Effects of pretreatments of Napier Grass with deionized water, sulfuric acid and sodium hydroxide on pyrolysis oil characteristics

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Table 1: Mineral composition of raw NGS and pretreated samples using NaOH, H_2SO_4 and deionized water

Pretreatment		Mineral Composition (mg/kg)					
	Ro	Na	K	Ca	Al	Fe	Si
Raw	0.0	12.85±1.05	3079.51±224.80	206.71±13.20	64.67±4.66	38.93±4.01	206.0±25.13
H_2O	0.4	4.63±0.34	1299.02±94.83	182.51±5.28	57.27±1.96	35.80±1.63	187.19±21.62
	0.9	2.67±0.22	1120.98±81.83	168.74±4.40	53.61±1.72	33.57±1.40	182.39±21.03
	2.1	2.40±0.15	1099.02±80.23	163.03±4.03	53.20±1.72	33.35±1.38	181.91±20.97
	2.4	1.99±0.12	974.63±71.14	147.56±3.04	52.98±1.72	31.74±1.21	180.47±20.80
	2.7	1.28±0.08	800.49±58.44	136.67±2.35	52.88±1.75	29.57±0.99	179.99±20.74
H_2SO_4	(w/w%)						
	0.5	4.10±0.24	988.20±62.56	166.15±3.80	51.18±1.44	33.65±2.90	219.22±30.62
	1.0	2.08±0.17	733.88±55.11	152.55±2.90	45.80±1.65	28.32±2.11	247.29±31.24
	1.5	1.48±0.14	483.88±27.21	105.33±2.10	39.98±1.35	24.99±1.90	253.78±31.37
	2.0	1.26±0.10	278.22±15.89	89.55±2.90	33.33±1.31	18.25±1.77	282.44±35.65
	2.5	0.47±0.07	142.88±12.63	52.75±2.90	30.78±1.28	16.75±1.69	338.79±38.85
NaOH	(w/w%)						
	0.5	387.14±24.33	873.35±34.76	169.51±3.20	57.61±1.66	32.65±2.80	78.78±2.85
	1.0	431.29±27.17	565.78±31.17	142.94±2.78	40.75±1.28	30.32±2.41	51.39±2.55
	1.5	459.56±26.14	334.15±23.14	123.81±2.40	29.38±1.15	27.99±2.00	36.69±2.19
	2.0	557.22±27.10	322.76±20.10	88.21±2.03	20.33±1.11	23.25±1.97	31.81±2.05
	2.5	593.20±28.07	290.48±18.07	53.67±1.40	14.13±1.08	21.75±1.59	26.42±1.99

Pretreatment	Proximate analysis (wt%)	(MJ/kg)	Ultimate analysis (wt%)

	Ro	A	VM	FC	HHV	C	H	N	S	O*	O/C	H/C
Raw	0.0	1.75±0.04	81.51±0.26	16.74±0.05	18.11±0.06	48.61±0.24	6.01±0.02	0.99±0.01	0.32±0.01	42.32±0.20	0.871	0.124
H_2O	0.4	1.40±0.02	84.21±0.27	14.39±0.04	18.22±0.06	48.97±0.24	5.99±0.02	0.82±0.01	0.30±0.01	42.52±0.21	0.868	0.122
	0.9	0.87±0.02	84.76±0.27	14.37±0.04	18.47±0.06	49.01±0.25	6.00±0.02	0.74±0.01	0.28±0.01	43.10±0.20	0.879	0.122
	2.1	0.75±0.02	85.01±0.26	14.25±0.04	18.67±0.06	49.07±0.25	5.99±0.02	0.75±0.01	0.29±0.01	43.16±0.20	0.879	0.122
	2.4	0.71±0.02	85.13±0.28	14.16±0.04	18.82±0.06	49.02±0.25	5.98±0.02	0.64±0.01	0.30±0.01	43.35±0.20	0.884	0.122
	2.7	0.63±0.02	85.21±0.28	14.17±0.03	19.17±0.07	49.12±0.24	5.98±0.02	0.61±0.01	0.29±0.01	43.38±0.21	0.883	0.122
H_2SO_4	Conc (w/w%)											
	0.5	0.78±0.02	88.28±0.27	10.94±0.03	18.62±0.05	50.34±0.25	5.76±0.02	0.79±0.01	0.23±0.01	42.10±0.21	0.836	0.114
	1.0	0.69±0.02	88.45±0.28	10.86±0.03	18.99±0.05	50.53±0.24	5.59±0.02	0.78±0.01	0.20±0.01	42.21±0.21	0.835	0.111
	1.5	0.53±0.02	88.76±0.29	10.71±0.03	19.64±0.06	50.63±0.25	5.45±0.03	0.71±0.01	0.21±0.01	42.47±0.20	0.839	0.108
	2.0	0.40±0.02	88.92±0.26	10.68±0.04	19.82±0.07	50.75±0.25	5.37±0.02	0.67±0.01	0.20±0.01	42.61±0.20	0.840	0.106
	2.5	0.34±0.02	89.09±0.29	10.57±0.03	19.98±0.06	50.81±0.25	5.31±0.03	0.59±0.01	0.19±0.01	42.76±0.20	0.841	0.105
NaOH	Conc (w/w%)											
	0.5	1.05±0.04	87.54±0.26	11.41±0.04	17.17±0.06	48.91±0.24	5.87±0.02	0.81±0.01	0.27±0.01	43.09±0.22	0.881	0.120
	1.0	1.08±0.03	87.16±0.26	11.77±0.04	17.09±0.06	48.84±0.24	5.83±0.02	0.69±0.01	0.19±0.01	43.38±0.21	0.888	0.119
	1.5	1.13±0.04	86.78±0.26	12.10±0.03	16.90±0.04	48.79±0.24	5.78±0.02	0.65±0.01	0.13±0.01	43.53±0.20	0.892	0.118
	2.0	1.20±0.04	86.23±0.27	12.57±0.04	16.77±0.06	48.74±0.25	5.72±0.02	0.59±0.01	0.10±0.01	43.65±0.21	0.896	0.117
	2.5	1.23±0.04	85.04±0.26	13.74±0.03	16.64±0.05	48.69±0.24	5.62±0.02	0.54±0.01	0.07±0.01	43.86±0.20	0.901	0.115

Table 2: Proximate and ultimate analyses of raw biomass and pretreated samples (dry basis).

Ash, (VM) volatile matter, (FC) fixed carbon, (HHV) higher heating value, (C) carbon, (H) hydrogen, (N)nitrogen, (S) sulfur, (O) oxygen, (Ro) severity factor
*By difference [O =100-(A+C+H+N+S)]

Table 3: Characteristics of leachate from aqueous pretreatment of Napier grass

Solvent	Ro	pH	Leachate Property Spgr @ 20°C	Sugar Concentration (°Bx)	g/L
H_2O					
	0.37	4.02	1.0120	3.11	31.47
	0.85	3.91	1.0130	3.36	34.04
	2.09	3.94	1.0126	3.26	33.01
	2.38	3.90	1.0126	3.26	33.01
	2.73	3.94	1.0131	3.39	34.35
H_2SO_4		Conc. (w/w%)			
	0.5	1.30	1.0602	14.88	157.79
	1.0	1.20	1.0610	15.07	159.70
	1.5	1.09	1.0615	15.18	161.16
	2.0	0.92	1.0617	15.23	161.73
	2.5	0.55	1.0621	15.32	162.74
NaOH		Conc. (w/w%)			
	0.5	13.70	1.0276	7.04	72.35
	1.0	13.72	1.0280	7.14	73.41
	1.5	13.92	1.0285	7.26	74.67
	2.0	>14.00	1.0287	7.31	75.20
	2.5	>14.00	1.0289	7.36	75.73

Table 4: Physicochemical characteristics of bio-oil from raw and pretreated Napier grass samples.

Property	Bio-oil			
	RNGS	WTNGS	ACTNGS	ALTNGS
Appearance	Dark black homogeneous liquid			
Physicochemical				
pH	2.95±0.01	2.92±0.01	2.68±0.01	3.26±0.01
Water content (wt%)	26.01±0.22	20.52±0.24	17.36±0.221	27.47±0.25
Viscosity (cp) @ 25 °C	2.71±0.13	2.81±0.16	2.96±0.17	2.17±0.15
Density (kg/m^3)@ 25 °C	1055±00	1077±00	1089±00	1032±00
HHV (MJ/kg)$_{dry}$	20.97±0.10	22.22±0.10	27.96±0.10	21.94±0.10
Ultimate analysis (wt%)				
C	45.32±0.81	46.01±0.82	48.95±0.82	45.12±0.79
H	7.17±0.13	6.59±0.12	6.02±0.11	7.39±0.11
N	0.81±0.03	0.77±0.03	0.72±0.03	0.95±0.03
S	0.10±0.00	0.11±0.00	0.15±0.00	0.11±0.00
O*	46.60±0.78	46.52±0.75	44.16±0.76	46.43±0.76

*By difference

Table 5: Chemical compounds detected in bio-oil from raw and pretreated samples

RT(min)	Compound name	RNGS	WTNGS	ALTNGS	ACTNGS
		Peak area (%)			
2.26	Benzene	4.83	2.60	8.15	1.45
2.96	Propanoic acid	13.19	0.29	-	-
3.05	1,2-Ethanediol, monoacatate	-	-	4.18	2.53
3.52	3-Penten-2-one	-	0.04	-	-
3.76	Butanoic acid, 2-methylpropyl ester	0.84	-	-	-
4.16	Cyclobutanethiol	-	-	1.13	-
4.18	Formic acid, 2-propenyl ester	-	-	-	2.24
4.19	Aziridine, 1-methyl	1.10	-	-	-
4.20	1-Hydroxy-2-butanone	5.89	0.05	-	-
4.37	Tert-Butyl methylcarbonate	0.38	-	-	-
4.77	Cyclohexane	-	-	3.93	-
4.80	1,2-Cyclopentanediol, trans-	-	1.14	-	0.19
4.81	Acetic acid, 2-ethylbutyl ester	1.73	-	-	-
5.19	Propanedioic acid propyl-	-	-	-	0.61
5.28	1,2-Amino-4-methyl-1-pentanol	-	0.91	0.63	-
5.37	2-[2-methyl-2-aminoethyl]benzofuran	0.62	-	-	-
5.62	Cyclopentane	0.34	0.03	-	-
6.04	Furfural	6.58	25.06	7.70	13.24
6.16	Betazole	0.41	-	-	-
6.88	2-Furanmethanol	0.84	0.66	3.32	0.82
7.36	1,2-Propanediol, diacetate	-	-	-	0.54
8.54	3-Hepten-1-ol, acetate	-	-	1.44	1.04
8.67	Propanenitrile, 3-(methylamino)-	-	-	3.25	1.72
8.69	Ethanone, 1-(2-furanyl)	0.84	0.96	-	-
9.53	Carbamic acid, phenyl-, butyl ester	-	-	-	0.11
10.46	2-Furancarboxaldehyde, 5-methyl-	3.37	3.75	-	0.88
11.20	Phenol	9.29	7.33	19.19	15.38
12.04	1,3-Dimethyl-5-(adamantyl-1)benzene	0.13	-	0.87	-
12.68	1,2-Cyclopentanedione, 3-methyl-	3.26	2.84	3.97	1.94
13.59	Phenol, 3-methyl-	4.41	3.78	3.32	1.71
14.28	Benzyl alcohol	1.25	-	-	0.99
14.31	P-Cresol	3.91	3.49	-	-
14.56	Mequinol	0.26	0.27	-	0.46
16.53	Phenol, 2-ethyl	-	1.17	1.16	0.55
17.08	Phenol, 4-ethyl-	4.02	4.59	1.79	1.99
18.01	Catechol	3.63	13.07	11.75	20.56
18.46	1,4:3,6-Dianhydro-alpha-d-glucopyranose	-	-	-	1.72
18.48	Pentanal, 2,2-dimethyl-, hydrazone	0.33	0.31	2.59	-
18.87	Furan, 2,3-dihydro-4-(1-methylpropyl)-,	-	-	-	2.21

	(S)-				
18.89	5-Hydroxymethylfurfural	-	4.25	-	-
19.12	3,4,5,7,8-Pentamethoxyflvone	-	-	1.48	-
19.77	1,2-Benzenediol, 4-methyl-	0.68	1.75	-	0.41
20.23	Phenylcyclopentyl sulfide	0.83	0.30	5.45	-
20.61	1,2-Benzenediol, 3-methyl-	-	2.83	2.31	1.16
20.88	d-Monnitol, 1,4-anhydro	-	0.76	-	0.49
22.13	N-Methyl-N-vinylthio-naphthalene-1-amine	-	-	7.26	1.01
22.14	Phenol, 2,6-dimethoxy-	3.15	1.98	-	-
22.62	Benzaldehyde, 2-hydroxy-	-	0.93	-	-
23.08	Benzenediol, 4-ethyl-	-	0.80	-	-
24.49	Benzonitrile, 2-chloro-6-nitro	0.20	-	-	-
24.59	4-Ethyl-3-oxabicyclo[4,4,0]decane	-	-	-	0.12
26.19	Levoglucosan	-	-	-	5.86
26.36	β-d-Glucopyranose 1 6-anhydro-	-	14.07	-	16.27