

# Aspen Plus® modeling and simulation of upgraded biofuel production in an industrial biomass direct liquefaction plant

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## Appendix A

The kinetic parameters of cellulose were studied by Yan *et al* [1]. In **Table S 1**,

**Table S 2** and

**Table S 3** are shown the values of T and k that have been fitted in the equation 4 in the main text, in order to find the  $k_0$  and Ea values.

**Table S 1.** Reaction rate at different temperatures for cellulose decomposition.

T (K)	k (s <sup>-1</sup> )
413	$7.17 \times 10^{-5}$
433	$1.77 \times 10^{-4}$
453	$7.65 \times 10^{-4}$
473	$3.06 \times 10^{-3}$
493	$1.13 \times 10^{-2}$

**Table S 2.** Reaction rate at different temperatures for glucose decomposition.

T (K)	k (s <sup>-1</sup> )
413	$2.27 \times 10^{-4}$
433	$5.60 \times 10^{-4}$
453	$1.18 \times 10^{-3}$
473	$3.39 \times 10^{-3}$
493	$7.52 \times 10^{-3}$

**Table S 3.** Reaction rate at different temperatures for 5-HMF decomposition.

T (K)	k (s <sup>-1</sup> )
413	$9.63 \times 10^{-4}$
433	$2.66 \times 10^{-3}$
453	$7.70 \times 10^{-3}$

473	$2.25 \times 10^{-2}$
493	$5.72 \times 10^{-2}$

## Appendix B

Simulations was made with different biomass composition. The **Table S 4**, **Table S 5** and **Table S 6** shown the stream results for each simulation.

**Table S 4.** Stream results (kg/h) for simulation with sample 1 of biomass.

Stream	FEEDREAC	INSOLVEN	GASPROD	LIQPROD	AQUEOUS	ORGANIC
2EH	0	46.57	28.83	17.74	0.04	17.73
H2O	12.38	4.99	21.57	0.39	7.91	8.50
CELL	30.96	0	0	11.40	0.18	0.39
GLUCOSE	4.64	0	0	5.15	0	0.26
GALACT	4.64	0	0	0.17	0	0
COUMARIL	12.38	0	0	0.35	0.01	0.01
XYLOSE	4.64	0	0	0.17	0	0.01
ARABIN	4.64	0	0	0.17	0	0
HMF	0	0.02	0.05	0.83	0.26	0.59
LA	0	1.84	2.59	15.03	1.85	13.72
FA	0	2.44	8.42	0.28	2.59	3.39
FURFURAL	0	8.72	11.51	2.94	0.39	4.36
PHENOL	0	6.63	7.50	10.44	0.25	10.32
Total	74.29	71.22	80.47	65.04	13.49	59.30

**Table S 5.** Stream results (kg/h) for simulation with sample 2 of biomass.

Stream	FEEDREAC	INSOLVEN	GASPROD	LIQPROD	AQUEOUS	ORGANIC
2EH	0	46.57	31.58	14.99	0.14	14.92
H2O	12.38	4.14	20.32	0.37	9.13	6.96
CELL	37.15	0	0	13.68	0.27	0.42
GLUCOSE	4.64	0	0	6.00	0	0.30
GALACT	4.64	0	0	0.17	0	0
COUMARIL	6.19	0	0	0.17	0	0
XYLOSE	4.64	0	0	0.17	0	0.01
ARABIN	4.64	0	0	0.17	0	0
HMF	0	0.03	0.06	0.94	0.37	0.59
LA	0	1.88	3.15	16.65	3.85	13.86
FA	0	2.63	9.42	0.31	3.53	3.28
FURFURAL	0	6.61	10.04	2.29	0.83	4.16
PHENOL	0	1.49	1.67	5.47	0.20	5.29
Total	74.29	63.35	76.26	61.38	18.34	49.80

**Table S 6.** Stream results (kg/h) for simulation with sample 3 of biomass.

Stream	FEEDREAC	INSOLVEN	GASPROD	LIQPROD	AQUEOUS	ORGANIC
2EH	0	46.57	31.47	15.10	0.07	15.08
H2O	12.38	4.86	22.69	0.36	10.31	7.34
CELL	27.86	0	0	10.26	0.20	0.31
GLUCOSE	6.19	0	0	5.03	0	0.25
GALACT	6.19	0	0	0.22	0	0
COUMARIL	9.29	0	0	0.26	0.01	0
XYLOSE	6.19	0	0	0.22	0	0.01
ARABIN	6.19	0	0	0.22	0	0
HMF	0	0.03	0.06	0.86	0.35	0.54
LA	0	2.17	3.17	15.38	2.88	13.26
FA	0	2.59	8.83	0.25	3.26	2.94
FURFURAL	0	12.16	16.34	3.46	0.79	5.50
PHENOL	0	4.72	5.30	7.90	0.26	7.70
Total	74.29	73.10	87.87	59.52	18.15	52.94

To calculate the yield and the biomass conversion some assumption was made: The liquefied biomass is composed by HMF, LA, FA, furfural, and phenol, and the non-liquefied biomass by cellulose, glucose, galactose, p-coumaryl alcohol, xylose, and arabinose.

## Appendix C

In sensitivity analysis the yield, conversion, stream flow, and the cooler duty was study. In the next tables the results for each analysis are shown.

**Table S 7.** Results of stream flow (kg/h) at different temperatures.

Temperature (°C)	FEEDREAC	INSOLVEN	GASPROD	LIQPROD	AQUEOUS	ORGANIC
128	74.29	49.90	27.60	96.60	9.56	71.65
144	74.29	55.47	45.92	83.84	10.98	67.30
160	74.29	71.22	80.47	65.04	13.49	59.30
176	74.29	119.28	147.85	45.72	14.16	50.15
192	74.29	269.34	319.28	24.34	46.42	0.00

**Table S 8.** Results of yield and conversion at different temperatures.

Temperature (°C)	Yield (%)	Conversion (%)					
		Biomass	Arabinose	Cellulose	p-Coumaryl alcohol	Galactose	Xylose
128	37.66	45.00	91.62	13.22	92.82	91.62	91.62
144	48.63	55.94	94.55	34.88	95.55	94.57	94.57

160	64.48	71.89	96.37	63.18	97.17	96.40	96.40
176	77.61	85.20	97.49	83.50	98.14	97.56	97.56
192	84.88	92.72	97.29	93.27	98.40	98.23	98.26

**Table S 9.** Results of cooler duty at different temperatures.

Temperature (°C)	Q <sub>cooler</sub> (kW)
413	-9.60
433	-13.48
453	-21.03
473	-37.54
493	-86.01

**Table S 10.** Results of stream flow (kg/h) at different purges.

Purge	FEEDREAC	INSOLVEN	GASPROD	LIQPROD	AQUEOUS	ORGANIC
0.05	74.29	74.28	82.82	65.75	13.78	60.27
0.1	74.29	71.22	80.47	65.04	13.49	59.30
0.15	74.29	68.59	78.43	64.44	13.20	58.48
0.2	74.29	66.26	76.62	63.93	12.90	57.80
0.3	74.29	62.33	73.51	63.11	12.28	56.69

**Table S 11.** Results of yield and conversion at different fraction purges.

Purge	Yield (%)	Conversion (%)					
		Biomass	Arabinose	Cellulose	p-Coumaryl alcohol	Galactose	Xylose
0.05	64.49	71.89	96.38	63.18	97.17	96.40	96.40
0.1	64.48	71.89	96.37	63.18	97.17	96.40	96.40
0.15	64.49	71.89	96.37	63.18	97.17	96.40	96.40
0.2	64.48	71.89	96.37	63.18	97.17	96.40	96.40
0.3	64.48	71.89	96.37	63.18	97.17	96.40	96.40

**Table S 12.** Results of cooler duty at different fraction purges.

Purge	Q <sub>cooler</sub> (kW)
0.05	-21.58
0.1	-21.03
0.15	-20.54
0.2	-20.09
0.3	-19.29

**Table S 13.** Results of stream flow (kg/h) at different biomass moisture.

<b>Q<sub>H2O</sub> (kg/h)</b>	<b>FEEDREAC</b>	<b>INSOLVEN</b>	<b>GASPROD</b>	<b>LIQPROD</b>	<b>AQUEOUS</b>	<b>ORGANIC</b>
9.9	71.79	68.78	73.65	66.93	9.07	63.04
11.14	73.03	70.01	77.09	65.95	11.32	61.09
12.38	74.29	71.22	80.47	65.04	13.49	59.30
13.62	75.51	72.41	83.75	64.17	15.57	57.62
14.86	76.75	73.58	86.97	63.36	17.59	56.08

**Table S 14.** Results of yield and conversion at different biomass moisture.

<b>Q<sub>H2O</sub> (kg/h)</b>	<b>Yield (%)</b>	<b>Conversion (%)</b>					
		<b>Biomass</b>	<b>Arabinose</b>	<b>Cellulose</b>	<b>p-Coumaryl alcohol</b>	<b>Galactose</b>	<b>Xylose</b>
9.9	64.49	71.89	96.38	63.18	97.17	96.40	96.40
11.14	64.48	71.89	96.38	63.18	97.17	96.40	96.40
12.38	64.48	71.89	96.37	63.18	97.17	96.40	96.40
13.62	64.48	71.89	96.37	63.18	97.17	96.40	96.40
14.86	64.48	71.89	96.37	63.18	97.17	96.40	96.40

**Table S 15.** Results of cooler duty at different moisture.

<b>Q<sub>H2O</sub> (kg/h)</b>	<b>Q<sub>cooler</sub> (kW)</b>
9.9	-18.68
11.14	-19.86
12.38	-21.03
13.62	-22.19
14.86	-23.33

**Table S 16.** Results of stream flow (kg/h) at different biomass/solvent ratio.

<b>Biomass/solvent ratio</b>	<b>FEEDREAC</b>	<b>INSOLVEN</b>	<b>GASPROD</b>	<b>LIQPROD</b>	<b>AQUEOUS</b>	<b>ORGANIC</b>
1.06	74.27	83.47	87.58	70.16	12.24	64.37
1.2	74.27	76.38	83.44	67.21	12.96	61.41
1.33	74.27	71.22	80.46	65.03	13.49	59.29
1.46	74.27	66.95	78.01	63.22	13.92	57.54
1.6	74.27	63.18	75.86	61.60	14.29	56.02

**Table S 17.** Results of yield and conversion at different biomass/solvent ratio.

<b>Biomass/solvent ratio</b>	<b>Yield (%)</b>	<b>Conversion (%)</b>					
		<b>Biomass</b>	<b>Arabinose</b>	<b>Cellulose</b>	<b>p-Coumaryl alcohol</b>	<b>Galactose</b>	<b>Xylose</b>
1.06	63.17	70.54	96.09	61.35	96.95	96.12	96.12

1.2	63.89	71.27	96.25	62.35	97.07	96.28	96.28
1.33	64.48	71.89	96.37	63.18	97.17	96.40	96.40
1.46	64.98	72.39	96.47	63.87	97.25	96.50	96.50
1.6	65.45	72.88	96.57	64.53	97.33	96.60	96.60

**Table S 18.** Results of cooler duty at different biomass/solvent ratio.

<b>Biomass/solvent ratio</b>	<b>Q<sub>cooler</sub> (kW)</b>
1.06	-22.42
1.2	-21.61
1.33	-21.03
1.46	-20.56
1.6	-20.14

**Table S 19.** Ea values (kJ/mol) for each deviation.

<b>Reaction</b>	<b>0%</b>	<b>10%</b>	<b>20%</b>	<b>-10%</b>	<b>-20%</b>
Arabinose	40.49	44.54	48.59	36.44	32.39
Cellulose	109.35	120.28	131.22	98.41	87.48
p-Coumaryl alcohol	44.31	48.74	53.17	39.88	35.45
Galactose	40.49	44.54	48.59	36.44	32.39
Glucose	74.37	81.80	89.24	66.93	59.49
HMF	87.13	95.84	104.56	78.42	69.70
Xylose	40.49	44.54	48.59	36.44	32.39

**Table S 20.** Results of stream flow (kg/h) at different Ea.

<b>Deviation (%)</b>	<b>FEEDREAC</b>	<b>INSOLVEN</b>	<b>GASPROD</b>	<b>LIQPROD</b>	<b>AQUEOUS</b>	<b>ORGANIC</b>
-20	74.27	80.61	99.59	55.29	11.26	74.36
-10	74.27	78.93	96.76	56.43	11.79	72.39
0	74.27	71.22	80.46	65.03	13.49	59.29
10	74.27	64.62	62.64	76.25	12.78	47.18
20	74.27	59.74	54.23	79.78	12.42	43.57

**Table S 21.** Results of yield and conversion at different Ea.

<b>Deviation (%)</b>	<b>Yield (%)</b>	<b>Conversion (%)</b>					
		<b>Biomass</b>	<b>Arabinose</b>	<b>Cellulose</b>	<b>p-Coumaryl alcohol</b>	<b>Galactose</b>	<b>Xylose</b>
-20	91.50	99.55	99.60	99.87	99.75	99.61	99.61
-10	88.47	96.36	98.79	97.28	99.16	98.80	98.80
0	64.49	71.89	96.37	63.18	97.17	96.40	96.40

10	34.61	41.96	89.63	7.61	90.95	89.70	89.70
20	25.49	31.99	73.76	0.39	74.61	73.87	73.88

**Table S 22.** Results of cooler duty at different Ea.

<b>Deviation (%)</b>	<b>Q<sub>cooler</sub> (kW)</b>
-20	-25.14
-10	-24.50
0	-21.03
10	-17.41
20	-15.48

## References

1. Yan, L.; Greenwood, A.A.; Hossain, A.; Yang, B. A Comprehensive Mechanistic Kinetic Model for Dilute Acid Hydrolysis of Switchgrass Cellulose to Glucose, 5-HMF and Levulinic Acid. *RSC Adv* **2014**, *4*, 23492–23504, doi:10.1039/C4RA01631A.