

Optimization of Biochar Production by Co-Torrefaction of Microalgae and Lignocellulosic Biomass Using Response Surface Methodology

Catarina Viegas ^{1,*}, Catarina Nobre ², Ricardo Correia ¹, Luísa Gouveia ³ and Margarida Gonçalves ¹

¹ METRICS, Mechanical Engineering and Resource Sustainability Center, Department of Science and Technology of Biomass, FCT-NOVA, Campus de Caparica, 2829-516 Caparica, Portugal; rjc07189@campus.fct.unl.pt (R.C.); mmpg@fct.unl.pt (M.G.)

² CoLAB BIOREF—Collaborative Laboratory for Biorefineries, Rua Amieira Apartado 1089, 4466-901 S. Mamede Infesta, Portugal; catarina-nobre@bioref-colab.pt

³ LNEG—Laboratório Nacional de Energia e Geologia, I.P./Bioenergy Unit, Estrada do Paço do Lumiar 22, 1649-038 Lisbon, Portugal; luisa.gouveia@lneg.pt

* Correspondence: cv.sousa@campus.fct.unl.pt

Table S1. Experimental design matrix using the RSM modelling technique (Cv – Microalgae sludge, Lc – Lignocellulosic biomass) and corresponding masses of Cv, Lc and water introduced in the reactor.

Run	Temperature (°C)	Time (min)	Lc Incorporation rate (%)	Moisture content (%)	Cv (g)	Added water (g)	Lc (g)	Total water in feed* (g)	Total feed mass (g)
1	300	60	50	30	3.5	4.9	10.0	5.6	18.4
2	300	60	25	15	12.0	2.2	5.0	2.9	19.2
3	300	60	25	15	12.0	2.2	5.0	2.9	19.2
4	300	45	0	45	11.0	8.5	0.0	8.8	19.5
5	300	45	100	5	0.0	0.0	20.0	1.0	20.0
6	300	45	50	5	10.0	0.0	10.0	1.0	20.0
7	300	45	0	5	20.0	0.0	0.0	1.0	20.0
8	300	30	50	30	5.5	5.6	10.0	6.4	21.1
9	300	15	25	45	5.2	7.5	5.0	8.0	17.7
10	300	15	0	45	11.0	8.0	0.0	8.6	19.0
11	300	15	50	5	10.0	0.0	10.0	1.0	20.0
12	275	60	0	70	7.0	15.2	0.0	15.6	22.2
13	275	45	25	30	8.5	4.9	5.0	5.6	18.4
14	250	60	0	15	16.0	1.9	0.0	2.7	17.9
15	250	60	50	5	10.0	0.0	10.0	1.0	20.0
16	250	45	50	30	3.5	4.9	10.0	5.6	18.4
17	250	45	25	30	8.5	4.9	5.0	5.6	18.4
18	250	45	25	30	8.5	4.9	5.0	5.6	18.4
19	250	45	25	15	12.0	2.0	5.0	2.9	19.0
20	250	45	25	15	12.0	2.0	5.0	2.9	19.0
21	250	30	25	45	5.2	7.5	5.0	8.0	17.7
22	250	30	25	45	5.2	7.5	5.0	8.0	17.7
23	250	30	50	15	8.0	2.2	10.0	3.1	20.2
24	250	30	25	5	15.0	0.0	5.0	1.0	20.0
25	250	15	50	30	5.5	5.6	10.0	6.4	21.1
26	250	15	0	5	20.0	0.0	0.0	1.0	20.0
27	250	15	0	5	20.0	0.0	0.0	1.0	20.0
28	225	60	25	5	15.0	0.0	5.0	1.0	20.0
29	225	45	0	45	11.0	8.0	0.0	8.6	19.0
30	225	15	25	15	12.0	2.0	5.0	2.9	19.0
31	200	60	25	45	5.2	7.5	5.0	8.0	17.7
32	200	60	50	30	5.5	5.6	10.0	6.4	21.1
33	200	60	0	5	20.0	0.0	0.0	1.0	20.0
34	200	30	25	15	12.0	2.0	5.0	2.9	19.0
35	200	30	25	15	12.0	2.0	5.0	2.9	19.0
36	200	30	50	5	10.0	0.0	10.0	1.0	20.0
37	200	15	0	70	7.0	15.2	0.0	15.6	22.2
38	200	15	50	30	3.5	4.9	10.0	5.6	18.4
39	200	15	25	30	8.5	4.9	5.0	5.6	18.4

*Total water in feed corresponds to the sum of the added water and the residual moisture present in the Cv and Lc biomasses introduced in the reactor.

Table S2. Equations generated by RSM software, with R², Adjusted R², Predicted R² and Adequate Precision for product yields

Parameter	Equation **	Model F-value	R ²	Adjusted R ²	Predicted R ²	Adequate Precision
Char Yield	$86.52 + 0.40 T - 0.62 t - 2.10 M + 0.14 I + 3.97 \times 10^{-3} (T \times M) - 1.53 \times 10^{-3} (T \times I) - 1.26 \times 10^{-3} (T^2) + 4.20 \times 10^{-3} (t^2) + 5.34 \times 10^{-3} (M^2) + 1.52 \times 10^{-3} (I^2)$	130.00	0.980	0.973	0.950	40.754
Condensate Yield	$-1.10 + 0.01 T - 0.30 t + 0.10 M + 9.70 \times 10^{-5} I - 1.20 \times 10^{-4} (T \times M) - 2.70 \times 10^{-4} (t \times M) - 5.39 \times 10^{-4} (M^2)$	26.19	0.859	0.827	0.698	16.900
Gas Yield	$-24.66 + 0.16 T + 0.24 t + 0.43 M - 0.07 I - 1.80 \times 10^{-3} (T \times t) - 3.28 \times 10^{-3} (T \times M) - 9.92 \times 10^{-3} (t \times M) - 1.40 \times 10^{-3} (M \times I)$	5.53	0.604 ¹	0.595	0.340	9.911
Aqueous Phase Yield	$-1.87 + 3.05 \times 10^{-3} T - 9.29 \times 10^{-3} t + 0.05 M + 0.08 I + 7.50 \times 10^{-5} (T \times t) - 2.20 \times 10^{-5} (t \times I) - 1.30 \times 10^{-5} (M \times I) - 4.42 \times 10^{-4} (M^2) - 5.64 \times 10^{-4} (I^2)$	30.58	0.908	0.878	0.611	27.606
Bio-oil Yield	$47.98 - 0.45 T + 0.38 t + 0.55 M - 0.42 I - 1.97 \times 10^{-3} (T \times M) + 1.88 \times 10^{-3} (T \times I) - 2.92 (t \times M) + 8.98 \times 10^{-4} (T^2) - 3.14 \times 10^{-3} (t^2)$	18.98	0.864	0.818	0.700	18.463

Note: p-value model is always 0.01%, and it means that there is only a 0.01% chance that an F-value this large could occur due to noise.

The equations did not undergo any transformations except the Condensate and Aqueous phase equations with a natural log transformation.

The Lak of Fit is not significant (< 4), except for the parameter Bio-oil (Lak of Fit of 6.06)

** Where T, t, M and I means temperature, residence time, moisture and incorporation rate of lignocellulosic material, respectively.

1 – a low R² suggests a dispersion of values that decrease the predictability of the model [39].

Table S3. Equations generated by RSM software, with R², Adjusted R², Predicted R² and Adequate Precision for char characterization

Parameter	Equation **	Model F-value	R ²	Adjusted R ²	Predicted R ²	Adeq. Precision
Ash	$18.09 - 0.16 T + 0.04 t + 0.02 M - 0.02 I - 1.53 \times 10^{-4} (T \times t) - 7.10 \times 10^{-5} (T \times M) + 9.40 \times 10^{-5} (T \times I) - 1.50 \times 10^{-4} (t \times M) - 5.90 \times 10^{-5} (M \times I) + 3.53 \times 10^{-4} (T^2) - 3.03 \times 10^{-4} (I^2)$	57.80	0.962	0.946	0.886	23.239
Volatile Matter	$-57.02 + 1.12 T - 0.06 t - 0.489 M + 0.39 I - 3.40 \times 10^{-3} (T \times t) + 3.68 \times 10^{-3} (t \times I) + 6.44 \times 10^{-3} (M \times I) - 2.26 \times 10^{-3} (T^2) + 5.52 \times 10^{-3} (t^2) - 3.38 \times 10^{-3} (I^2)$	41.07	0.943	0.920	0.874	27.313
Fixed carbon	$116.76 - 0.80 T - 0.74 t - 0.54 M + 0.16 I + 3.12 \times 10^{-3} (T \times t) + 1.42 \times 10^{-3} (T \times M) - 9.18 \times 10^{-4} (T \times I) + 2.73 \times 10^{-3} (t \times M) + 1.66 \times 10^{-3} (T^2)$	80.69	0.964	0.952	0.920	39.412
O/C ratio	$0.88 - 1.67 \times 10^{-3} T + 3.46 \times 10^{-3} t + 9.30 \times 10^{-3} M - 1.98 \times 10^{-4} I - 2.60 \times 10^{-5} (T \times t) - 9.50 \times 10^{-5} (M \times I)$	60.89	0.921	0.910	0.871	26.910
H/C ratio	$2.48 - 3.74 \times 10^{-3} T - 5.96 \times 10^{-3} t + 1.14 \times 10^{-3} M + 1.85 \times 10^{-3} I - 3.10 \times 10^{-5} (T \times t) + 1.13 \times 10^{-4} (t^2)$	102.92	0.954	0.944	0.923	35.734
Char adsorption capacity	$273.18 - 0.80 T - 0.66 t - 2.74 M + 0.20 I + 9.55 \times 10^{-3} (T \times M)$	38.40	0.857	0.835	0.786	19.010

Note: p-value model is always 0.01%, and it means that there is only a 0.01% chance that an F-value this large could occur due to noise. The equations did not undergo any transformations except Ash equation with a natural log transformation. The Lak of Fit is not significant (<4), except for parameters Volatile Matter (Lak of Fit of 9.18) and Char adsorption capacity (Lak of Fit of 108.61).

** Where T, t, M and I means temperature, residence time, moisture and incorporation rate of lignocellulosic material, respectively.

Table S4. Equations generated by RSM software, with R², Adjusted R², Predicted R² and Adequate Precision for Q_{input} and Q_{output}.

Parameter	Equation **	Model F-value	R ²	Adjusted R ²	Predicted R ²	Adeq. Precision
Q _{input}	$1.66 + 6.89 \times 10^{-4} T - 4.70 \times 10^{-3} t + 3.36 \times 10^{-2} M + 6.367 \times 10^{-3} I$	59.44	0.878	0.863	0.821	27.054
Q _{output}	$0.38 + 8.30 \times 10^{-5} T - 1.94 \times 10^{-3} t - 8.35 \times 10^{-3} M + 2.19 \times 10^{-3} I + 1.3 \times 10^{-5} (T \times M) - 1.20 \times 10^{-5} (T \times I) - 2.10 \times 10^{-5} (t \times M) + 1.50 \times 10^{-5} (t \times I) + 4.80 \times 10^{-5} (M^2)$	193.09	0.988	0.983	0.972	49.376

Note: p-value model is always 0.01%, and it means that there is only a 0.01% chance that an F-value this large could occur due to noise.

The Lak of Fit is not significant (< 4).

** Where T, t, M and I means temperature, residence time, moisture and incorporation rate of lignocellulosic material, respectively.