A co-solvent hydrolysis strategy for the production of biofuels: Process synthesis and technoeconomic analysis

Wangyun Won,[a,b] Ali Hussain Motagamwala,[a,b] James A. Dumesic,[a,b] Christos T. Maravelias*[a,b]

[a] Department of Chemical and Biological Engineering, University of Wisconsin-Madison, Madison, WI 53706, USA

[b] DOE Great Lakes Bioenergy Research Center, University of Wisconsin-Madison, 1552 University Ave, Madison, WI 53726, USA

SUPPLEMENTARY MATERIAL

* Corresponding author (Email: maravelias@wisc.edu)

A. Data regression for liquid-liquid equilibrium of GVL-toluene-water system

To accurately model the liquid-liquid equilibrium (LLE) in the toluene-based extractor and liquid-liquid separator, we conducted the LLE experiments for a mixture of GVL/toluene/water at different temperatures (near the operating temperature of the separation processes) and corrected the key coefficients of the non-random two-liquid (NRTL) model based on the experimental data obtained. The NRTL model can be written as (Renon and Prausnitz, 1968)

$$\ln\gamma_i = \frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_k x_k G_{ki}} + \sum_j \frac{x_j G_{ij}}{\sum_k x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_m x_m \tau_{mj} G_{mj}}{\sum_k x_k G_{kj}} \right) \quad (1)$$

where

$$G_{ij} = \exp\left(-\alpha_{ij}\tau_{ij}\right) \quad (2a)$$

$$\tau_{ij} = a_{ij} + b_{ij}/T + e_{ij}\ln T + f_{ij}T \quad (2b)$$

$$\alpha_{ij} = c_{ij} + d_{ij}(T - 273.15) \quad (2c)$$

In the above, the subscripts (i.e., i, j, k, and m) denote components. γ_i represents the activity coefficient of component i, x_j indicates the mole fraction of component j in the liquid phase considered, and T is temperature. The binary parameters a_{ij}, b_{ij}, e_{ij}, and f_{ij} are unsymmetrical, e.g., a_{ij} may not be equal to a_{ji}. Here, we chose a_{ij} and b_{ij} to be estimated, while fixing $c_{ij} = 0.3$ and others equal to zero. The experimental data used for the estimation of the parameters are presented in Table A.1. We used default parameter values in Aspen Plus database as the initial point for parameter estimation. The regression results are summarized in Table A.2.

Table A.1. LLE experimental data (mole fraction of components in organic and aqueous phases) for a mixture of GVL/toluene/water.

Temperature	Organic phase			Aqueous phase		
(K)	Water	GVL	Toluene	Water	GVL	Toluene
313	0.06121	0.77429	0.16450	0.86357	0.13201	0.00442
323	0.10863	0.68242	0.20895	0.84203	0.15202	0.00595
333	0.15344	0.61521	0.23135	0.82543	0.16772	0.00685
343	0.19926	0.56204	0.23870	0.81813	0.17432	0.00755
353	0.25627	0.49873	0.24500	0.81578	0.17590	0.00832

Table A.2. NRTL parameter values for a mixture of GVL/toluene/water.

Parameter	Component i	Component j	Default*	Estimates*
a_{ij}	Water	Toluene	0	14.215
	Toluene	Water	0	-0.524
	Water	GVL	0	-3.121
	GVL	Water	0	7.568
	Toluene	GVL	0	34.707
	GVL	Toluene	0	3.627
b_{ij}	Water	Toluene	0	-2471.831
	Toluene	Water	0	19.061
	Water	GVL	0	1363.416
	GVL	Water	0	-919.849
	Toluene	GVL	0	4241.894
	GVL	Toluene	0	-954.991

* a_{ij} is dimensionless, and b_{ij} is in K.

Figure A.1 demonstrates fitting results of the experimental data (symbols) to the regression phase equilibria model (lines). In process analysis, the liquid-liquid equilibrium for the mixture of GVL/toluene/water was calculated from these estimated curves.

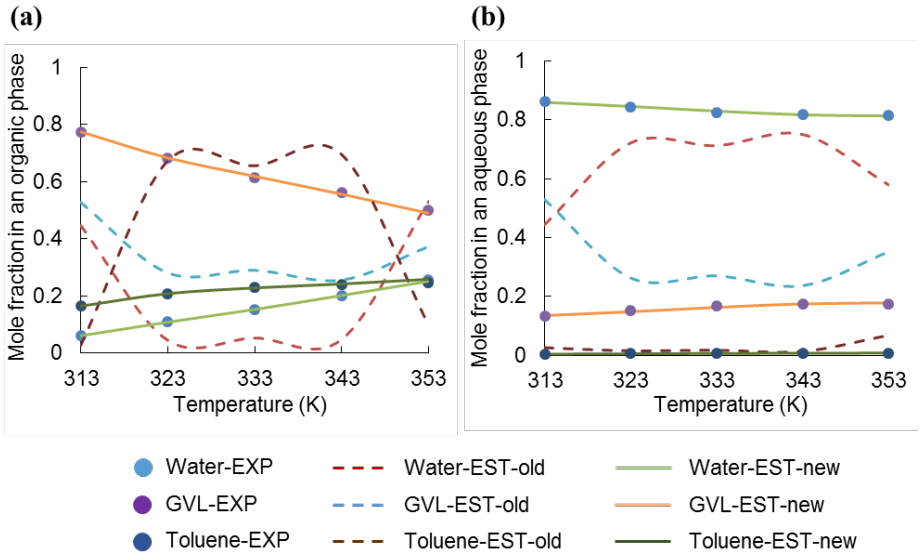

Figure A.1. LLE experimental data (points) and fitting results (lines). NRTL was used to calculate liquid activity coefficients for a mixture of GVL/toluene/water. The experimental data represent average values of multiple experiments. EXP: experimental data, EST: estimated data (using process model).

B. Heat integration

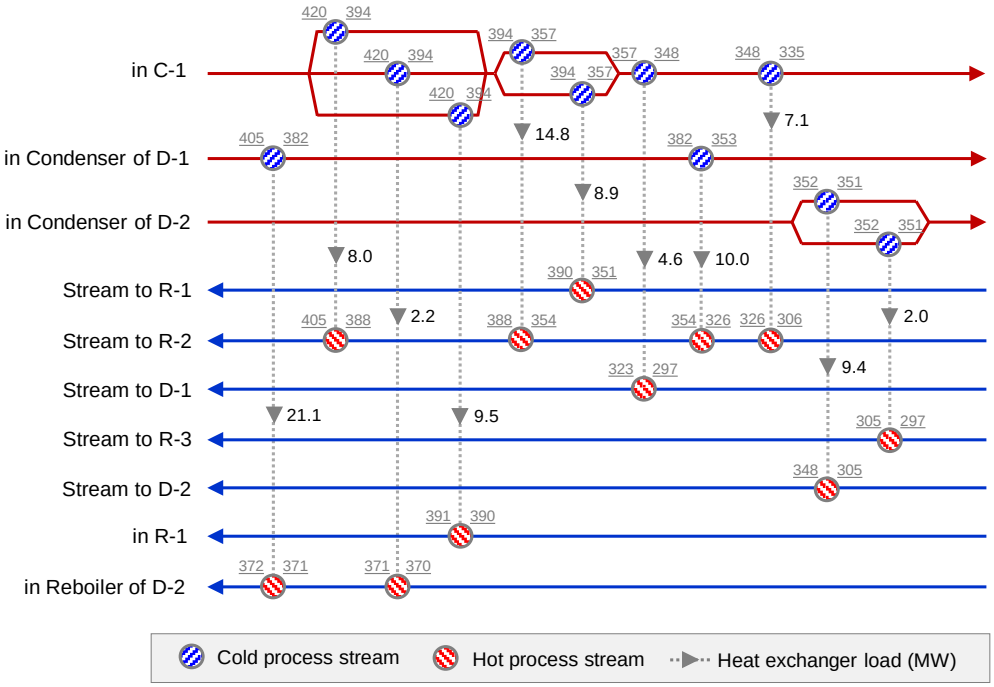

Figure B.1. Heat exchanger network. Numbers in black denote heat load (MW) and underlined numbers in grey denote temperature (K).

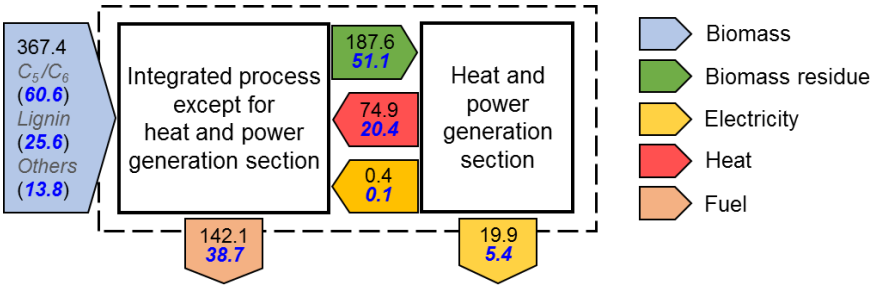

Figure B.2. Energy flow diagram after heat integration. Numbers in black represent energy content (MW) and numbers in blue (bold and italic) indicate energy flows as percentage of the energy content of biomass feedstock.

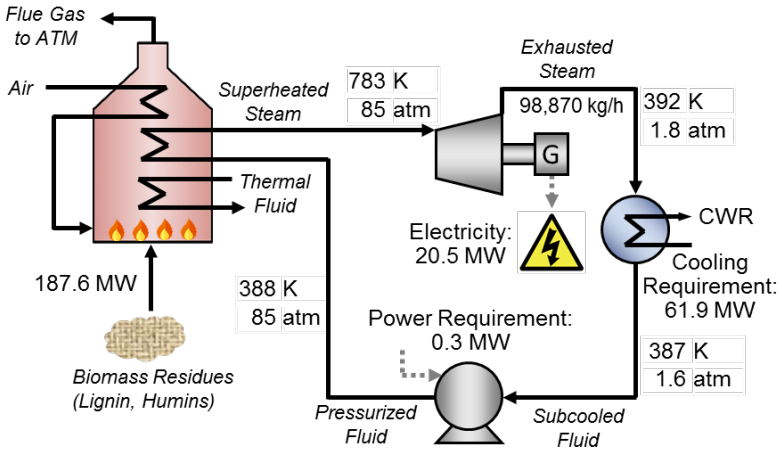

Figure B.3. Process flow diagram for the heat and power generation section.

C. Important stream information and ethanol yield

Table C.1. Process stream information for selected streams in the flowsheet shown in Fig. 2. (Abbreviations: GVL, γ-Valerolactone; HMF, 5-hydroxymethylfurfural).

Stream number	1	8	9	11	13	15	18	19	20	22	24	28	29	31
Mass flow (ton/h)														
Cellulose	31.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Hemicellulose	18.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Toluene	0.0	91.8	91.8	79.2	0.0	0.0	199.7	0.0	0.0	0.0	0.0	0.1	0.0	0.1
GVL	0.0	468.1	468.1	260.1	166.6	166.1	214.1	5.5	5.5	5.5	0.0	202.0	85.5	203.4
H_2O	0.0	138.0	138.0	4.2	133.2	124.3	1.2	124.9	124.9	162.5	0.1	0.0	0.0	0.2
H_2SO_4	0.0	9.0	9.0	0.0	9.0	8.4	0.0	8.4	0.0	0.0	0.0	0.0	0.0	0.0
C_6 sugar	0.0	30.7	30.7	1.7	28.7	26.8	1.6	25.5	25.5	3.3	0.0	1.6	0.7	1.6
C_5 sugar	0.0	16.9	16.9	0.7	16.1	15.1	0.9	14.3	14.3	1.9	0.0	0.8	0.4	0.8
HMF	0.0	12.6	12.6	4.5	7.4	6.9	3.6	4.1	4.1	4.1	0.0	3.4	1.5	3.4
Furfural	0.0	15.7	15.7	3.6	11.5	10.8	3.5	8.0	8.0	8.0	0.0	3.3	1.4	3.3
Levulinic acid	0.0	9.4	9.4	1.5	7.6	7.4	4.0	3.8	3.8	3.8	0.0	3.8	1.6	2.2
Formic acid	0.0	3.7	3.7	0.6	3.0	2.9	1.6	1.5	1.5	1.5	0.0	1.5	0.6	0.9
Ethanol	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	17.7	17.7	0.0	0.0	0.0
CO_2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	16.9	0.0	0.0	0.0	0.0
Lignin	13.3	16.6	16.6	2.4	13.8	0.6	0.8	0.2	0.2	0.2	0.0	0.8	0.3	0.8
Humins	0.0	8.0	8.0	0.0	8.0	0.3	0.2	0.1	0.1	0.1	0.0	0.2	0.1	0.2
Total flow (ton/h)	64.1	820.5	820.5	358.4	405.1	369.5	431.3	196.5	188.1	225.7	17.8	217.6	92.1	216.9
Temperature (K)	298	420	298	298	298	298	299	299	299	305	311	473	473	481
Pressure (atm)	1	20	20	20	20	1	1	1	1	1	1	1	35	20

Table C.2. Fuel production rates for different strategies.

Strategy	Strategy A		Strategy B (Han et al., 2015)	Strategy C (Humbird et al., 2011)
	Basic	Alternative		
Fuel production rate (10^6 GGE yr^{-1})	35.7	38.4	39.8	40.2

D. Economic evaluation

Table D.1. List of major economic parameters and assumptions.

Corn stover price ($ per ton) [a]	58.5
Sulfuric acid price ($ per ton) [b]	35.0
Lime price ($ per ton) [b]	99.0
Water price ($ per ton) [b]	0.23
Electricity price ($ per kWh) [a]	0.057
Toluene price ($ per ton) [c]	669.0
Gypsum disposal ($ per ton) [b]	30.9
RuSn(1:4)/C catalyst ($ per kg) [d]	540.0
Yeast price ($ per gallon of ethanol) [e]	0.01
Wastewater treatment cost ($ per ton) [b]	36.0
Refrigerated water ($ per ton) [f]	0.185
Internal rate of return (%) [a]	10.0
Plant financing by equity (%) [a]	40.0
Plant life (years) [a]	30.0
Income tax rate (%) [a]	35.0
Interest rate for debt financing (%) [a]	8.0
Term for debt financing (years) [a]	10.0
General plant depreciation (years) [a]	7.0
Steam plant depreciation (years) [a]	20.0
Working capital (% of fixed capital investment) [a]	5.0
On-stream percentage after startup (%) [a]	96.0
Startup time (years) [a]	0.25
Revenue and costs during startup	
Revenue (% of normal) [a]	50.0
Variable costs (% of normal) [a]	75.0
Fixed costs (% of normal) [a]	100.0
Construction period (years) [a]	3.0
First 12 months' expenditures (%) [a]	8.0
Next 12 months' expenditures (%) [a]	60.0
Last 12 months' expenditures (%) [a]	32.0

[a] Taken from Humbird et al. (2011)
[b] Taken from Kazi et al. (2010)
[c] Taken from S&P Global Platts
[d] Taken from Sen et al. (2012) (10% of the catalyst is refurbished every 3 months)
[e] Taken from McAloon et al. (2000); yeast is utilized as a raw material for fermentation
[f] Taken from Turton et al. (2008)

Table D.2. Cost of major equipment units.

Section	Equipment type	Equipment ID	Equipment cost ($)	Installed cost ($)	Calculation method
Two-Stage Biomass conversion Reaction	Reactor	R-1/R-2	26,070,195	59,480,124	Scaled on area[a,c]
	Pump	P-1/P-2/P-3/P-4/ P-5	165,308	380,209	APEA[b]
	Separator	S-1	11,737,916	12,207,432	Scaled on flow[a]
	Vessel	V-1	151,840	182,208	Scaled on flow[a]
Liquid-liquid Separation	Cooler	C-1	2,156,925	4,745,236	APEA[b]
	Separator	S-2	35,008	52,511	APEA[b]
Solid Recovery	Separator	S-3/S-6	12,053,991	12,536,150	Scaled on flow[a,d]
	Separator	S-7	65,723	118,301	APEA[b]
Extraction/ Toluene Separation	Extractor	E-1	121,350	266,971	APEA[b]
	Column	D-1	921,433	1,653,015	APEA[b]
GVL Production	Reactor	R-4	128,202	256,404	APEA[b,e]
	Pump	P-6	47,217	108,600	APEA[b]
Fermentation	Reactor package	R-3	4,567,766	5,938,096	Scaled on flow[a]
Wastewater Treatment	Package	-	32,245,661	32,245,661	Scaled on flow[a,f]

[a] The cost is estimated using exponential scaling expression (based on size and cost data presented in the NREL reports (Humbird et al., 2011)).

[b] The cost is determined using Aspen Process Economic Analyzer (APEA, 2011)

[c] If the cost is estimated following the approach of Davis et al. (2015), the cost is 100.2 MM$.

[d] If the cost is estimated based on the cost data in Davis et al. (2015), the cost is 23.1 MM$.

[e] If the reactor cost is estimated using the scaling expression for the condensation reactor (573 K, 62 atm) in Davis et al. (2015), which is the most similar reactor to R-4 (473 K, 35 atm), the cost is 2.5 MM$.

[f] The cost is scaled based on mass flow rate following the approach of Humbird et al. (2011). If the cost is scaled based on both mass flow rate and chemical oxygen demand (COD) (Davis et al., 2013), the cost is 54.9 MM$.

E. Discounted cash flow for the process design

Table E.1. Discounted cash flow calculations.

Year	-2	-1	0	1	2	3	4	5	6	7	8
Fixed capital investment	11,277,781	84,583,359	45,111,125								
Land	1,848,000										
Working capital			17,621,533								
Loan payment				31,513,537	31,513,537	31,513,537	31,513,537	31,513,537	31,513,537	31,513,537	31,513,537
Loan interest payment	1,353,334	11,503,337	16,916,672	16,916,672	15,748,923	14,487,754	13,125,691	11,654,663	10,065,953	8,350,147	6,497,075
Loan principal	16,916,672	143,791,711	211,458,399	196,861,533	181,096,919	164,071,136	145,683,289	125,824,416	104,376,832	81,213,441	56,196,980
Ethanol sales				99,089,968	113,245,678	113,245,678	113,245,678	113,245,678	113,245,678	113,245,678	113,245,678
By-product (electricity) credit				8,361,557	9,556,066	9,556,066	9,556,066	9,556,066	9,556,066	9,556,066	9,556,066
Total annual sales				107,451,526	122,801,744	122,801,744	122,801,744	122,801,744	122,801,744	122,801,744	122,801,744
Annual manufacturing cost											
Feedstock				39,567,938	45,220,500	45,220,500	45,220,500	45,220,500	45,220,500	45,220,500	45,220,500
Baghouse bags				431,272					431,272		
Other variable costs				16,696,288	17,809,374	17,809,374	17,809,374	17,809,374	17,809,374	17,809,374	17,809,374
Fixed operating costs				10,293,354	10,293,354	10,293,354	10,293,354	10,293,354	10,293,354	10,293,354	10,293,354
Total product cost				66,988,852	73,323,228	73,323,228	73,323,228	73,323,228	73,754,500	73,323,228	73,323,228
Annual depreciation											
General plant writedown				14.29%	24.49%	17.49%	12.49%	8.93%	8.92%	8.93%	4.46%
Depreciation charge				42,172,533	72,274,691	51,616,347	36,860,387	26,354,144	26,324,632	26,354,144	13,162,316
Remaining value				252,946,661	180,671,971	129,055,624	92,195,236	65,841,092	39,516,460	13,162,316	0
Steam plant writedown				3.75%	7.22%	6.68%	6.18%	5.71%	5.29%	4.89%	4.52%
Depreciation charge				2,149,180	4,137,315	3,826,687	3,540,129	3,274,204	3,028,911	2,801,385	2,591,625
Remaining value				55,162,290	51,024,975	47,198,288	43,658,158	40,383,954	37,355,043	34,553,658	31,962,034
Net revenue				(20,775,711)	(42,682,413)	(20,452,272)	(4,047,692)	8,195,504	9,627,747	11,972,841	27,227,500
Losses forward					(20,775,711)	(63,458,123)	(83,910,395)	(87,958,087)	(79,762,583)	(70,134,836)	(58,161,995)
Taxable income				(20,775,711)	(63,458,123)	(83,910,395)	(87,958,087)	(79,762,583)	(70,134,836)	(58,161,995)	(30,934,495)
Income tax				0	0	0	0	0	0	0	0
Annual cash income				8,949,137	17,964,979	17,964,979	17,964,979	17,964,979	17,533,707	17,964,979	17,964,979
Discount factor	1.2100	1.1000	1.0000	0.9091	0.8264	0.7513	0.6830	0.6209	0.5645	0.5132	0.4665
Annual present value				8,135,579	14,847,090	13,497,354	12,270,322	11,154,838	9,897,320	9,218,875	8,380,795
Total capital investment + interest	17,519,729	105,695,366	79,649,330								

Year	9	10	11	12	13	14	15	16	17	18	19
Fixed capital investment											
Land											
Working capital											
Loan payment	31,513,537	31,513,537	0	0	0	0	0	0	0	0	0
Loan interest payment	4,495,758	2,334,336	0	0	0	0	0	0	0	0	0
Loan principal	29,179,201	0	0	0	0	0	0	0	0	0	0
Ethanol sales	113,245,678	113,245,678	113,245,678	113,245,678	113,245,678	113,245,678	113,245,678	113,245,678	113,245,678	113,245,678	113,245,678
By-product (electricity) credit	9,556,066	9,556,066	9,556,066	9,556,066	9,556,066	9,556,066	9,556,066	9,556,066	9,556,066	9,556,066	9,556,066
Total annual sales	122,801,744	122,801,744	122,801,744	122,801,744	122,801,744	122,801,744	122,801,744	122,801,744	122,801,744	122,801,744	122,801,744
Annual manufacturing cost											
Feedstock	45,220,500	45,220,500	45,220,500	45,220,500	45,220,500	45,220,500	45,220,500	45,220,500	45,220,500	45,220,500	45,220,500
Baghouse bags			431,272					431,272			
Other variable costs	17,809,374	17,809,374	17,809,374	17,809,374	17,809,374	17,809,374	17,809,374	17,809,374	17,809,374	17,809,374	17,809,374
Fixed operating costs	10,293,354	10,293,354	10,293,354	10,293,354	10,293,354	10,293,354	10,293,354	10,293,354	10,293,354	10,293,354	10,293,354
Total product cost	73,323,228	73,323,228	73,754,500	73,323,228	73,323,228	73,323,228	73,323,228	73,754,500	73,323,228	73,323,228	73,323,228
Annual depreciation											
General plant writedown											
Depreciation charge											
Remaining value											
Steam plant writedown	4.46%	4.46%	4.46%	4.46%	4.46%	4.46%	4.46%	4.46%	4.46%	4.46%	4.46%
Depreciation charge	2,557,238	2,556,665	2,557,238	2,556,665	2,557,238	2,556,665	2,557,238	2,556,665	2,557,238	2,556,665	2,557,238
Remaining value	29,404,796	26,848,131	24,290,893	21,734,229	19,176,991	16,620,326	14,063,088	11,506,424	8,949,186	6,392,521	3,835,284
Net revenue	42,425,520	44,587,515	46,490,006	46,921,851	46,921,278	46,921,851	46,921,278	46,490,579	46,921,278	46,921,851	46,921,278
Losses forward	(30,934,495)	0	0	0	0	0	0	0	0	0	0
Taxable income	11,491,025	44,587,515	46,490,006	46,921,851	46,921,278	46,921,851	46,921,278	46,490,579	46,921,278	46,921,851	46,921,278
Income tax	4,021,859	15,605,630	16,271,502	16,422,648	16,422,447	16,422,648	16,422,447	16,271,703	16,422,447	16,422,648	16,422,447
Annual cash income	13,943,120	2,359,349	32,775,742	33,055,868	33,056,069	33,055,868	33,056,069	32,775,541	33,056,069	33,055,868	33,056,069
Discount factor	0.4241	0.3855	0.3505	0.3186	0.2897	0.2633	0.2394	0.2176	0.1978	0.1799	0.1635
Annual present value	5,913,244	909,631	11,487,697	10,532,618	9,575,166	8,704,643	7,913,360	7,132,913	6,539,967	5,945,388	5,404,931
Total capital investment + interest											

Year	20	21	22	23	24	25	26	27	28	29	30
Fixed capital investment											
Land											(1,848,000)
Working capital											(17,621,533)
Loan payment	0	0	0	0	0	0	0	0	0	0	0
Loan interest payment	0	0	0	0	0	0	0	0	0	0	0
Loan principal	0	0	0	0	0	0	0	0	0	0	0
Ethanol sales	113,245,678	113,245,678	113,245,678	113,245,678	113,245,678	113,245,678	113,245,678	113,245,678	113,245,678	113,245,678	113,245,678
By-product (electricity) credit	9,556,066	9,556,066	9,556,066	9,556,066	9,556,066	9,556,066	9,556,066	9,556,066	9,556,066	9,556,066	9,556,066
Total annual sales	122,801,744	122,801,744	122,801,744	122,801,744	122,801,744	122,801,744	122,801,744	122,801,744	122,801,744	122,801,744	122,801,744
Annual manufacturing cost											
Feedstock	45,220,500	45,220,500	45,220,500	45,220,500	45,220,500	45,220,500	45,220,500	45,220,500	45,220,500	45,220,500	45,220,500
Baghouse bags		431,272					431,272				
Other variable costs	17,809,374	17,809,374	17,809,374	17,809,374	17,809,374	17,809,374	17,809,374	17,809,374	17,809,374	17,809,374	17,809,374
Fixed operating costs	10,293,354	10,293,354	10,293,354	10,293,354	10,293,354	10,293,354	10,293,354	10,293,354	10,293,354	10,293,354	10,293,354
Total product cost	73,323,228	73,754,500	73,323,228	73,323,228	73,323,228	73,323,228	73,754,500	73,323,228	73,323,228	73,323,228	73,323,228
Annual depreciation											
General plant writedown											
Depreciation charge											
Remaining value											
Steam plant writedown	4.46%	2.23%									
Depreciation charge	2,556,665	1,278,619									
Remaining value	1,278,619	0									
Net revenue	46,921,851	47,768,625	49,478,516	49,478,516	49,478,516	49,478,516	49,047,244	49,478,516	49,478,516	49,478,516	49,478,516
Losses forward	0	0	0	0	0	0	0	0	0	0	0
Taxable income	46,921,851	47,768,625	49,478,516	49,478,516	49,478,516	49,478,516	49,047,244	49,478,516	49,478,516	49,478,516	49,478,516
Income tax	16,422,648	16,719,019	17,317,481	17,317,481	17,317,481	17,317,481	17,166,535	17,317,481	17,317,481	17,317,481	17,317,481
Annual cash income	33,055,868	32,328,225	32,161,035	32,161,035	32,161,035	32,161,035	31,880,708	32,161,035	32,161,035	32,161,035	32,161,035
Discount factor	0.1486	0.1351	0.1228	0.1117	0.1015	0.0923	0.0839	0.0763	0.0693	0.0630	0.0573
Annual present value	4,913,544	4,368,531	3,950,854	3,591,685	3,265,168	2,968,335	2,674,965	2,453,169	2,230,154	2,027,413	1,843,102
Total capital investment + interest											(1,115,771)

References

A. McAloon, F. Taylor, W. Yee, K. Ibsen, R. Wooley, *National Renewable Energy Laboratory Report*, NREL/TP-580-28893, 2000.

Aspen Process Economic Analyzer (APEA) V7.3, Aspen Technology Inc., Cambridge, 2011.

D. Humbird, R. Davis, L. Tao, C. Kinchin, D. Hsu, A. Aden, P. Schoen, J. Lukas, B. Olthof, M. Worley, D. Sexton, and D. Dudgeon, *National Renewable Energy Laboratory Report*, NREL/TP-5100-47764, 2011.

F. K. Kazi, J. Fortman, R. Anex, G. Kothandaraman, D. Hsu, A. Aden, and A. Dutta, *National Renewable Energy Laboratory Report*, NREL/TP-6A2-46588, 2010.

H. Renon and J. M. Prausnitz, *AIChE Journal*, 1968, 14, 135-144.

J. Han, J. S. Luterbacher, D. M. Alonso, J. A. Dumesic, and C. T. Maravelias, *Bioresource Technology*, 2015, 182, 258-266.

R. Davis, L. Tao, E. C. D. Tan, M. J. Biddy, G. T. Beckham, C. Scarlata, J. Jacobson, K. Cafferty, J. Ross, J. Lukas, D. Knorr, and P. Schoen, *National Renewable Energy Laboratory Report*, NREL/TP-5100-60223, 2013.

R. Davis, L. Tao, C. Scarlata, E. C. D. Tan, J. Ross, J. Lukas, and D. Sexton, *National Renewable Energy Laboratory Report*, NREL/TP-5100-62498, 2015.

R. Turton, R. C. Bailie, W. B. Whiting, J. A. Shaeiwitz, *Analysis, Synthesis, and Design of Chemical Processes*, 4th edition, Prentice Hall, 2012.

S. M. Sen, D. M. Alonso, S. G. Wettstein, E. I. Gürbüz, C. A. Henao, J. A. Dumesic, and C. T. Maravelias, Energy and Environmental Science, 2012, 5, 9690-9697.

S&P Global Platts. http://www.platts.com/news-feature/2014/petrochemicals/pgpi/toluene.