

**Upgrading of Napier grass pyrolytic oil using microporous and hierarchical mesoporous zeolites: products distribution, composition and reaction pathways**

MOHAMMED, Isah Yakub, ABAKR, Yousif Abdalla, YUSUP, Suzana, ALABA, Peter Adeniyi, MORRIS, Kenobi Isima, SANI, Yahaya Muhammad and KABIR, Feroz Kabir <<http://orcid.org/0000-0002-3121-9086>>

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**Table 1:** Treatment condition and characteristics of zeolite

Catalyst	C <sub>NaOH</sub> (mol/L)	(Si/Al) <sup>a</sup> (mol/mol)	(S <sub>BET</sub> ) <sup>b</sup>	(S <sub>micro</sub> ) <sup>c</sup>	(S <sub>meso</sub> ) <sup>d</sup>	(V <sub>micro</sub> ) <sup>c</sup>	(V <sub>meso</sub> ) <sup>d</sup>	total acidity (mmol/g)
			surface area (m <sup>2</sup> /g)			volume (cm <sup>3</sup> /g)		
ZSM-5	0.00	20.76	385.20	356.54	11.67	0.14	0.01	3.81
0.2HZSM-5	0.20	13.79	369.43	274.66	115.55	0.10	0.17	3.00
0.3HZSM-5	0.30	12.51	374.88	240.23	175.09	0.11	0.28	2.96

<sup>a</sup>determined by X-ray fluorescence; <sup>b</sup>Brunauer–Emmett–Teller (BET) method; <sup>c</sup>t-plot method; <sup>d</sup>Barrett, Joyner and Halenda (BJH) method

**Table 2:** Physicochemical properties of raw and upgraded [pyrolytic oil](#)

Property	Raw	Thermal	ZSM-5	0.2HZSM-5	0.3HZSM-5
Density (g/cm <sup>3</sup> )	0.98±0.0	0.95±0.0	0.91±0.0	0.9±0.0	0.9±0.0
pH	3.71±0.01	3.6±0.01	3.92±0.01	3.88±0.01	3.92±0.01
HHV (MJ/kg)	29.18±0.10	35.90±0.10	40.46±0.10	42.08±0.10	43.43±0.10
C (wt %)	53.87±1.71	60.93±1.72	72.86±1.70	74.82±1.73	74.75±1.72
H (wt %)	6.45±0.07	7.50±0.10	7.36±0.09	8.62±0.11	8.55±0.10
N (wt %)	1.35±0.01	1.10±0.01	0.34±0.01	0.39±0.01	0.24±0.01
S (wt %)	0.76±0.01	0.13±0.01	0.12±0.01	0.14±0.01	0.22±0.01
O*(wt %)	37.57±1.01	30.34±1.01	19.32±1.01	16.24±1.01	16.03±1.01

Value are the mean (n =3) ± standard deviation

**Table 3:** Group of organic compound in the deoxygenated [pyrolytic oil](#) identified by GC-MS.

Composition (%)	Raw	Thermal	ZSM-5	0.2HZSM-5	0.3HZSM-5
HC	4.67	5.20	20.67	13.56	3.94
ARHC	2.53	0.00	13.33	20.40	26.87
MARHC	2.18	10.34	3.56	0.00	0.00
PHOL	28.15	65.91	41.25	43.12	47.70
MPHOL	37.87	5.03	0.00	0.00	0.00
AAK	16.88	4.35	12.69	3.71	2.01
MEST	4.68	9.18	8.50	11.75	11.00
OVAC	3.05	0.00	0.00	7.46	8.48

(HC) hydrocarbons, (ARHC) aromatic hydrocarbons, (MARHC) methoxy aromatic hydrocarbons, (PHOL) phenol, (MPHOL) methoxy phenol, (AAK) acids, aldehydes and ketones, (MEST) methylester and (OVAC) other value added chemical

**Table 4:** Gas composition from GC-TCD analysis

Composition (vol %)	Thermal	ZSM-5	0.2HZSM-5	0.3HZSM-5
H <sub>2</sub>	1.35	1.61	1.51	1.42
CH <sub>4</sub>	33.42	24.66	17.14	12.18
CO	25.34	27.72	32.92	36.88
CO <sub>2</sub>	9.03	28.01	30.43	32.35

**Table 5:** Composition of upgraded pyrolytic oil (organic phase) over regenerated 0.3HZSM-5 catalyst.

Composition (%)	Cycle			
	1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>	4 <sup>th</sup>
HC	7.32	6.46	8.59	2.50
ARHC	40.94	25.40	12.58	10.42
MARHC	0.00	2.89	10.33	12.66
PHOL	44.70	50.12	62.28	63.32
MPHOL	0.00	0.00	0.00	2.46
AAK	0.00	3.38	2.81	5.03
MEST	7.04	11.75	3.41	3.61

(HC) hydrocarbons, (ARHC) aromatic hydrocarbons, (MARHC) methoxy aromatic hydrocarbons (PHOL) phenol, (MPHOL) methoxy phenol, (AAK) acids, aldehydes and ketones and (MEST) methyl ester

**Table 6.** Gas composition from regenerated 0.3HZSM-5 catalyst

Composition (vol %)	Cycle			
	1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>	4 <sup>th</sup>
H <sub>2</sub>	1.23	1.29	1.21	1.30
CH <sub>4</sub>	12.78	12.08	12.41	12.80
CO	35.22	33.78	30.44	29.53
CO <sub>2</sub>	31.87	30.01	30.82	28.77

**Table 7:** Characteristic of fresh and regenerated 0.3HZSM-5 after 4 cycle.

Catalyst	$(S_{\text{BET}})^{\text{a}}$	$(S_{\text{micro}})^{\text{b}}$	$(S_{\text{meso}})^{\text{c}}$	$(V_{\text{micro}})^{\text{b}}$	$(V_{\text{meso}})^{\text{c}}$
	surface area ( $\text{m}^2/\text{g}$ )			volume ( $\text{cm}^3/\text{g}$ )	
Fresh 0.3HZSM-5	374.88	240.23	175.09	0.11	0.28
Regenerated 0.3HZSM-5	208.95	88.47	192.55	0.05	0.09

<sup>a</sup>Brunauer–Emmett–Teller (BET) method; <sup>b</sup> t-plot method; <sup>c</sup>Barrett, Joyner and Halenda (BJH) method