Valorization of Napier grass via intermediate pyrolysis: Optimization using response surface methodology and pyrolysis products characterization

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Table 1: Range of independent variables and experimental levels

Variables	**Experimental levels**		
	-1	**0**	**+1**
Temperature (^{o}C): A	450	600	750
Nitrogen flow (L/min): B	5	15	25
Heating rate (^{o}C/min): C	10	30	50

Table 2: Characteristics of Napier grass biomass used

Standard used	Property	NGS (this study)	Strezov et al. (2008)	Lee et al. (2010)	Braga et al. (2014)	Sousa et al. (2016)	De Conto et al. (2016)
	Proximate analysis (wt%)						
BS EN 14774-1:2009	Moisture Content[a]	75.27 ± 0.21	12.40	9.43	10.04	-	10.63
BS EN 15148:2009	Volatile Matter[b]	81.51 ± 0.26	66.90	72.58	65.00	-	72.54
BS EN 14775:2009	Ash Content[b]	1.75 ± 0.04	2.90	9.68	6.90	-	8.26
	Fixed Carbon[c]	16.74 ± 0.05	-	-	14.66	-	19.20
BS EN 14918:2009	HHV(MJ/kg)	18.05 ± 0.07	-	-	15.61	-	15.77
	Ultimate analysis (wt%) dry basis						
	Carbon (C)	51.61 ± 0.24	41.6	42.4	44.5	41.85	39.63
	Hydrogen (H)	6.01 ± 0.02	4.83	5.96	5.4	6.77	6.31
	Nitrogen (N)	0.99 ± 0.01	0.43	1.71	1.4	0.72	1.7
	Sulfur (S)	0.32 ± 0.01	-	0.09	-	48.64	0.2
	Oxygen (O)[c]	41.07 ± 0.02	-	45.32	31.8	-	52.16
	O/C (atomic ratio)	0.8	-	-	-	-	-
	H/C (atomic ratio)	0.12	-	-	-	-	-
NREL/TP-510-42618	Structural composition (wt%)						
	Cellulose	38.75 ± 2.30		66.59	39.14	-	30.37
	Hemicellulose	19.76 ± 1.68			19.9	-	31.31
	Lignin	26.99 ± 1.29		26.72	6.18	-	26.02
	Extractives	12.07 ± 0.32		-		-	14.86
BS EN 15290:2011	Atomic absorption analysis of ash (mg/kg)						
	Sodium (Na)	12.85±1.05	-	-	-	-	-
	Potassium (K)	3079.51±224.80	-	-	-	-	-
	Calcium (Ca)	206.71±13.20	-	-	-	-	-
	Aluminum (Al)	64.67±4.66	-	-	-	-	-
	Iron (Fe)	38.93±4.01	-	-	-	-	-
	Silicon (Si)	206.0±25.13	-	-	-	-	-

Notes: [a] as received at harvest; [b] dry basis; [c] by difference; (NGS) Napier grass stem. Values are the means (n =3) ± standard deviations

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Table 3: CCD Experimental Design Matrix and Response

	Actual level factors			Coded level factors			Response (%)		
Runs	**Temperature (^oC) (A)**	**N_2 flow (L/min)(B)**	**Heating rate (^oC/min)(C)**	**A**	**B**	**C**	**Bio-oil**	**Bio-char**	**Non-condensable**
1	600	25	30	0	1	0	48.12	21.67	30.21
2	750	25	10	1	1	-1	37.11	19.61	43.28
3	600	15	30	0	0	0	48.67	22.96	28.37
4	600	15	10	0	0	-1	46.13	23.18	30.70
5	750	5	10	1	-1	-1	38.87	19.23	41.90
6	600	15	30	0	0	0	49.42	22.89	27.69
7	450	5	10	-1	-1	-1	30.11	41.29	28.61
8	750	5	50	1	-1	1	39.37	18.79	41.83
9	450	25	10	-1	1	-1	29.99	46.41	23.60
10	600	15	30	0	0	0	49.88	21.13	28.98
11	450	25	50	-1	1	1	38.37	42.83	18.79
12	600	15	30	0	0	0	48.97	21.89	29.14
13	600	5	30	0	-1	0	52.06	21.89	26.05
14	600	15	30	0	0	0	49.20	20.44	30.36
15	600	15	30	0	0	0	50.16	20.83	29.01
16	750	15	30	1	0	0	37.85	20.59	41.57
17	450	5	50	-1	-1	1	37.09	42.09	20.81
18	450	15	30	-1	0	0	34.22	43.89	21.89
19	600	15	50	0	0	1	50.89	19.22	29.89
20	750	25	50	1	1	1	36.92	19.42	43.66

Responses are the average values (n= 2)

Table 4(a): ANOVA test for bio-oil response model and respective model term

Source	Sum of squares	df	Mean square	F-value	prob >F	Remark
Model	1014.97	9	112.77	171.60	< 0.0001	significant
A	41.35	1	41.35	62.92	< 0.0001	significant
B	4.90	1	4.90	7.46	0.0211	significant
C	41.79	1	41.79	63.59	< 0.0001	significant
A^2	487.13	1	487.13	741.20	< 0.0001	significant
B^2	1.55	1	1.55	2.36	0.1556	
C^2	1.91	1	1.91	2.91	0.1187	
AB	3.63	1	3.63	5.52	0.0407	significant
AC	28.34	1	28.34	43.12	< 0.0001	significant
BC	0.06	1	0.06	0.10	0.7642	
Residual	6.57	10	0.66			
Lack of Fit	5.00	5	1.00	3.18	0.1151	not significant
Pure Error	1.57	5	0.31			
Cor Total	1021.54	19				
Std. Dev.	0.81		R-Squared	0.9936		
Mean	42.67		Adj R-Squared	0.9878		
C.V.	1.90		Pred R-Squared	0.9518		
PRESS	49.28		Adeq Precision	36.4925		

Table 4(b): ANOVA test for bio-char response model and respective model term

Source	Sum of squares	df	Mean square	F-value	prob >F	Remark
Model	1911.12	9	212.35	151.22	< 0.0001	significant
A	1413.01	1	1413.01	1006.27	< 0.0001	significant
B	4.42	1	4.42	3.15	0.1065	
C	5.40	1	5.40	3.84	0.0784	
A^2	292.88	1	292.88	208.58	< 0.0001	significant
B^2	0.05	1	0.05	0.04	0.8491	
C^2	1.42	1	1.42	1.01	0.3380	
AB	2.94	1	2.94	2.09	0.1788	
AC	0.58	1	0.58	0.41	0.5361	
BC	2.14	1	2.14	1.53	0.2450	
Residual	14.04	10	1.40			
Lack of Fit	8.35	5	1.67	1.47	0.3421	not significant
Pure Error	5.69	5	1.14			
Cor Total	1925.16	19				
Std. Dev.	1.18		R-Squared	0.9927		
Mean	26.51		Adj R-Squared	0.9861		
C.V.	4.47		Pred R-Squared	0.9411		
PRESS	113.31		Adeq Precision	32.8072		

Table 4(c): ANOVA test for non-condensable gas response model and respective model term

Source	**Sum of squares**	**df**	**Mean square**	**F-value**	**prob >F**	Remark
Model	1093.29	9	121.48	69.74	< 0.0001	significant
A	970.91	1	970.91	557.41	< 0.0001	significant
B	0.01	1	0.01	0.01	0.9339	
C	17.15	1	17.15	9.85	0.0105	significant
A^2	24.57	1	24.57	14.11	0.0037	significant
B^2	1.03	1	1.03	0.59	0.4601	
C^2	6.64	1	6.64	3.81	0.0795	
AB	13.09	1	13.09	7.52	0.0208	significant
AC	20.83	1	20.83	11.96	0.0061	significant
BC	1.47	1	1.47	0.85	0.3794	
Residual	17.42	10	1.74			
Lack of Fit	13.47	5	2.69	3.41	0.1020	not significant
Pure Error	3.95	5	0.79			
Cor Total	1110.71	19				
Std. Dev.	1.32		R-Squared	0.9843		
Mean	30.82		Adj R-Squared	0.9702		
C.V.	4.28		Pred R-Squared	0.8903		
PRESS	121.87		Adeq Precision	27.3167		

Table 5(a): Optimization condition (constraints)

Constraints		Lower	Upper	Lower	Upper	
Name	**Goal**	**Limit**	**Limit**	**Weight**	**Weight**	**Importance**
Temperature	is in range	450	750	1	1	3
Nitrogen flow	is in range	5	25	1	1	3
Heating rate	is in range	10	50	1	1	3
Bio-oil Yield	maximize	29.9921	52.0642	1	1	5
Bio-char Yield	minimize	18.7939	46.4071	1	1	1
Non-condensable gas Yield	minimize	18.7939	43.6589	1	1	1

Table 5(b): Optimized solutions

Solutions				Yield (%)				
Number	**Temperature (^oC)**	**Nitrogen flow (L/min)**	**Heating rate (^oC/min)**	**Bio-oil**	**Bio-char**	**Non-condensable gas**	**Desirability**	
1	**599.68**	**5.00**	**50.00**	**51.9376**	**20.0643**	**27.9981**	**0.9260**	**Selected**
2	599.80	5.00	49.38	51.9284	20.1068	27.9648	0.9258	
3	595.63	5.00	47.74	51.8548	20.5494	27.5958	0.9244	
4	590.77	25.00	50.00	50.6973	21.1272	28.1755	0.8817	
5	591.73	25.00	49.71	50.6956	21.0801	28.2244	0.8814	
6	594.45	25.00	49.71	50.7087	20.8416	28.4497	0.8812	
7	591.70	25.00	49.32	50.6836	21.1339	28.1825	0.8812	
8	578.88	25.00	49.99	50.5248	22.2634	27.2119	0.8782	

Table 6: Bio-oil yield predicated at optimized condition and experimental value

Run	Temperature	Nitrogen flow	Heating rate	Bio-oil Yield (wt %)	
	(^{o}C)	(L/min)	(^{o}C/min)	Experimental	Predicted
1	600	5	50	51.56	5136.6942
2	600	5	50	48.14	51.9436.62
3	600	5	50	52.02	51.9436.62
Average				**50.57**	**51.94**

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Table 7: Physicochemical properties of bio-oil produced at optimized condition compared with the ASTM D7544-12 specifications

Property	**Organic phase**	**ASTM-Grade G**	**ASTM-Grade D**	**Aqueous phase**
Appearance	Black	-	-	Dark brown
pH	3.71±0.01	Report	Report	2.09±0.01
Water content (wt%)	7.24±0.21	30 max.	30 max.	62.44±0.25
Density (g/cm^3)[1]	0.981±0.0	1.1-1.3	1.1-1.3	1.052±0.0
Viscosity (cSt)[2]	2.04±0.17	125 max.	125 max.	1.20±0.14
Solid (wt%)[3]	<0.100	2.5 max.	0.25 max	0.00
Ash (wt%)	0.012±0.0	0.25 max	0.15 max	-
Carbon (wt%)	51.14±1.72			15.27±1.43
Hydrogen (wt%)	6.22±0.07			13.80±0.09
Nitrogen (wt%)	0.78±0.01			1.45±0.03
Sulfur (wt%)	0.20±0.01	0.05 max.	0.05 max.	0.10±0.01
Oxygen (wt%)[4]	41.66±1.01			69.38±1.27
HHV (MJ/kg)	26.42±0.10	15 min.	15 min.	14.55±0.10

[1]Measured at 20^{o}C; [2]Measured at 40^{o}C; [3]ethanol insoluble (0.1µm filter); [4]by difference. Max: maximum value; Min: minimum value. Values are the means (n =3) ± standard deviations (SD)

Table 8(a): GC-MS analysis of organic phase bio-oil obtained at optimized condition

RT (min)	Compound	Formula	Area%
	Organic Phase		
3.85	1,3-DIMETHYL-1-CYCLOHEXENE	C_8H_{14}	4.67
4.03	1H-IMIDAZOLE-2-METHANOL	$C_4H_6ON_2$	3.05
5.13	PHENOL	C_6H_6O	8.43
5.76	PHENOL, 2-METHYL-	C_7H_8O	4.06
5.93	PHENOL, 3-METHYL-	C_7H_8O	4.96
6.06	PHENOL, 2-METHOXY-	$C_7H_8O_2$	7.65
6.51	PHENOL, 2,4-DIMETHYL-	$C_8H_{10}O$	2.50
6.64	PHENOL, 3-ETHYL-	$C_8H_{10}O$	8.20
6.86	CREOSOL	$C_8H_{10}O_2$	3.68
7.03	BENZALDEHYDE, 4-METHYL-	C_8H_8O	13.41
7.47	PHENOL, 4-ETHYL-2-METHOXY-	$C_9H_{12}O_2$	5.39
7.73	2-METHOXY-4-VINYLPHENOL	$C_9H_{10}O_2$	6.74
7.96	PHENOL, 2,6-DIMETHOXY-	$C_8H_{10}O_3$	8.85
8.57	1,2,3-TRIMETHOXYBENZENE	$C_9H_{12}O_3$	2.18
8.63	PHENOL, 2-METHOXY-4-(1-PROPENYL)-, (Z)-	$C_{10}H_{12}O_2$	2.44
9.05	4-ETHYLBIPHENYL	$C_{14}H_{14}$	2.53
9.30	4-METHYL-2,5-DIMETHOXYBENZALDEHYDE	$C_{10}H_{12}O_3$	1.74
10.08	PHENOL, 2,6-DIMETHOXY-4-(2-PROPENYL)-	$C_{11}H_{14}O_3$	3.12
10.43	DESASPIDINOL	$C_{11}H_{14}O_4$	1.73
19.06	1,4-BENZENEDICARBOXYLIC ACID, BIS(2-ETHYLHEXYL) ESTER	$C_{24}H_{38}O_4$	4.68

Table 8(b): GC-MS analysis of aqueous phase bio-oil obtained at optimized condition

RT (min)	Compound	Formula	Area%
	Aqueous Phase		
3.31	1,2,4,5-CYCLOHEXANETETROL, (1.ALPHA.,2.ALPHA.,4.ALPHA.,5.BETA.)-	$C_6H_{12}O_4$	3.24
3.85	CARBONIC ACID, 2,2,2-TRICHLOROETHYL CYCLOHEXYLMETHYL ESTER	$C_{10}H_{15}O_3Cl_3$	8.65
4.06	Z,Z-6,28-HEPTATRIACTONTADIEN-2-ONE	$C_{37}H_{70}O$	6.51
4.52	CYCLOHEXENE, 3,5-DIMETHYL-	C_8H_{14}	4.28
4.58	BUT-3-EN-1-YL 2-METHYLBUTANOATE	$C_9H_{16}O_2$	3.86
4.70	UNDECANOIC ACID, 11-MERCAPTO-	$C_{11}H_{22}O_2S$	4.03
5.15	PHOSPHONIC ACID, (P-HYDROXYPHENYL)-	$C_6H_7O_4P$	6.25
5.36	FURAN, TETRAHYDRO-2,5-DIMETHOXY-	$C_6H_{12}O_3$	2.75
5.56	2-ETHYL-5-PROPYLCYCLOPENTANONE	$C_{10}H_{18}O$	5.11
6.06	IMIDAZOLE, 2-AMINOCARBONYL-1-METHYL-	$C_5H_7ON_3$	7.14
6.64	1,3,5-CYCLOHEPTATRIENE, 1-METHOXY-	$C_8H_{10}O$	4.22
6.91	2-PROPENAMIDE, N-(4-AMINOBUTYL)-3-(3,4-DIHYDROXYPHENYL)-, (E)-	$C_{13}H_{18}O_3N_2$	11.20
7.04	BENZENE, (ETHENYLOXY)-	C_8H_8O	5.31
7.38	1,2-BENZENEDIOL, 3-METHOXY-	$C_7H_8O_3$	5.91
7.96	PHENOL, 2,6-DIMETHOXY-	$C_8H_{10}O_3$	9.14
8.56	PHENOL, 4-METHOXY-3-(METHOXYMETHYL)-	$C_9H_{12}O_3$	3.37
9.04	BENZENE, 1,2,3-TRIMETHOXY-5-METHYL-	$C_{10}H_{14}O_3$	2.14
9.10	2-PROPANONE, 1-(4-HYDROXY-3-METHOXYPHENYL)-	$C_{10}H_{12}O_3$	2.51
10.08	PHENOL, 2,6-DIMETHOXY-4-(2-PROPENYL)-	$C_{11}H_{14}O_3$	2.02
10.42	BENZENEMETHANOL, 2,5-DIMETHOXY-, ACETATE	$C_{11}H_{14}O_4$	2.34

Table 9: Physicochemical properties of NGS bio-char produced at 50 ^{o}C/min and 5 L/min nitrogen flow at different pyrolysis temperature

Pyrolysis temperature (°C)			
Property	450	600	750
Proximate analysis (wt%) dry basis			
Ash	10.47±0.29	13.40±0.31	14.49±0.30
Volatile matter (VM)	19.41±0.21	15.09±0.17	12.70±0.13
Fixed carbon (FC)	70.12±0.51	71.51±0.51	72.81±0.50
FC/(VM+FC)	0.78	0.83	0.85
HHV (MJ/kg)	29.06±0.01	27.60±0.01	26.71±0.01
Ultimate analysis (wt%) dry basis			
Carbon (C)	72.21±0.41	79.78±0.44	85.86±0.42
Hydrogen (H)	5.20±0.01	3.61±0.01	2.67±0.01
Nitrogen (N)	1.16±0.01	0.98±0.00	0.66±0.00
Sulfur (S)	0.30±0.00	0.18±0.00	0.11±0.00
Oxygen (O)	21.13±0.22	15.45±0.20	10.70±0.21
O/C (mole ratio)	0.22	0.15	0.09
Physisorption analysis			
Surface area (BET) (m^2/g)	0.014	0.126	0.293
Pore volume (cm^3/g)	0.008	0.100	0.130

Values are the means (n =3) ± standard deviations (SD)