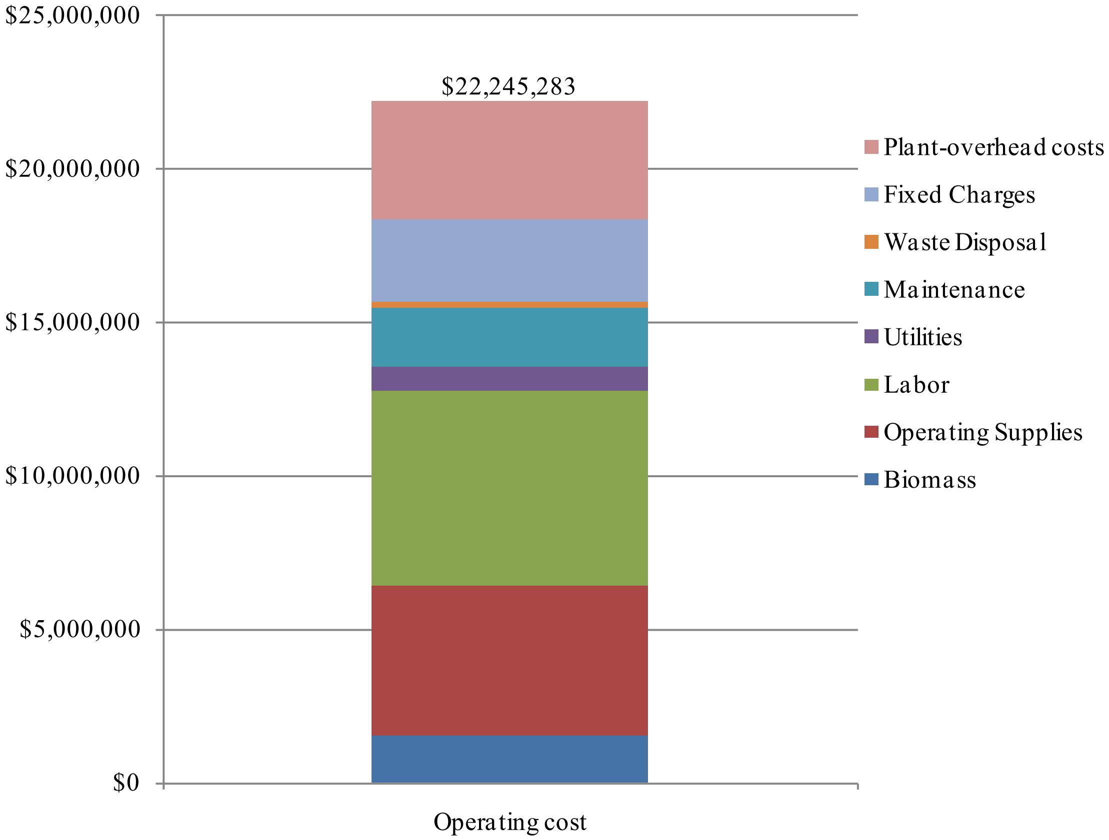

Fig. S5 The operating cost of the whole process

3 Some background data for this LCA study

3.1 LCI data for petrochemical production of phenol - formaldehyde resins (PF)

Wilson et al. has developed an life-cycle inventory of formaldehyde-base resins used in wood composites in terms of resources, emissions, energy and carbon.[16] The LCI for the production of PF is shown in Table S7, in which the environmental burdens of the delivery of chemicals to the resin plants are ignored.

Table S7 LCI data for conventional PF production route

Materials, Energy and Emissions	Value	Units
Phenol	2.44E-01	kg /kg_{PF}
Methanol	2.09E-01	kg /kg_{PF}
Sodium hydroxide	6.10E-02	kg /kg_{PF}
Process water	3.34E-01	kg /kg_{PF}
Cooling water from river (20℃)	1.56E-02	kg /kg_{PF}
Electricity	3.56E-02	kWh /kg_{PF}
Natural gas	8.21E-03	Nm^3 /kg_{PF}
Propane	2.93E-06	L /kg_{PF}
Carbon dioxide	1.76E-02	kg /kg_{PF}
Carbon monoxide	3.81E-05	kg /kg_{PF}

3.2 LCI data for petrochemical production of calcium acetate

Overcash et al has presented gate-to-gate process energy use for a calcium acetate manufacturing process, in which calcium hydroxide and acetic acid were used as raw materials.[17] On the basis of the work of Overcash et al, LCI data for petrochemical production of calcium acetate is shown in Table S8.

Table S8 LCI data for petrochemical production of calcium acetate

Materials, Energy and Emissions	Value	Units
Calcium hydroxide	4.69E-01	kg /$kg_{\text{Calcium acetate}}$
Acetic acid	7.59E-01	kg /$kg_{\text{Calcium acetate}}$
Steam (6bar)	1.53E+00	MJ /$kg_{\text{Calcium acetate}}$
Electricity	1.05E-03	MJ /$kg_{\text{Calcium acetate}}$
Natural gas	9.32E-01	MJ /$kg_{\text{Calcium acetate}}$
Carbon dioxide	5.22E-02	kg /$kg_{\text{Calcium acetate}}$

3.3 The GWP100a, CED, EI-99 metric for some chemicals and utilities

Cradle-to-gate LCIA results according to the GWP100a, CED, EI-99 metric for some chemicals and utilities used in this process are listed in Table S9. All the data is mainly based on ecoinvent 2.2 database, and a few of the data is derived from some LCA documents. These LCA documents are listed in the last row in Table S9.

Table S9 The GWP100a, CED, EI-99 metric for some chemicals and utilities

Substance	GWP100a ($kg_{CO2\text{-}eq}$/kg)	$CED_{non\text{-}renewable}$ (MJ_{eq}/kg)	EI-99 (Points/kg)
Materials			
Fertilizer [a]	1.66E+00	2.93E+01	1.66E-01
Sulfuric acid (98 wt. %)	1.20E-01	2.02E+00	4.00E-02
Process water	2.45E-05	2.79E-04	1.83E-06
Activated carbon [b]	2.94E-01	5.92E+00	1.76E-02
Calcium hydroxide	9.90E-01	5.50E+00	3.00E-02
Hydrochloric acid (32 wt. %)	8.53E-01	1.75E+01	6.00E-02
Ethyl acetate [c]	3.14E+00	9.63E+01	3.36E-01
Sodium hydroxide	1.10E+00	2.14E+01	6.00E-01
Phenol	3.48E+00	1.21E+02	4.40E-01
Formaldehyde (37 wt.%) [c]	4.14E-01	1.82E+01	6.25E-02
Calcium oxide [d]	1.31E+00	7.30E+00	2.80E-02
Methanol [c]	7.64E-01	4.08E+01	1.35E-01
Energy			
Diesel [e]	1.29E-02	1.20E+00	6.43E-03
Electricity [e]	4.90E-01	9.87E+00	2.00E-02
Steam (6 bar) [e]	1.00E-01	1.56E+00	5.77E-03
Cooling water from river (20℃)	0.00E+00	0.00E+00	0.00E+00
Waste treatment			
Waste liquid [f]	2.19E-02	2.42E-01	5.00E-04
Solid waste [f]	1.34E-02	6.52E-01	4.22E-02

[a] Values based on the work of Hasler et al.[18]

[b] Values based on the work of Arena et al.[19]

[c] Values based on the work of Amelio et al.[20]

[d] Values based on the works of Huijbregts et al. and Alvarez-Gaitan et al.[21, 22]

[e] Functional unit for diesel as well as steam is MJ and for electricity kWh

[f] Values based on the works of Rerat et al.[23]

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Bale Moving Forklift*4	1.25 ton/h	$14,021
Concrete Storage Slab	30 m*29 m*3.5 m	$87,631
Discharge Conveyor	0.75 kw/ton	$9,785
Bale Transport Conveyor	90 w/ton	$77,845
Bale Unwrapping Conveyor	5.5 kw	$29,210
Continuous Spray Rotary Drum	2.2 kw, 2.5 ton/h	$185,089
Rotary Dryer	2.2 kw	$99,519
Biomass Feeding Bin	Φ1.5*4.3 m	$6,047
Screw Feeder	0.75 kw/ton	$23,733
Pyrolysis Fluid Bed	Φ1.2 m*2 m	$122,099
Non-condensible Gas Blower	90 kw	$31,357
Pyrolysis Vapor Cyclones*2	3600 m^3 of gas per hour	$184,316
Bio-oil Condenser*2	600 m^2 of heat transfer area	$291,722
Electro-Static Precipitator	30 kw	$42,705
Condenser Water Pump*3	90 kw	$62,527
Ice making machine	53 /kw, 592 kg of ice per hour	$20,000
Condenser Oil Pump	5 kw	$6,952
Cooling Tower	Φ 8.8m*6.5m	$438,898
Wash Percolater	4 m^3	$31,459
Solids Combustor	Φ0.3 m*0.8 m	$35,680
Combustor Cyclones	3360 m^3 of gas per hour	$161,343
Combustion Gas Blower	85 kw	$9,084
Sub 2		
Settling Tank	3 m^3	$35,965
Filter, vacuum rotary drum	3 kw, 600 kg of filtrate /(m^2.h)	$185,089
Vacuum pump	10 kw	$28,655
Settling Tank	3 m^3	$35,965
Filter, vacuum rotary drum	3 kw, 600 kg of filtrate /(m^2.h)	$185,089
Vacuum pump	10 kw	$28,655
Mixer	10 kw, 3m^3	$73,805
Vaccum freeze dryer	130 kw, 1.2 ton water per hour	$365,261
Mixer	10 kw, 3 m^3	$73,805
Filter, vacuum rotary drum	3 kw, 600 kg of filtrate /(m^2.h)	$185,089
Evaporation crystallizer	1000 kg of acetic ether per	$452,879
Settling Tank	3 m^3	$35,965

Filter, vacuum rotary drum	3 kw, 600 kg of filtrate /(m^2.h)	$185,089
Vacuum pump	10 kw	$28,655
Sub 3		
Mixer*2	10 kw, 3 m^3	$147,610
Sub 4		
Evaporator	600 kg of water per hour	$349,285
Mixer	10 kw, 3 m^3	$73,805
Evaporator	600 kg of water per hour	$349,285
Mixer*4	3 kw, 0.8 m^3	$104,268
Filter, vacuum rotary drum*4	3 kw, 75 kg of filtrate /(m^2.h)	$212,611
Vacuum pump*4	10 kw	$114,620
Evaporator*2	50 kg of methanol per hour	$190,110

4.2 Methodology for estimation of the operating cost and direct production cost

Table S3 Variable costs employed in the estimation of the direct production costs (Source: www.alibaba.com and refs). [6-8]

Item	Value
Cotton straw	$83/metric ton
Transport	$0.71/(ton.mile)
Sulfuric acid 98 wt.%	$300/metric ton
Process water	$1.0/metric ton
Activated carbon	$1500/metric ton
Calcium hydroxide	$110/metric ton
Hydrochloric acid 32 wt.%	$190/metric ton
Ethyl acetate	$1200/metric ton
Calcium oxide	$160/metric ton
Methanol	$700/metric ton
Sodium hydroxide	$500/metric ton
Phenol	$1300/metric ton
Formaldehyde 37 wt.%	$400/metric ton
Cooling water from river	$0.15/metric ton
Average hourly wage	$21/h
Electricity	$0.061/kwh
Steam (6 bar)	$20/metric ton
Solids disposal cost	$22.23/metric
Waste water disposal cost	$1.30/metric ton

The operating cost is divided into three classifications as follows: (1) direct production costs, which mainly involve expenditures for raw materials, direct operating labor, supervisory and clerical labor directly connected to the manufacturing operation, utilities, plant maintenance and repairs. Some variable cost parameters, such as the prices of cotton straw, phenol, and utilities, average hourly wage and water treatment cost, are listed on the Table S3；(2) fixed charges, essentially include expenses directly associated with depreciation, property taxes, insurance. Some assumptions for the estimation of fixed charges, such as depreciation period, type of depreciation and property tax rate, are listed on the Table S4；(3) plant-overhead costs, which are used for medical services, warehouses, safety services, warehouses and so on. The estimation of fixed charges and plant-overhead costs can be based on the method of 'Percentage of total-capital investment'.[4] However the estimation of direct production costs is slightly complex. Chemical engineering principles, such as material balance and energy balance, and the methodology proposed by Overcash et.al are used for calculation of the expenditures for raw materials and utilities.[5] The method of estimating labor requirements is based on adding up the various principal processing steps on the flow sheet and plant capacity, and the cost for direct supervisory and clerical labor averages about 15 percent of the cost for operating labor.[1] The method for estimation of the expenditures for plant maintenance and repairs is the same as that for estimation of fixed charges.

Table S4 Assumptions for the estimation of the fixed charges

Item	Value/method
Equipment depreciation period	20 years
Building depreciation period	40 years
Amortization period	5 years
Type of depreciation or amortization	Straight-line
Property tax rate	2% of FCI
Insurance rate	1% of FCI

4.3 Methodology for estimation of the operating cost and direct production cost

Table S5 Assumptions or parameters for the calculation of IRR

Item	Value
Service life	20 years
Construction period	1 years
Income tax rate	39%
Annual capacity in the first year	30%
Annual capacity in the second year	50%
Annual capacity in the third year	80%
Salvage value at end of service life	Working capital+land+salvage value of buildings
Levoglucosan	15$/kg
Renewable phenol resin	2800$/metric ton
Road de-icer	700$/metric ton

The 20-year facility IRR is calculated on the basis of a cash flow sheet in order to perform a profitability evaluation.[1] The determination or estimation of the market prices for the three chemicals is important for calculation of IRR. Levoglucosan is advertised for sale at \$1500/kg and \$20~90/kg on the carbosynth's Web site and the Alibaba Web site, respectively.[9, 10] The purity of the levoglucosan sold at the carbosynth's Web site is 3% higher than that of the levoglucosan produced via the process. Moreover, from an economic perspective, mass production will lower the cost. Therefore, the price of the levoglucosan produced via the process is set at \$15/kg in this analysis. The phenolic resins from America are priced around \$4000/ton (¥25.5/kg) on the Guidechem Web site.[11] Considering that about 50wt% of the phenol used in the renewable phenol resin produced via the process is replaced and the phenolic resin is not as good as those phenolic resins based on petrochemical synthesis in quality and performance, the renewable phenol resin was valued at \$2800/ton. Food grade calcium acetate is priced at about \$1200/ton on the Alibaba Web site.[12] The deicer produced via the process is, at best, an industrial grade mixture of calcium salts. Hence the mixture is pegged at \$700/ton. Some necessary parameters for the calculation of the cash flow sheet, such as construction period, income tax rate and product prices, are showed in Table S5.

Moreover, the cash flow sheet also involves so-called general expenses. The general expenses, including research and development, administrative, distribution, marketing expenses etc, are estimated at about 4% of the operating costs per year.[5] The cash flow sheet is listed in Table S6.

Table S6 The cash flow sheet

Year	Annual capacity	Cash flow
0	0	-\$26,240,599
1	30%	-\$12,199,189
2	50%	\$2,381,781
3	80%	\$13,413,186
4	100%	\$15,232,873
5	100%	\$15,232,873
6	100%	\$20,350,000
7	100%	\$20,350,000
8	100%	\$20,350,000
9	100%	\$20,350,000
10	100%	\$20,350,000
11	100%	\$20,350,000
12	100%	\$20,350,000
13	100%	\$20,350,000
14	100%	\$20,350,000
15	100%	\$20,350,000
16	100%	\$20,350,000

17	100%	$20,350,000
18	100%	$20,350,000
19	100%	$20,350,000
20	100%	$26,701,958

4.4 The average delivery distance

Since the biorefinery plant is located at the center of a square rural area, where cotton straw is uniformly distributed, the distance traveled by a truck delivering the cotton straw is uncertain and should be a random variable. Therefore, the average transportation distance to this plant, namely the random variable expectation, will be supposed to be the actual distance traveled by trucks delivering all the cotton straw. A formula of computation of the average delivery distance was given by Brown et al, but the deduced method and details of this formula was not provided.[13] We give a following deduced method and steps of this formula.

Fig. S1 A square with a side of length 2

Firstly, if F is the feedstock delivered annually to the plant, Y is the annual yield of cotton straw and f is the fraction of the acreage around the plant devoted to feedstock production, the square rural area should has a side of length $(F/(Y*f))^{0.5}$. Suppose that the average distance from a random point in the square to the center of the square is r_{ave} if the horizontal and vertical ordinate of the point all follow U (-1, 1).

Secondly, a square with a side of length 2 is considered as depicted in Fig. S1.

The average distance from a random point in the square to the center of the square (I) can be calculated as following if the horizontal and vertical ordinate of the point all follow U (-1, 1):

$$I=\int_{-1}^{1}\int_{-1}^{1}\sqrt{x^2+y^2}*\frac{1}{2}*\frac{1}{2}dxdy=\int_{0}^{1}\int_{0}^{1}\sqrt{x^2+y^2}dxdy$$

$$Let:\ x=r\cos\varphi,\mathrm{y}=\sin\varphi$$

$$So:$$

$$I=\int_{0}^{\frac{\pi}{4}}d\varphi\int_{0}^{\sec\varphi}r^2dr+\int_{\frac{\pi}{4}}^{\frac{\pi}{2}}d\varphi\int_{0}^{\csc\varphi}r^2dr$$

$$I=\frac{1}{3}(\sqrt{2}+Ln(1+\sqrt{2}))$$

Finally, the two squares are similar.

$$\because \frac{r_{ave}}{I} = \frac{\sqrt{\frac{F}{Yf}}}{2}$$

$$\therefore r_{ave} = \frac{1}{6}\sqrt{\frac{F}{Yf}}(\sqrt{2} + Ln(1+\sqrt{2}))$$

A 'tortuosity factor' τ is defined as the ratio of actual distance to the straight-line distance from the plant. Therefore, the average delivery distance, which is expressed as r_{square} in this following formula, should be:

$$r_{square} = \frac{1}{6}\tau\sqrt{\frac{F}{Yf}}(\sqrt{2} + Ln(1+\sqrt{2}))$$

In this study, F, Y, f and τ are assumed to be 18000 ton/year, 5 ton/acre per year, 60% and 1.5, respectively. Therefore, the average delivery distance is 1.76 miles.

5 Investment and production cost

5.1 The investment

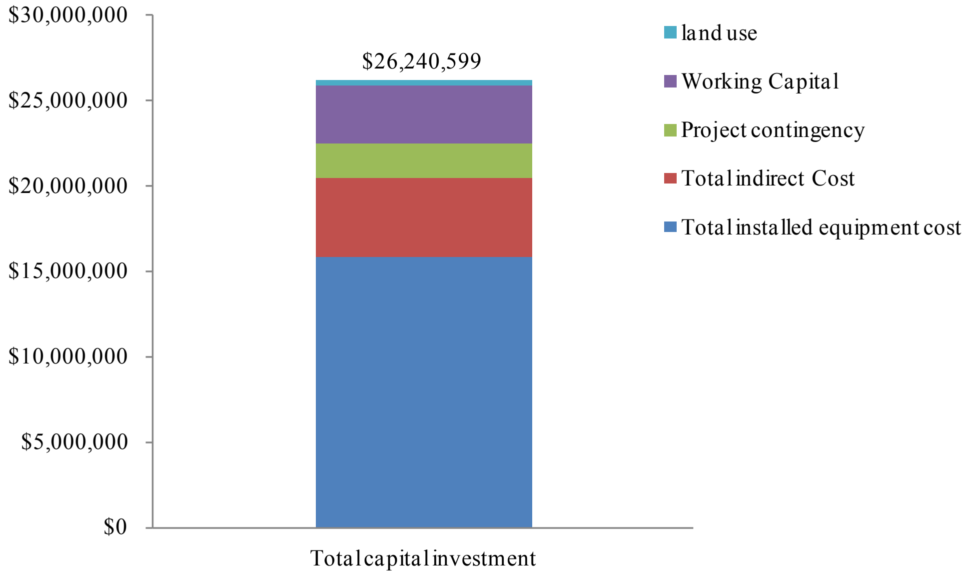

Fig. S2 Total capital investment of the process

As showed in Fig. S2, which represents total capital investment as the summation of total installed equipment cost, total indirect cost, project contingency, working capital cost, and land use, the total capital investment for the biorefinery process amounts to \$26.2 million, while the total installed equipment cost of the whole process is \$15.7 million. Such a scale of investment is one order smaller than the investment scale of biofuel plants.[7, 14, 15] However, Chemicals have normally higher added value than fuels. And this allows chemical plants can be operated with smaller scale of economies than fuel plants when the two kinds of plants have the same profit margin. Since the biorefinery process consists of four sub-processes, it is important to know the percentage of the total installed equipment cost for each sub-process.

Fig. S3 shows the relative weightings (percentage) of the four sub-processes represented in the total installed equipment cost of the whole process. Bio-oil preparation and separation (sub 1), extraction of levoglucosan (sub 2) and preparation of deicer (sub 4) separately contribute 38%, 34% and 25% of the total installed equipment cost, respectively. The really amazing thing about this figure is that production of renewable phenol resin (sub 3) is the smallest (only 3%) contributor to the total installed equipment cost. The reason is that the production of renewable phenol resin requires a minimum number of unit operations or equipments in comparison with other three sub-processes. From an economic point of view, the sub-process 4, the preparation of deicer, seemingly is not feasible or cost-effective because the total installed cost for the sub-process 4 accounts for 25% of the total but the selling price (\$700/ton) and the production rate (37kg/h) of the deicer are all comparatively low. On the other hand, it can be expected that the extraction of levoglucosan and the production of renewable phenol resin are all cost-effective because levoglucosan is a high added-value product and the production of renewable phenol resin needs relatively small equipment investment.

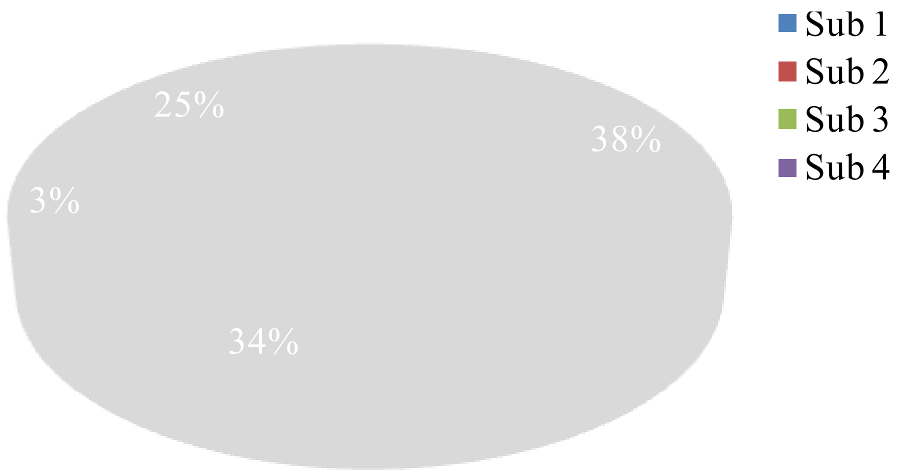

Fig. S3 The percentage of the total installed equipment cost for each sub-process

5.2 The production cost

Determination of the necessary capital investment is only one part of a complete cost estimate. Another equally important part is the estimation of costs for operating the plant or process. Fig. S4 shows the annual direct production costs for cotton straw to levoglucosan, renewable phenol resin and deicer. Similar to Fig. S3, the direct production cost of the whole process is breakdown to each sub-process area in Fig. S4.

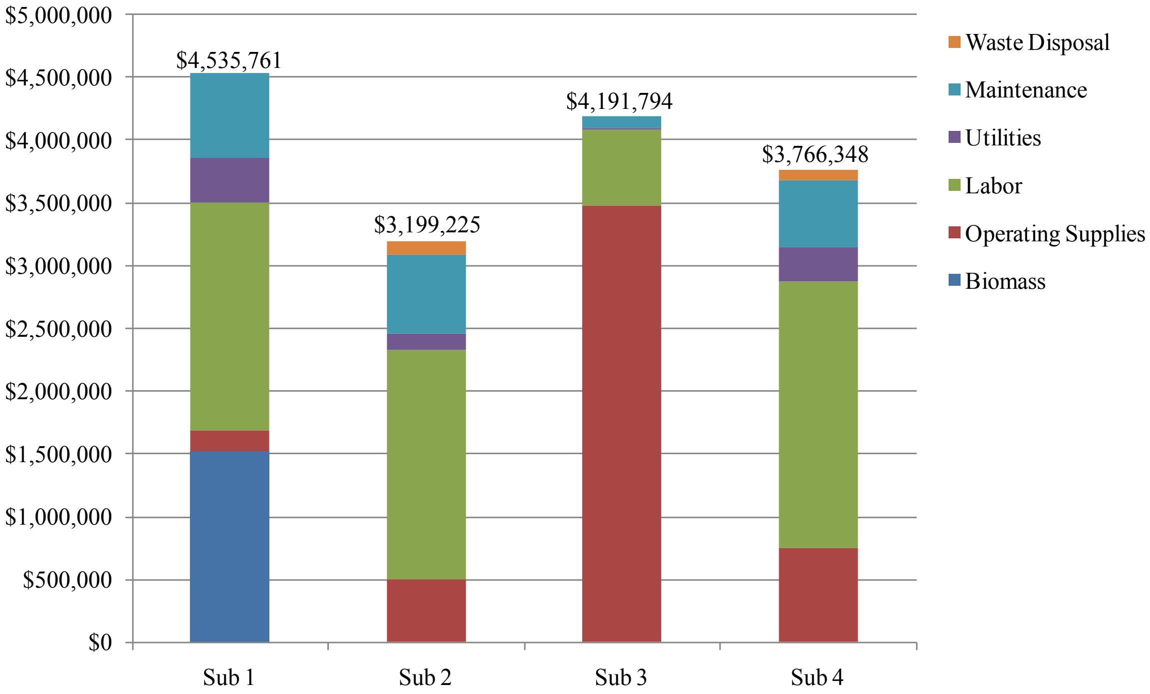

Fig. S4 The annual direct production costs

The direct production costs of the four sub-processes vary from around $3.2 million/year to $4.5 million/year, and total up to $15.7 million/year. There is not much difference between the annual direct production cost of sub 4 (preparation of deicer) and the annual direct production cost of sub 2 (extraction of levoglucosan) or sub 3 (production of renewable phenol resin). However, in consideration of the yearly outputs and product prices of the three chemicals, it can be also inferred that sub 4 (preparation of deicer) is not cost-effective. The labor costs of sub 1 (bio-oil preparation and separation), 2 (extraction of levoglucosan) and 4 (preparation of deicer) are the largest contributors to the annual direct production costs of the three sub-processes, respectively. This is because each of the three sub-processes contains quite a number of unit operations or equipments, which require a number of operating labor and a certain amount of direct supervisory and clerical labor for operation. On the basis of the same reason, the maintenance costs of the three sub-processes account for the certain proportion of the annual direct production costs of the three sub-processes. The operating supplies of sub 3 (production of renewable phenol resin) comprise the vast majority of the annual direct production cost of this sub-process because a substantial number of phenol and formaldehyde are used in the sub-process. Direct production cost is only part of operating cost. The operating cost include all expenses directly connected with the manufacturing operation or the physical equipment of a process plant itself. However, unlike direct production cost, operating cost is not appropriate for being breakdown to process area because it includes plant-overhead costs, which are reserved for hospital and medical services, safety services, salvage services and warehouse facilities, etc.

As shown in Fig. S5, the operating cost of the whole process is around \$22.2 million/year. The annual direct production cost, fixed charge and plant-overhead cost of the whole process account for about 71%, 12% and 17% of the operating cost, respectively. These percents are basically similar to other techno-economic analyses of some biorefinery processes via fast paralysis.[7, 8] However, the labor cost of the whole process occupies about 29% of the operating cost; In comparison with prodcution of biofuels,[7, 8, 15] this percent is remarkably higher. There could be three reasons to explain this. Firstly, production of chemicals usually needs more purification steps or equipments than production of fuels. Secondly, not one chemical but three chemicals are produced in this birefinery process. Finally, mass production of biofuels usually is a continuous process, while the production of the three chemicals contains some batch steps. These reasons could result in more labor requirement in this birefinery process.

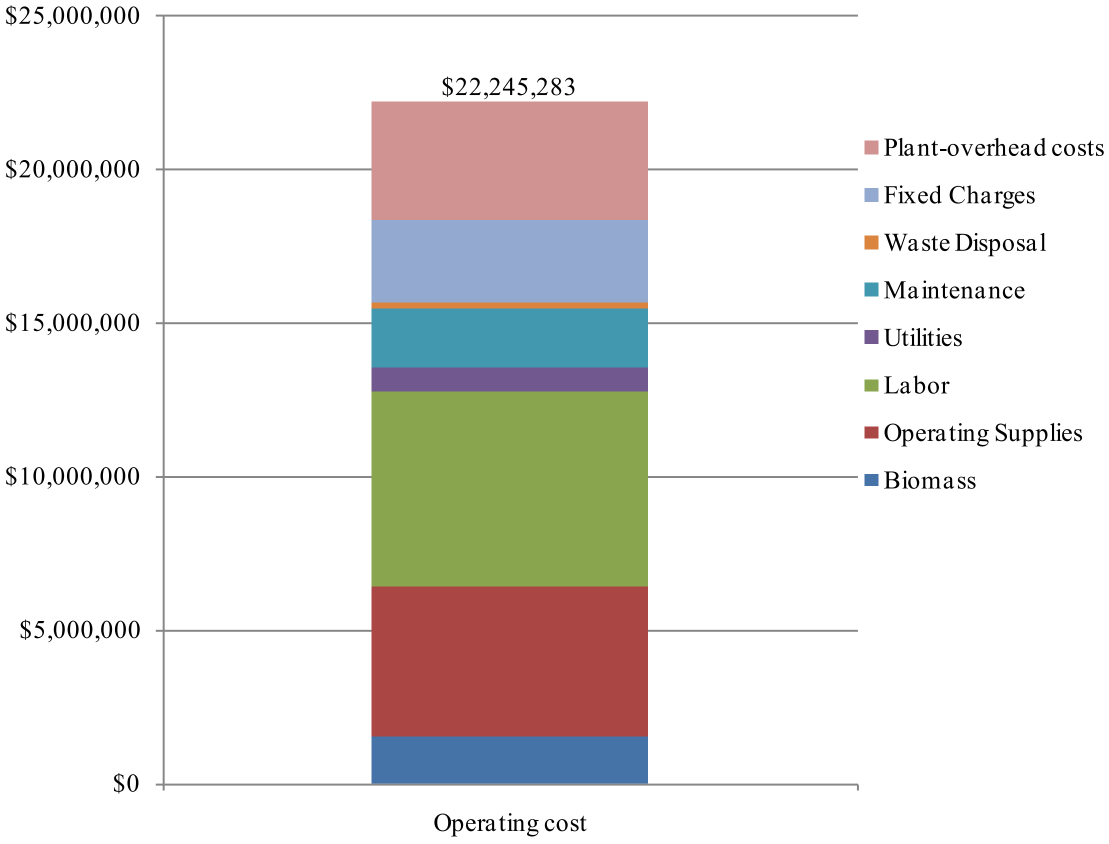

Fig. S5 The operating cost of the whole process

6 Some background data for this LCA study

6.1 LCI data for petrochemical production of phenol - formaldehyde resins (PF)

Wilson et al. has developed an life-cycle inventory of formaldehyde-base resins used in wood composites in terms of resources, emissions, energy and carbon.[16] The LCI for the production of PF is shown in Table S7, in which the environmental burdens of the delivery of chemicals to the resin plants are ignored.

Table S7 LCI data for conventional PF production route

Materials, Energy and Emissions	Value	Units
Phenol	2.44E-01	kg /kg_{PF}
Methanol	2.09E-01	kg /kg_{PF}
Sodium hydroxide	6.10E-02	kg /kg_{PF}
Process water	3.34E-01	kg /kg_{PF}
Cooling water from river (20℃)	1.56E-02	kg /kg_{PF}
Electricity	3.56E-02	kWh /kg_{PF}
Natural gas	8.21E-03	Nm^3 /kg_{PF}
Propane	2.93E-06	L /kg_{PF}
Carbon dioxide	1.76E-02	kg /kg_{PF}
Carbon monoxide	3.81E-05	kg /kg_{PF}

6.2 LCI data for petrochemical production of calcium acetate

Overcash et al has presented gate-to-gate process energy use for a calcium acetate manufacturing process, in which calcium hydroxide and acetic acid were used as raw materials.[17] On the basis of the work of Overcash et al, LCI data for petrochemical production of calcium acetate is shown in Table S8.

Table S8 LCI data for petrochemical production of calcium acetate

Materials, Energy and Emissions	Value	Units
Calcium hydroxide	4.69E-01	kg /$kg_{\text{Calcium acetate}}$
Acetic acid	7.59E-01	kg /$kg_{\text{Calcium acetate}}$
Steam (6bar)	1.53E+00	MJ /$kg_{\text{Calcium acetate}}$
Electricity	1.05E-03	MJ /$kg_{\text{Calcium acetate}}$
Natural gas	9.32E-01	MJ /$kg_{\text{Calcium acetate}}$
Carbon dioxide	5.22E-02	kg /$kg_{\text{Calcium acetate}}$

6.3 The GWP100a, CED, EI-99 metric for some chemicals and utilities

Cradle-to-gate LCIA results according to the GWP100a, CED, EI-99 metric for some chemicals and utilities used in this process are listed in Table S9. All the data is mainly based on ecoinvent 2.2 database, and a few of the data is derived from some LCA documents. These LCA documents are listed in the last row in Table S9.

Table S9 The GWP100a, CED, EI-99 metric for some chemicals and utilities

Substance	GWP100a (kg$_{\mathrm{CO2\text{-}eq}}$/kg)	CED$_{\text{non-renewable}}$ (MJ$_{\mathrm{eq}}$/kg)	EI-99 (Points/kg)
Materials			
Sulfuric acid (98 wt. %)	1.20E-01	2.02E+00	4.00E-02
Process water	2.45E-05	2.79E-04	1.83E-06
Activated carbon [a]	2.94E-01	5.92E+00	1.76E-02
Calcium hydroxide	9.90E-01	5.50E+00	3.00E-02
Hydrochloric acid (32 wt. %)	8.53E-01	1.75E+01	6.00E-02
Ethyl acetate [b]	3.14E+00	9.63E+01	3.36E-01
Sodium hydroxide	1.10E+00	2.14E+01	6.00E-01
Phenol	3.48E+00	1.21E+02	4.40E-01
Formaldehyde (37 wt.%) [b]	4.14E-01	1.82E+01	6.25E-02
Calcium oxide [c]	1.31E+00	7.30E+00	2.80E-02
Methanol [b]	7.64E-01	4.08E+01	1.35E-01
Energy			
Diesel [d]	1.29E-02	1.20E+00	6.43E-03
Electricity [d]	4.90E-01	9.87E+00	2.00E-02
Steam (6 bar) [d]	1.00E-01	1.56E+00	5.77E-03
Cooling water from river (20℃)	0.00E+00	0.00E+00	0.00E+00
Waste treatment			
Waste liquid [e]	2.19E-02	2.42E-01	5.00E-04
Solid waste [e]	1.34E-02	6.52E-01	4.22E-02

[a] Values based on the work of Arena et al.[18]

[b] Values based on the work of Amelio et al.[19]

[c] Values based on the works of Huijbregts et al. and Alvarez-Gaitan et al.[20, 21]

[d] Functional unit for diesel as well as steam is MJ and for electricity kWh

[e] Values based on the works of Rerat et al.[22]

References

1 K. A. Kobe, *Plant Design and Economics for Chemical Engineers*, McGraw-Hill, 1991.

2 G. Towler and R. K. Sinnott, *Chemical engineering design: principles, practice and economics of plant and process design*, Elsevier, 2012.

3 R. Snow, T. Allen, B. Ennis and J. Litster, *Perry's chemical engineers' handbook*, 2008.

4 M. Morales, M. Ataman, S. Badr, S. Linster, I. Kourlimpinis, S. Papadokonstantakis, V. Hatzimanikatis and K. Hungerbuhler, *Energy Environ. Sci.*, 2016, **9**, 2794-2805.

5 Q. Li, Y. Zhang and G. Hu, *Bioresour. Technol.*, 2015, **191**, 88-96.

6 Y. Zhang, T. R. Brown, G. Hu and R. C. Brown, *Bioresour. Technol.*, 2013, **127**, 358-365.

7 E. Henrich, N. Dahmen and E. Dinjus, *Biofuels, Bioprod. Bioref.*, 2009, **3**, 28-41.

8 C. Jiménez-González, S. Kim and M. R. Overcash, *Int. J. Life. Cycle. Ass.*, 2000, **5**, 153-159.

9 Alibaba, Levoglucosan, https://www.alibaba.com/product-detail/Levoglucosan-498-07-7_521299548.html?spm=a2700.7724838.0.0.rlFtq8, accessed 05/01/2017, 2017.

10 Carbosynth, Levoglucosan, http://www.carbosynth.com/carbosynth/website.nsf/(w-productdisplay)/186B041DE4AA69F080256D8F003304BA, accessed 05/01/2017, 2017.

11 Guidechem, The phenolic resin 551 from America, http://china.guidechem.com/trade/pdetail7363823.html, accessed 05/01/2017, 2017.

12 Alibaba, Calcium Acetate BP/USP, https://www.alibaba.com/product-detail/Calcium-Acetate-BP-USP_60154097956.html?spm=a2700.7724838.0.0.Ds8gK7&s=p, accessed 05/01/2017, 2017.

13 M. M. Wright, R. C. Brown and A. A. Boateng, *Biofuels, Bioprod. Bioref.*, 2008, **2**, 229-238.

14 M. Wright and R. C. Brown, *Biofuels, Bioprod. Bioref.*, 2007, **1**, 191-200.

15 Y. N. Zhang, T. R. Brown, G. P. Hu and R. C. Brown, *Biomass Bioenergy*, 2013, **51**, 99-108.

16 J. B. Wilson, *Wood Fiber Sci.*, 2010, **42**, 125-143.

17 S. Kim and M. Overcash, *J. Chem. Technol. Biot.*, 2003, **78**, 995-1005.

18 N. Arena, J. Lee and R. Clift, *J. Clean Prod.*, 2016, **125**, 68-77.

19 A. Amelio, G. Genduso, S. Vreysen, P. Luis and B. Van der Bruggen, *Green Chem.*, 2014, **16**, 3045-3063.

20 J. P. Alvarez-Gaitan, G. M. Peters, H. V. Rowley, S. Moore and M. D. Short, *Int. J. Life. Cycle. Ass.*, 2013, **18**, 1291-1301.

21 M. A. Huijbregts, S. Hellweg, R. Frischknecht, H. W. Hendriks, K. Hungerbühler and A. J. Hendriks, *Environ. Sci. Technol.*, 2010, **44**, 2189-2196.

22 C. Rerat, S. Papadokonstantakis and K. Hungerbühler, *J. Air Waste Manage.*, 2013, **63**, 349-366.