

**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<sub>2</sub>SO<sub>4</sub> 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 <sub>2</sub> O	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 <sub>2</sub> SO <sub>4</sub>	(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
NaOH	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
	(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	

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Pretreatment

Proximate analysis (wt%)

(MJ/kg)

Ultimate analysis (wt%)

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	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 <sub>2</sub> O	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 <sub>2</sub> SO <sub>4</sub>	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 <sub>2</sub> O	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 <sub>2</sub> SO <sub>4</sub>	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			
<i>Physicochemical</i>				
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 <sup>3</sup> )@ 25 °C	1055±00	1077±00	1089±00	1032±00
HHV (MJ/kg) <sub>dry</sub>	20.97±0.10	22.22±0.10	27.96±0.10	21.94±0.10
<i>Ultimate analysis (wt%)</i>				
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	Peak area (%)	
				ALTNGS	ACTNGS
2.26	Benzene	4.83	2.60	8.15	1.45
2.96	Propanoic acid	13.19	0.29	-	-
3.05	1,2-Ethanediol, monoacetate	-	-	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	Levoglucozan	-	-	-	5.86
26.36	$\beta$ -d-Glucopyranose 1 6-anhydro-	-	14.07	-	16.27

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