

Effect of Variation HCl Concentration on Natural Zeolite Dealumination to The Content of Liquid Smoke Compounds by Hydrodeoxygenation Process

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Abstract: Recently, for its direct use as a renewable energy resource of pyrolysis biomass, liquid smoke has received increased attention. Unfortunately, the composition of liquid smoke is very complex that cause to obvious changes in chemical properties of the liquid smoke. Therefore, the hydrodeoxygenation method required to handle this issue. The Objective of this research was the hydrodeoxygenation of liquid smoke to remove oxygenated compounds with decreased concentration of ketones and increased phenol concentration using sarulla natural zeolite dealuminated with 3M, 5M and 7M HCl concentrations at 90°C in the H₂ atmosphere. Characterization of hydrodeoxygenation product was analyzed content by gas chromatography-mass spectrometry (GC-MS). The results showed a decrease in phenol content and a rise in carbonyl at 7 M HCl dealumination while 5 M HCl dealumination increased phenol content and reduced carbonyl compounds. Treatment with concentration of 5 M HCl results in a better content of liquid smoke.

1 INTRODUCTION

Liquid smoke, a by-product of the charcoal industry, is high economic in aspects of its discharge into the atmosphere. Liquid smoke is derived from dew condensation due to the decay of organic compounds during pyrolysis. The quantity of liquid pyrolysis smoke is 90.75% phenol compound, 3.71 % carbonyl and 1.81% alcohol, an antimicrobial as a meat preservative (Hadanu & Apituley, 2016).

Liquid smoke produced from pyrolysis has a higher water and oxygen content and a lower heating value than fossil fuels, which can be achieved by upgrading, i.e. hydrodeoxygenation (HDO) (Bulushev & Ross, 2011). HDO method can reduce the water and oxygen content and increase the heating value of biomass (S. P. Zhang et al., 2003).

A catalyst is necessary in the HDO process to reduce the oxygenate compound content in liquid smoke. Several studies have used catalysts Pd/C, Ru/C and Pt/C (300°C, 3 MPa H₂, 60 minutes) (Oh et al., 2016) stored (23°C, 20% RH) for 12 weeks

almost no change in color and physicochemical properties. The water content changed from 1.3% to 3.4% is still in the dry category (<6%), the acidity was reduced from 70.2 to 71 mg-KOH/g and HHV from 762 Da to 867 Da. Likewise for bio oil after HDO with Pt/Al₂O₃, Ni/HY, Pd/C catalyst (260°C, 70 Bar, 2 hours), after 140 hours there was no change in content except 0.8% to 2.9% aldehyde and 30% phenol to 27% (Alvarez-Galvan et al., 2019; Liu et al., 2019; Mortensen et al., 2011).

In the other hand, with high temperatures (above 300°C) and high H₂ pressure (2-10 MPa), the catalyst often becomes inactive due mainly to coke and water-induced structural changes (Mortensen et al., 2011). In terms of costs as well as unnecessary protection. Lercher and Jones show that cyclohexane-forming phenol hydrodeoxygenation can be performed at relatively low temperatures using bi-functional metallic acid catalysts (Mäki-Arvela & Murzin, 2017; Mo et al., 2018). Therefore research has carried out the HDO process with ethanol solvents which act as hydrogen donors and

the catalyst used was natural zeolite. This study was to determine the composition of compounds from liquid smoke using natural zeolite as a catalyst without the addition of metals.

2 RESEARCH METHODS

2.1 Materials

In this research using commercial liquid smoke, natural zeolite purchased at bratachem. Ethanol (p.a), hydrogen gas and nitrogen gas.

2.2 Activation Natural Zeolite

Zeolite was sieved with the size in 100 mesh and then washed with distilled water for 24 hours then filtered and dried at 110°C. The zeolite activation was carried out by varying the HCl concentrations of 3M, 5M and 7M for 60 minutes at 90°C. After that, filtered and washed to neutral pH and then dried. Activated zeolite was calcined at 500°C for 1 hour while running nitrogen gas 10 mL/min (Sihombing et al., 2018).

2.3 Pretreatment of Liquid Smoke

Conventional liquid smoke was distilled to separate water content. Distillation was carried out at 90°C. After the liquid smoke was water-free, it was prepared to be used for the cycle of hydrodeoxygenation.

2.4 Hydrodeoxygenation of Liquid Smoke

The hydrodeoxygenation process was carried out by adding natural zeolite to liquid smoke at a ratio of 1% (w / w), then 96% ethanol was added, and refluxed at 90°C while flowing 10 mL/min hydrogen gas for 5 hours. After that, GC-MS measured the components of the compounds.

3 RESULTS AND DISCUSSION

3.1 Identification of Components of Liquid Smoke Compounds

GC-MS characterization was carried out to determine the content of compounds in bio-oil. In accordance with the main purpose of the research

was to vary the catalyst with different concentrations can affect component compounds in liquid smoke, i.e increase the content of phenols and reduce the content of oxygenate compounds. GC-MS results can be seen in Fig. 1-3.

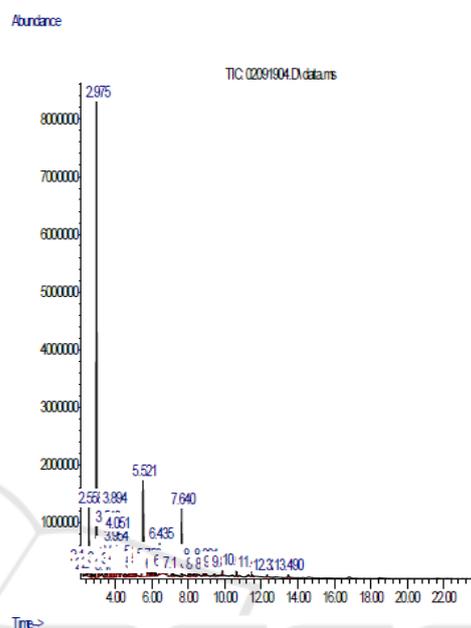


Figure 1: GC-MS chromatogram analysis of liquid smoke in 3M HCl Zeolite.

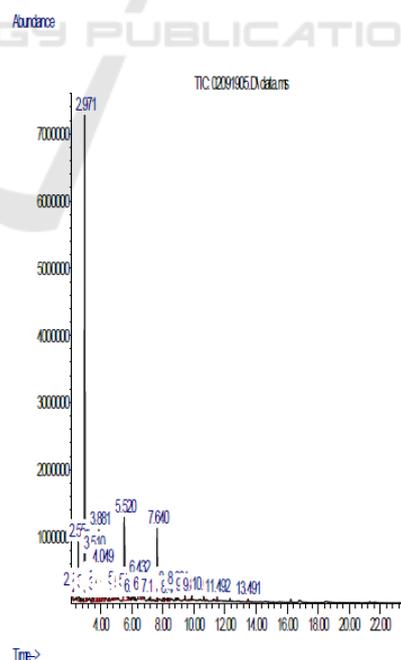


Figure 2: GC-MS chromatogram analysis of liquid smoke in 5M HCl Zeolite.

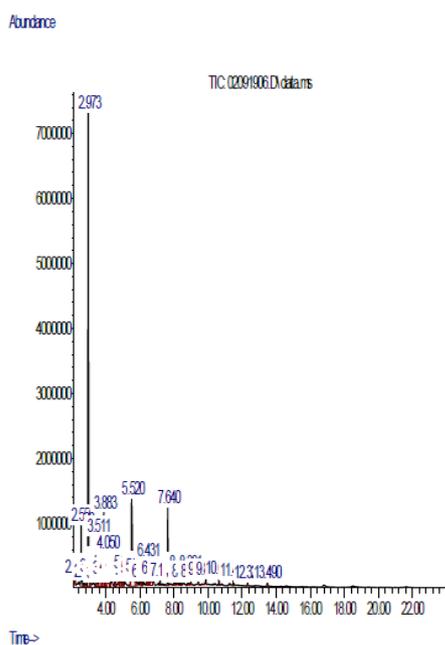


Figure 3: GC-MS chromatogram analysis of liquid smoke in 7M HCl Zeolite.

There was more than 30 types of compound components in liquid smoke which are shown in the Table 1-3.

Table 1: Characterization GC-MS of liquid smoke in 3M HCl Zeolite.

No	% Area	Compounds
1	0.28	1,2-Ethandiol
2	0.17	Furan,tetrahydro-2-methyl
3	5.50	Furanone,dihydro
4	0.53	Furanone,5-methyl
5	35.71	Phenol
6	0.81	Phenyl alcohol
7	0.29	2-piperidinone
8	3.28	1,2-cyclopentanedion
9	2.23	Pentanoic acid
10	1.97	Ethyl,4-hydroxybutanoate
11	0.63	Pentanoic acid,4-oxo,ethyl ester
12	6.05	2-furanmethanol,tetrahydro
13	2.74	Phenol,4-methyl
14	2.64	Tetrahydrofurfurylacetate
15	0.85	Phenol,2-methoxy
16	0.39	3,hydroxy-2-methyl
17	0.79	2-cyclopenten-1-one-3-ethyl
18	0.44	3-methylmorpholine
19	0.62	Dihydro-citronella
20	1.13	2-furanone,5-methyl
21	0.38	Methyl ester
22	1.08	2,2-dimethyl,1-one-2-silacyclo
23	0.45	Ethyl,5-oxohexanone
24	0.71	5-ethyldehydro
25	13.66	1,2-benzenediol
26	1.46	Cyclopropanecarboxamide
27	0.36	Phenol-d6
28	0.27	Tertramethylguanid
29	0.45	2-methyl-3-isothiazolone
30	0.28	2-penten,3-ethyl-2-methyl
31	0.32	Phenol,3,4-dimethoxy
32	2.13	3-methyl-1-hexene
33	0.24	3-isobuthyldihydropyrazin
34	0.67	7,7-dimethylbicyclo
35	0.39	2-n-propylthiacyclohexane
36	0.42	Cyclohexane,ethyl
37	3.95	Phenol,2,6-dimethoxy
38	0.48	1-methoxy-2,6,6-trymethyl
39	0.32	3-buten-2-ol,2-methyl
40	1.00	Benzaldehyde,3-hydroxy
41	0.26	Phosphonic acid
42	0.73	Benzoic acid,4-hydroxy
43	0.42	Methylparaben
44	0.51	Ethanone
45	0.47	7,8-dimethylbenzocyclooctene
46	0.57	2,4-dihydroxy,3-methoxy
47	0.39	Benzaldehyde,4-hydroxy
48	0.24	Ethanone
49	0.24	Aspidinol

Table 2: Characterization GC-MS of liquid smoke in 5M HCl Zeolite.

No	% Area	Compunds
1	0.27	Propanoic acid
2	0.63	2-butanone
3	5.37	Furanone-dihydro
4	0.52	Furanone,5-methyl
5	40.02	Phenol
6	0.80	Furanone,3-methyl
7	0.35	2-piperidinone
8	3.45	1,2-cyclopentenedione
9	2.26	Pentanoic acid,4-oxo
10	2.08	Ethyl,4-hydroxybutanoate
11	0.55	Pentanoic acid,4-oxo ethyl ester
12	6.09	2-furanmethanol,tetrahydro
13	2.92	Phenol,4-methyl
14	2.31	2-furanmethanol,tetrahidro-acet
15	0.93	Phenol,2-methoxy
16	0.31	3-hydroxy,2=methyl
17	076	2-cyclopentene,1-one-3-ethyl
18	0.51	2-propenyl,2-ethylbutanone
19	0.83	2-furanone-5-methyl
20	0.50	Ethane,1,1-diethoxy
21	0.69	2,2-dimethyl-1-oxa
22	0.52	2-furanone,dihydro-5-pentyl
23	12.87	1,2-benzenediol
24	1.12	2-propanoic acid,2-methyl-ethyl
25	0.13	3-cis-methoxy-5-cus-methyl
26	2.23	Butanoid acid,butyl ester
27	0.67	2,3-dihydroxy-acetophenone
28	0.39	Cyclohexane ethyl
29	4.64	Phenol,2,6-dimethoxy
30	0.54	2,6-dimethyl-4-oxa
31	0.23	1-hydroxy,2-pentanone
32	1.02	Benzaldehyde,3-hydroxy
33	0.25	Cyclopentaneacetic acid
34	0.76	Benzoic acid,4-hydroxy
35	0.51	Ethanone
36	0.62	2,3,5-trimethoxytoluene
37	0.48	Ethanone
38	0.44	Benzaldehyde,4-hydroxy
39	0.42	Aspinidiol

Table 3: Characterization GC-MS of liquid smoke in 7M HCl Zeolite.

No	% Area	Compunds
1	0.28	Propanoic acid
2	0.47	2-ethylbutanal
3	5.31	2-furanone,dihydro
4	0.56	Furanone,5-methyl
5	36.57	Phenol
6	0.83	Phenol
7	0.39	2-piperidinone
8	3.38	1,2-cyclopentanedione
9	2.29	Pentanoic acid
10	1.96	Ethyl,4-hydroxybutanoate
11	0.52	Pentanoic acid,4-oxo,ethyl
12	5.98	Tetrahydrofurfurilalkohol
13	2.66	Phenol,4-methyl
14	2.14	2-furanmethanol
15	0.94	Phenol,2-methoxy
16	0.41	Maltol
17	0.85	2-cyclopenten,1-one
18	0.75	4-acetylbutric acid
19	1.11	Furanone,5-methyl
20	0.65	Methylester of,4,4-dimethoxy
21	0.99	Methyl-2,3,4-trimethyl
22	0.73	Gamma,hexalactone
23	13.15	1,2-benzenediol
24	1.40	2-propanoic acid
25	0.52	N-methylthiazolone
26	0.39	Methyltriacelatone
27	2.22	Butanoic acid
28	0.65	1,4-benzenediol
29	1.25	7,7-dimethylbicyclo
30	0.48	3,6-dihydro-6,6-dimethyl
31	4.55	Phenol,2,6-dimethoxy
32	0.51	Naphthalenone,octahydro
33	0.20	1-hydroxy-2-pentanone
34	0.94	Vanilin
35	0.28	Cyclopentaneacetic acid
36	0.75	Benzoic acid,4-hydroxy
37	0.40	Methylparaben
38	0.41	Ethanone
39	0.54	2,3,5-trimethoxytoluene
40	0.51	Benzamide,diethyl,4-hydroxy
41	0.45	Benzaldehyde,4-hydroxy
42	0.28	Ethanone
43	0.34	Ethylisovanillymandelate

The high peak indicates a compound most contained in bio-oil, namely phenol compounds in the form of syringol and guaiacol. It can be seen from the three tables above that phenol compounds and oxygenate compounds are the main components of bio-oil. Relative to other products, the syringol compound has the highest and most important appearance for all bio-oils. There is also a significant percentage of guaiacol after syringol relative to other

compounds. Both of these compounds originate from lignin cracking, while furan, acetate, and aromatic compounds are derived from degradation of cellulose and hemicellulose (C. Zhang et al., 2016).

It appears that phenol compounds, both syringol and guaiacol, have increased concentrations in this case characterized by the percentage of the area on the GC-MS chromatogram. It can be concluded that the HDO reaction in bio-oil takes place which is characterized by a decrease in the concentration of oxygenate compounds such as ketones and an increase in alcohol concentration in this case represented by phenols.

But there was a decline in phenol levels at 7 M zeolite concentration. The possibility of zeolite with a concentration of 7M has not been able to be a good catalyst in the HDO process.

4 CONCLUSIONS

Generally, the results showed a decrease in phenol content and a rise in carbonyl at 7 M HCl dealumination while 5 M HCl dealumination increased phenol content and reduced carbonyl compounds. Treatment with concentration of 5 M HCl results in a better content of liquid smoke.

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