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Research article

Catalytic upgrading of palm oil derived bio-crude oil for bio-hydrocarbon enrichment using protonated zeolite-Y as catalyst

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Abstract: This research was conducted to study upgrading bio-crude oil (BCO) produced by pyrolysis of palm oil without the use of a catalyst, using protonated zeolite-Y designated as H-Y. Preparation of H-Y was carried out by subjecting zeolite-Y synthesized from rice husk silica (RHS) and food grade aluminium foil (FGAF) to a cation exchange process using ammonium nitrate solution with different concentrations of 2.0, 2.5, 3.0, and 3.5 M to obtain (H-Y) samples with different protonation extents. To confirm the formation of Na-Y, the sample was characterized using XRD and SEM, and to evaluate the protonation, the Na-Y and H-Y samples were analyzed using XRF. Characterization using XRD showed that the Na-Y sample is faujasite, which is the characteristic phase of zeolite-Y, and supported by the existence of particles with octahedral structure as seen by SEM. Successful protonation resulted in a reduction of Na content up to 89.948% from that of the Na-Y, which was demonstrated by the XRF results. Catalytic upgrading experiments demonstrated that H-Y zeolites functioned to increase the bio-hydrocarbon content from 80.23% in the BCO to practically 100% in the upgraded oil. In addition, no acids were identified in the upgraded fuels, implying that H-Y zeolite is a promising catalyst for BCO upgrading for bio-hydrocarbon enrichment of the oil.

Keywords: pyrolysis; bio-crude oil; catalytic upgrading; zeolite-Y; bio-hydrocarbon

1. Introduction

In search of renewable energy sources, the production of liquid hydrocarbons from biomass or bio-hydrocarbons has been considered as one of the priorities by many workers around the globe. Biohydrocarbons are composed of hydrocarbons with different numbers of carbon, and from fuel point of view they can be distinguished into biogasoline, which is a mixture of hydrocarbons with carbon chain of C_5-C_{12}, kerosene fuel or bioavture, which is a mixture of hydrocarbons with carbon chain of C_{13}-C_{17}, and biodiesel, which is a mixture of C_{18}-C_{28} [1,2]. The opportunity to produce bio-hydrocarbons is supported by the development of pyrolysis technology, in which biomass is subjected to thermal treatment in the absence or limited oxygen to produce products in the forms of gas, liquid, and solid [3]. The liquid product is generally known as pyrolysis oil or bio-crude oil (BCO) which is a complex mixture consisting of a large number of compounds including hydrocarbons together with oxygenated organic compounds, such as acids, aldehydes, ketones, ester, and phenols [4–7].

The presence of non-hydrocarbon components is the main limitation that prevents direct use of BCO as a fuel for ignition machines. To eliminate the oxygenated components of the BCO, two upgrading treatments have been developed, known as hydro treatment upgrading and catalytic upgrading. In the hydro treatment method, hydrogen is reacted with BCO to reduce its oxygen content by the formation of water, thus increasing the hydrocarbon content of the upgraded fuel [6,8]. The main drawback of the hydro treatment method is the need to use large volumes of hydrogen and relatively high pressure. Due to this limitation, catalytic upgrading is more desirable since in this method no need to use hydrogen, and can be carried out at atmospheric pressure. produces hydrocarbon rich upgraded fuel.

The major catalysts used for BCO upgrading reported in literatures are zeolites since this type of material has been acknowledged to have a good ability to promote deoxygenation during pyrolysis through three mechanisms, i.e., by decarbonylation, decarboxylation, and dehydrogenation [8]. The most widely used zeolites reported in previous work are HZSM-5 and zeolite-Y [3,9–11]. Other catalysts that have been reported for the same purpose are activated natural zeolites with different Si/Al ratios [12], β-zeolites [13], and NiN-supported natural bentonite [14].

In this study, the BCO obtained by pyrolysis of palm oil without the use of a catalyst was subjected to catalytic upgrading using protonated zeolite-Y (H-Y) as catalyst. The H-Y zeolite was selected since this zeolite is cheaper than HZSM-5 and can be synthesized with a much simpler procedure than that required for the preparation of HZSM-5. Preparation of H-Y was conducted in two stages, starting with the synthesis of zeolite-Y (Na-Y) from rice husk silica and food grade aluminium foil using the hydrothermal method, followed by protonation of the Na-Y through ion exchange using aluminium nitrate solution with different concentrations to produce zeolite H-Y with different protonation levels. The use of ammonium nitrate solution with different concentrations was intended to obtain the H-Y zeolites with different protonation levels. Successful formation of Na-Y and H-Y zeolites was confirmed by characterization using XRD and SEM techniques, while the protonation was evaluated by analysis using XRF technique. The Na-Y and H-Y zeolites were then utilized for catalytic upgrading of BCO produced by pyrolysis of palm oil without the use of a catalyst. The chemical compositions of both BCO and upgraded fuels were then analyzed using GC-MS.

2. Materials and methods

Sodium hydroxide and nitric acid (reagent grade) were purchased from Aldrich. Rice husk (RH) and food grade aluminum foil were obtained from local sources in the City of Bandar Lampung. Crystallization process of zeolite was conducted using a polytetrafluoroethylene (PTFE) lined stainless steel autoclave, and calcination of zeolite was performed using a Nabertherm electrical furnace (Lilienthal, Germany). XRD characterization was performed using a PANalytical type Empyrean diffractometer and SEM characterization using a scanning electron microscope model Zeiss EVO MA 10. XRF analysis was conducted on the PANalytical Epsilon 3 instrument. Pyrolysis experiment was carried out using a laboratory scale pyrolysis unit, and bio-oil resulted was analyzed using the GCMS-QP2010 SE SHIMADZU instrument. The MS Library systems NIST62.LIB and WILEY229.LIB were applied to identify the components of the BCO and upgraded oils. To determine the relative percentage of each component of the samples identified, the peak area of the component was divided by the total area of all identified components.

2.1. Procedure

2.1.1. Extraction of RHS

The RHS was obtained utilizing the sol-gel process as reported in a previous study [4]. Typically, a mixture of 50 g dried husk with 500 mL of 1.5% NaOH was boiled for 30 min, and then left at room temperature for 24 h. The mixture was filtered and the filtrate, which contains silica (silica sol), was collected and then neutralized (pH of 6.8–7.0) with HNO_3 solution (10%) to transform silica from sol to gel, followed by aging of the gel for 24 hours. The excess of acid was removed by repeated rinsing of the gel with distilled water, and then the gel was oven dried at 110 °C for eight hours. To obtain a sample with a relatively homogeneous size, the silica was ground into powder and sieved with a 250 mesh sieve.

2.1.2. Zeolite preparation

Zeolite-Y was synthesized from RHS, sodium hydroxide, and aluminum foil with the composition to satisfy the formula of $Na_2O.Al_2O_3.4.8SiO_2.xH_2O$. In contrast to the other three components, in this molecular formula, the amount of H_2O is uncertain depending on the further treatment applied to the sample, for example, calcination. For this reason, the amount of H_2O in the molecular formula of the zeolite is expressed as x. Typical procedure for zeolite preparation consists of dissolving 8.0 g NaOH in 250 mL of distilled water, and 175 mL of the solution was used to dissolve 28.8 g of RHS and the rest (75 mL) to dissolve 5.4 g aluminum foil. The two solutions were then thoroughly mixed using a laboratory blender. The mixture was transferred into a Teflon lined stainless autoclave and allowed to stand at room temperature for 24 hours to age. After aging treatment was completed, the sample was subjected to crystallization by placing the autoclave in an oven at 100 °C for 48 hours. After the completion of crystallization process, the autoclave was allowed to cool to ambient temperature, and then the sample inside the autoclave was filtered. The solid was collected and rinsed with distilled water to remove the excess of alkali, and then oven dried

at 80 °C for twenty four hours. The dry sample was ground into 250 mesh powder and finally calcined at 550 °C for six hours.

2.1.3. Preparation of protonated zeolite-Y (HY)

Conversion of zeolite-Y into zeolite H-Y was conducted by ion exchange adopting the method described in previous work by others [15]. Zeolite-Y was mixed with ammonium nitrate solution with the ratio of 1 g zeolite/10 mL ammonium nitrate solution of different concentrations of 2.0; 2.5; 3.0; and 3.5 M. The mixture was sealed and placed on a hotplate stirrer for 6 hours at 80 °C. After the completion of the experiment, the mixture was filtered and the solid was oven dried at 80 °C for 8 hours, and finally calcined at 550 °C for 6 hours to obtain protonated zeolite-Y (H-Y zeolite).

2.1.4. Zeolite characterization

The XRD pattern for phase identification was produced by PANalytical type Empyrean diffractometer, using CuKα (λ = 1.54 Å) radiation with the energy of 40 kV and current of 100 mA. The pattern was recorded over the 2θ range of 5–90°, with a scanning rate was $0.06°s^{-1}$. The phase identification was done by comparing the pattern with that of the standard listed in the International Zeolite Association (IZA) files. The surface morphology of the sample was examined using SEM technique. The instrument was operated at 30 KV, with an electron acceleration voltage of 20 kV, and the sample was scanned at different magnifications to produce micrographs that display a better image of the surface.

2.1.5. Pyrolysis experiments

Pyrolysis experiment was performed in a laboratory scale pyrolysis reactor with a schematic arrangement as shown in Figure 1. The first experiment was carried out to produce bio crude oil (BCO) by pyrolysis of palm oil without the use of catalyst. The typical experiment was conducted by transferring 350 mL of palm oil into the inside chamber of the reactor and then the reactor was heated. The cracking products were passed into the condenser and the condensed liquid was collected. The liquid produced was collected for 60 minutes and then transferred into a separatory funnel to allow separation between water phase and organic phase (BCO), which was then used in catalytic upgrading experiment. For the catalytic upgrading experiment, an aliquot of 100 mL of BCO was mixed with 5 g of the catalyst, and then the mixture was transferred into the reactor. The mixture was then pyrolyzed and liquid product (upgraded oil) was collected for 30 minutes. The BCO and upgraded fuel were analyzed by GC-MS and the chemical components of the samples were tentatively identified with the aid of MS Library systems NIST62.LIB and WILEY229.LIB. For component identification, the GC-MS analysis was conducted to evaluate the effect of protonation of the zeolite on the chemical composition of the upgraded fuel.
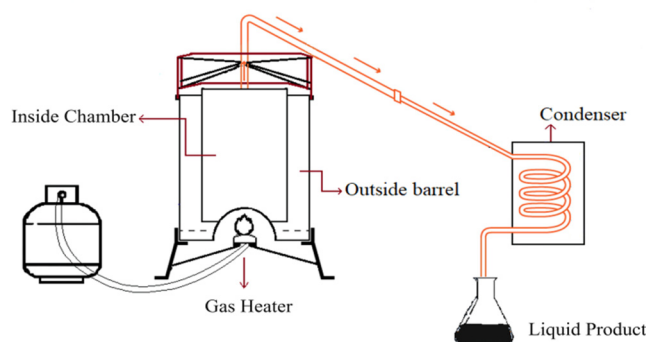
Figure 1. Schematic of laboratory scale pyrolysis reactor used in this study.

3. Results and discussion

3.1. Characterization of synthesized zeolite-Y

To see if the zeolite-Y was successfully prepared using the method applied, the sample produced was analyzed using XRD and SEM. Characterization of the sample using XRD produced the diffraction pattern as shown in Figure 2. As can be seen in Figure 2, the XRD pattern (diffractogram) of the synthesized sample is characterized by the presence of sharp peaks, which confirm the existence of the sample as crystalline material, although the existence of an amorphous state should also be acknowledged. In addition, it can be seen that the XRD pattern of the sample is identical to the pattern of the standard zeolite-Y, more specifically faujasite type. Concerning this result of XRD characterization, it is concluded that preparation of zeolite-Y was accomplished as expected.
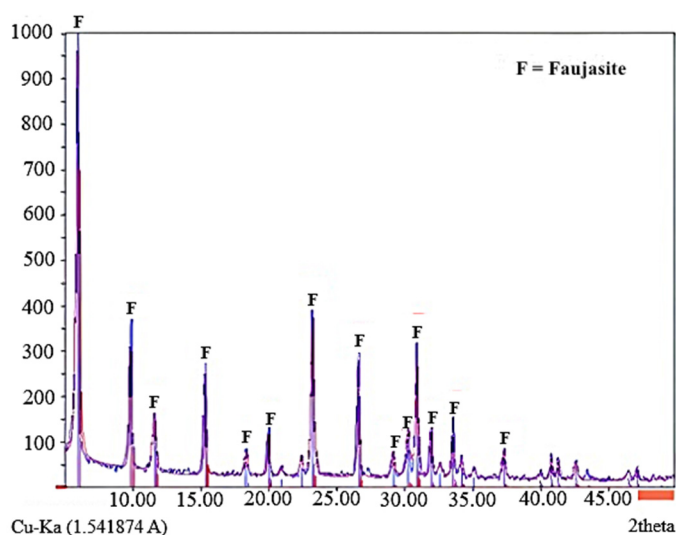

Figure 2. The XRD pattern of the zeolite-Y synthesized in this study.

For further confirmation, the positions (2θ) of some characteristic diffraction peaks of the sample were compared with those of the standard zeolite-Y available in the International Zeolite Association (IZA) Data Base as shown in Table 1. As can be seen in the data, no significant difference in the position (2θ) of the seven peaks is listed in Table 1, although the difference in the relative intensity should be noted, which is most likely due to different crystallinity between the sample synthesized and the standard zeolite. Without ignoring the differences found, based on XRD characteristics presented in Figure 2 and Table 1, it can be concluded that the zeolite-Y has been successfully prepared.

Table 1. Comparison of XRD data of synthesized zeolite-Y and standard zeolite-Y (IZA database).

Standard zeolite-Y		Synthesized zeolite-Y	
2θ (°)	Relative intensity (%)	2θ (°)	Relative intensity (%)
6.183	100	6.209	100
10.104	9.09	10.097	34.47
11.854	7.34	11.819	14.92
15.600	10.46	15.557	23.64
18.621	4.10	18.548	6.13
20.288	3.96	20.191	12.60
37.575	0.14	20.191	7.13

Another unique feature of zeolites is the shape of the particle, in which each zeolite has its particle shape. For this reason, characterization using SEM is an important part of zeolite investigation. In this respect, the zeolite-Y synthesized was also characterized using SEM, and the micrographs of the sample with different magnifications are shown in Figure 3.

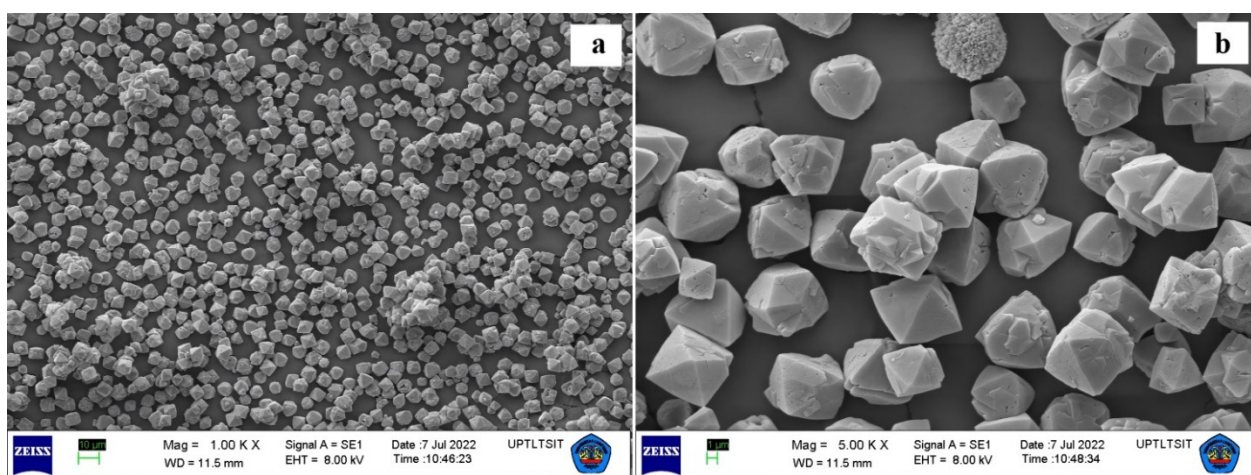
Figure 3. Micrograph of the zeolite-Y synthesized with magnification: (a) 1000 x and (b) 5000 x.

As can be seen in Figure 3, the existence of crystallite particles is displayed by the micrographs even at low magnification (1000 x). By increasing the magnification to 5000 x, the presence of particles with octahedral structure, which is the characteristic shape of zeolite-Y, can be observed

more evidently. This shape of particles observed in this study is in agreement with the shape of zeolite-Y reported in other studies [16,17].

3.2. Characterization of protonated zeolite-Y

To investigate the extent of zeolite-Y protonation accomplished, the samples produced from ion exchange experiments with NH_4NO_3 solution of different concentrations were analyzed using XRF to determine the Na contents before and after ion exchange treatments. The results obtained are shown in Table 2.

Table 2. The results of ion exchange experiments with NH_4NO_3 solution of different concentrations.

$[NH_4NO_3]$, M	Na content (%)	Na reduction (%)
-	1.15	0
2.0	0.83	27.82
2.5	0.72	37.95
3.0	0.58	49.65
3.5	0.12	89.95

As displayed by the experimental data in Table 2, the ion exchange treatment resulted in reduction of Na contents of the zeolite, confirming that some of the Na^+ ions in the zeolite-Y have been replaced by H^+ ions. The data also indicate that the reduction of Na^+ content increased with increased concentration of NH_4NO_3 solution, with the highest reduction of 89.948% was achieved with the use of 3.5 M NH_4NO_3 solution.
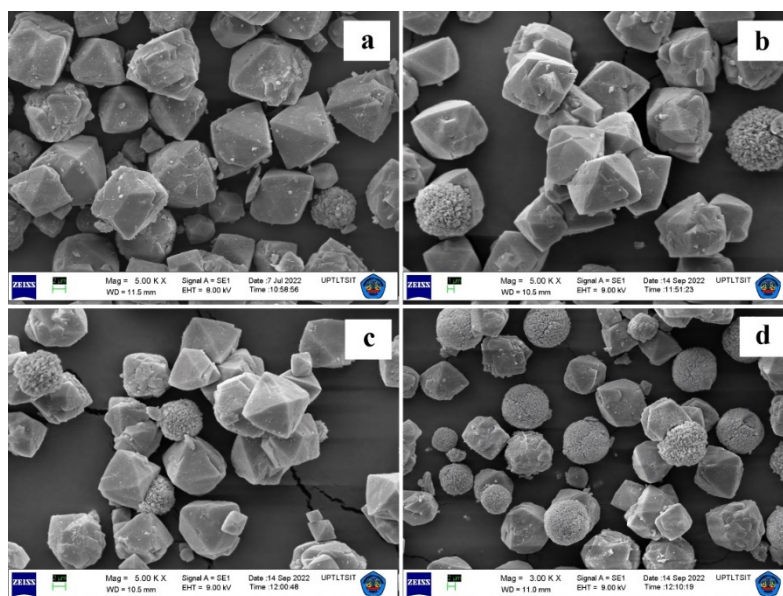

Figure 4. SEM micrographs of protonated zeolite-Y: (a) H-Y1, (b) H-Y2, (c) H-Y3, and (d) H-Y4.

To study the effect of protonation treatments applied, the protonated samples produced using NH_4NO_3 solution with different concentrations were analyzed using SEM, and the diffractograms

obtained are compiled in Figure 4. For simplicity, the protonated samples are specified as H-Y1, H-Y2, H-Y3, and H-Y4, which refer to the NH_4NO_3 concentration of, 2.0, 2.5, 3.0, and 3.5 M, respectively. As the case with the micrograph of the unprotonated zeolite-Y presented in Figure 4, the micrographs of the protonated samples shown in Figure 4 are characterized by the existence of crystalline particles with octahedral shape, implying the samples retain their particle shape although some of the Na^+ ions have been replaced by H^+ ions. However, protonation also led to the formation of spherical clusters, and with increased concentrations of NH_4NO_3 led to formation of more clusters as seen in the micrograph of the H-Y4 sample. In this respect, the micrographs also suggest that protonation most likely led to a decrease in the crystallinity of the samples.

3.3. The results of pyrolysis experiments

In this study, the BCO was produced by pyrolysis of palm oil without the use of catalyst and the BCO was analyzed using GC-MS. The chromatogram of the sample is shown in Figure 5.
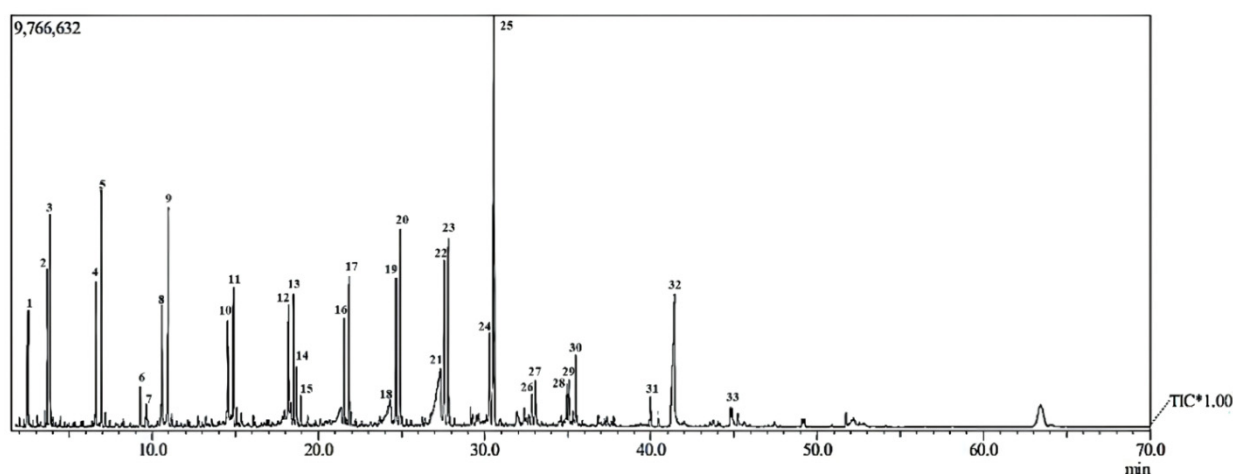

Figure 5. GC-chromatogram of BCO obtained by pyrolysis of palm oil without catalyst.

It is typical of BCO to be produced by pyrolysis of biomass reported in the literature [3,4]. The GC chromatogram in Figure 5 indicates that the BCO consists of a large number of compounds. The components of the BCO were then identified with the aid of the MS Library system NIST12.LIB and WILEY229.LIB. These databases also provide a similarity index (SI), which indicates the agreement between the MS data for compounds found in the sample with those of the standard compounds provided in the database. The identified components of the BCO sample with the aid of the above MS Library systems are listed in Table 3. In this respect, it should be acknowledged that some of the components were not identified, mostly because of their very small quantities, below the limit of detection of the instrument used. With respect to the distribution of products, the possibility of some error in the relative percentage of the compounds should be acknowledged. This limitation should be taken into account since in the GC-MS analysis the relative percentage of the compound detected is calculated based on the peak area of the compound and does not take into account the difference in peak is of different compounds although they have the same quantity.

Table 3. The chemical composition of the BCO obtained by pyrolysis of palm oil without the use of a catalyst.

Peak No.	Retention time (Min)	SI (%)	Compound name	Molecular formula	Category	Relative percentage (%)
1	2.475	94	1-Hexene	C_6H_{12}	Hydrocarbon	2.39
2	3.694	97	1-Heptene	C_7H_{14}	Hydrocarbon	2.17
3	3.861	96	Heptane	C_7H_{16}	Hydrocarbon	3.01
4	6.605	96	1-Octene	C_8H_{16}	Hydrocarbon	2.89
5	6.941	95	Octane	C_8H_{18}	Hydrocarbon	4.69
6	9.279	96	Ethylbenzene	C_8H_{10}	Hydrocarbon	0.90
7	9.645	94	Benzene	C_8H_{10}	Hydrocarbon	0.91
8	10.598	96	1-Nonene	C_9H_{18}	Hydrocarbon	3.03
9	10.967	96	Nonane	C_9H_{20}	Hydrocarbon	5.11
10	14.552	98	1-Decene	$C_{10}H_{20}$	Hydrocarbon	2.75
11	14.890	96	Decane	$C_{10}H_{22}$	Hydrocarbon	3.26
12	18.202	96	1-Undecene	$C_{11}H_{22}$	Hydrocarbon	3.04
13	18.505	96	Undecane	$C_{11}H_{24}$	Hydrocarbon	2.62
14	18.660	95	2-Undecene	$C_{11}H_{22}$	Hydrocarbon	1.21
15	21.351	85	Undecanoic Acid	$C_{11}H_{22}O_2$	Acid	0.92
16	21.551	95	1-Dodecene	$C_{12}H_{24}$	Hydrocarbon	2.25
17	21.828	97	Dodecane	$C_{12}H_{26}$	Hydrocarbon	3.11
18	24.292	86	Dodecanoic Acid	$C_{12}H_{24}O_2$	Acid	1.15
19	24.666	96	1-Tridecene	$C_{13}H_{26}$	Hydrocarbon	3.41
20	24.921	97	Tridecane	$C_{13}H_{28}$	Hydrocarbon	4.43
21	27.331	91	Tetradecanoic Acid	$C_{14}H_{28}O_2$	Acid	7.35
22	27.573	98	1-Tetradecene	$C_{14}H_{28}$	Hydrocarbon	3.94
23	27.803	97	Tetradecane	$C_{14}H_{30}$	Hydrocarbon	4.17
24	30.293	97	1-Pentadecene	$C_{15}H_{30}$	Hydrocarbon	2.25
25	30.553	97	Pentadecane	$C_{15}H_{32}$	Hydrocarbon	12.25
26	32.856	98	1-Hexadecene	$C_{16}H_{32}$	Hydrocarbon	0.80
27	33.043	96	Hexadecane	$C_{16}H_{34}$	Hydrocarbon	1.21
28	34.935	93	1-Heptadecene	$C_{17}H_{34}$	Hydrocarbon	1.31
29	35.075	97	8-Heptadecene	$C_{17}H_{34}$	Hydrocarbon	1.33
30	35.475	96	Heptadecane	$C_{17}H_{36}$	Hydrocarbon	1.79
31	39.979	94	2-Heptadecanone	$C_{17}H_{34}O$	Ketone	0.84
32	41.405	92	Octadecanoic Acid	$C_{18}H_{36}O_2$	Acid	8.19
33	44.788	93	Oleic Acid	$C_{18}H_{34}O_2$	Acid	1.32

With respect to the categorization method found in the literature, the identified components of the BCO produced from the experiment without the use of catalyst (Figure 5) were classified into three more common categories of chemical compounds. The three categories are hydrocarbon, acid, and ketone, as indicated in Table 3. Categorizing the components of BCO is also useful to estimate the relative composition of the BCO as a base to compare the composition of BCO samples obtained

from different experiments. To determine the relative percentage of each component of the BCO, the following Eq (1) was used:

$$\%i = \frac{A_i}{A_t} \, x \, 100 \tag{1}$$

i = component i
A_i = peak area of component i
A_t = total peak of all identified components

To calculate the relative composition of the BCO in terms of general categories, the relative percentages of all components in the category were then added. Using this calculation approach, the results for the BCO obtained by pyrolysis of palm oil without catalyst (Figure 5) are presented in Table 3. As can be seen in Table 3, the main component of the BCO is a hydrocarbon category that contributes 80.23% to the composition, followed by 18.93% acid and 0.84% ketone. It is also observed that the hydrocarbon fraction of the BCO consists of linear alkanes and their corresponding alkenes, as indicated by the presence of two peaks at each carbon number. This pattern is in agreement with that of BCO derived from cork granules reported by others [18].

The upgraded oils obtained from catalytic upgrading experiments using Na-Y and H-Y zeolites as catalysts were analyzed using GC-MS and the GC chromatograms obtained are shown in Figure 6. As displayed in Figure 6, the appearance of chromatograms of the upgraded oils using H-Y catalysts is very similar, suggesting that the oils are composed of mostly the same compounds. A different pattern was observed for the upgraded oil using the Na-Y catalyst, in which more compounds were observed and distributed at a longer retention time range, suggesting the presence of compounds with higher molecular weight in the sample.

Due to the complexity of its chemical composition, it is very difficult to describe the characteristics of BCO based on a single component. For practical reasons, the components of BCO were commonly assigned to more general categories of organic compounds. As an example, Yoo et al. [19] divided the components of liquid fuel obtained by pyrolysis of wild reed were grouped into oxygenate, phenolic, aliphatic hydrocarbon, monocyclic aromatic, polycyclic aromatic, and nitrogen-containing species. In another study, the components of BC produced by pyrolysis of grass biomass (Napier grass) the components of liquid fuel obtained by pyrolysis of Napier were divided into hydrocarbon, aromatic, phenol, alcohol, and other oxygenates [20].

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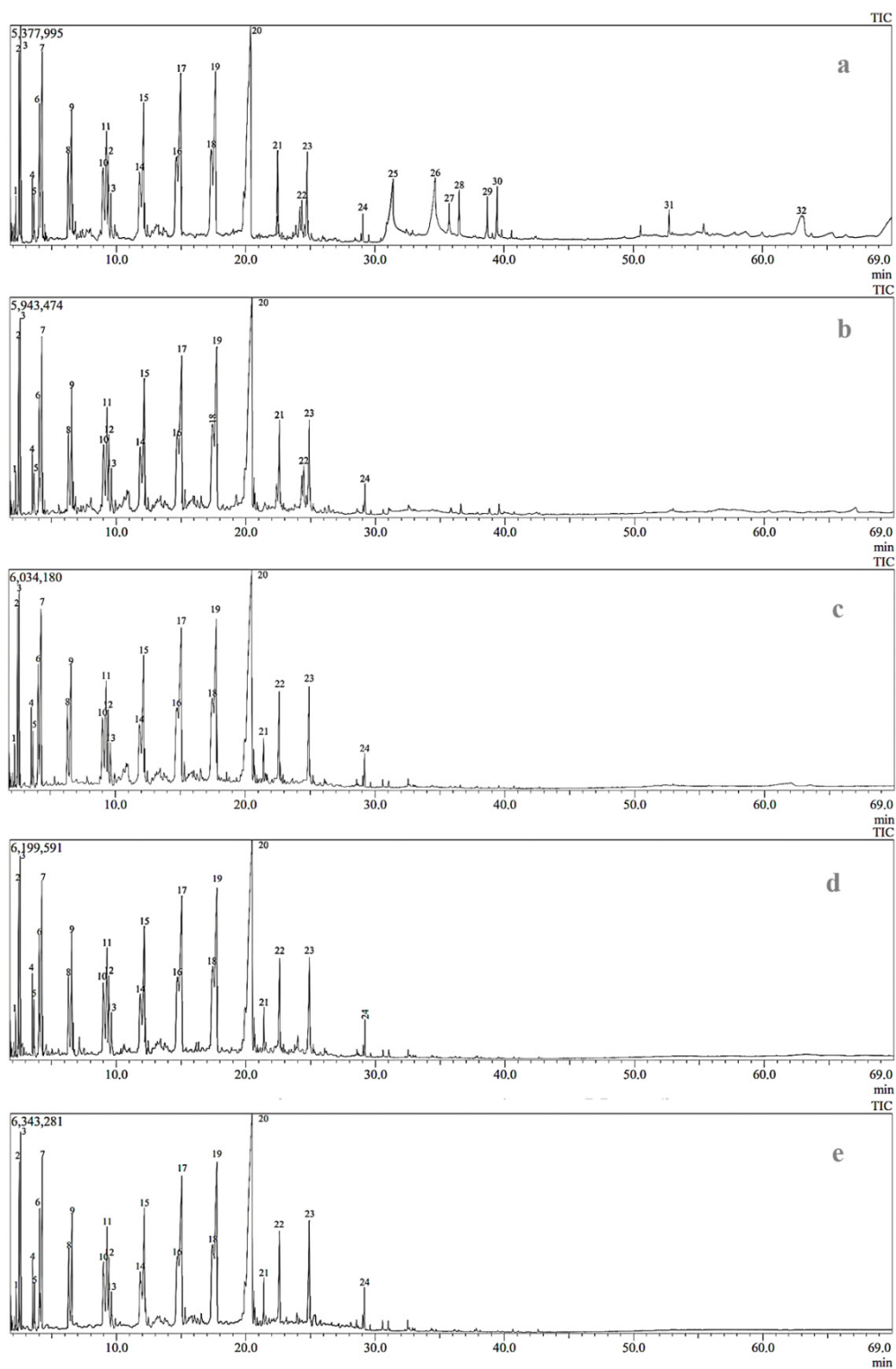
Figure 6. Chromatogram of upgraded fuel using different catalysts: (a) zeolite-Y, (b) H-Y1, (c) H-Y2, (d) H-Y3, and (e) H-Y4.

The components of the samples produced from upgrading experiments (upgraded oils) were identified and their relative percentages were calculated in the same way as applied to the BCO produced without catalyst, and the results are summarized in Table 4.

Table 4. Chemical constituents of the upgraded oils produced using original zeolite-Y (Na-Y) and protonated zeolite-Y (H-Y) as catalysts.

Chemical component	Catalyst				
	Na-Y	H-Y1	H-Y2	H-Y3	H-Y4
Cyclohexene	0.60	0.48	0.47	0.52	0.44
1-Octene	3.30	3.18	2.39	2.63	2.34
Octane	4.38	3.50	3.44	3.56	3.21
2-Octene	0.46	nd	0.36	nd	nd
Ethylbenzene	0.90	0.78	0.93	nd	0.80
1,3-dimethylbenzene	nd	0.66	nd	nd	nd
1-Nonene	3.57	2.77	2.66	nd	0.66
Nonane	6.86	5.11	5.10	5.56	2.48
4-Nonene	nd	nd	nd	nd	4.77
1-Decene	3.32	2.56	2.44	nd	2.31
Decane	4.44	3.46	3.36	nd	3.26
Cyclopropane, octyl-	nd	3.14	3.00	3.51	nd
4-Undecene	nd	0.81	0.96	nd	2.90
Undecane	nd	3.82	3.63	nd	nd
5-Undecene	nd	1.77	1.69	nd	3.54
Isopentylbenzene	nd	nd	0.68	nd	nd
1-Dodecene	4.02	3.25	3.14	2.01	1.30
Dodecane	6.16	5.02	5.04	4.29	1.73
2-Dodecene	nd	nd	nd	2.15	1.70
6-Dodecene	nd	nd	nd	nd	4.89
Cyclodecane	6.66	nd	nd	nd	nd
Cyclododecane	2.56	2.74	5.46	nd	nd
1-Tridecene	nd	2.81	8.27	nd	nd
Tridecane	9.57	8.54	nd	5.62	5.82
1-Tetradecene	nd	nd	3.85	nd	4.59
3-Tetradecene	nd	nd	2.14	3.23	nd
5-Tetradecene	nd	nd	8.62	9.09	9.55
6-Tetradecene	nd	nd	nd	1.35	1.89
Tetradecane	nd	8.24	nd	3.98	7.64
Cyclotetradecane	nd	6.25	0.69	2.92	nd
1-Pentadecene	3.70	nd	1.72	1.20	0.87
Pentadecane	22.23	nd	nd	nd	22.1
Cyclohexylhexane	0.82	nd	nd	nd	nd
1-Hexadecene	nd	nd	6.92	nd	1.12
3-Hexadecene	nd	nd	nd	0.68	2.65
Hexadecane	2.25	2.16	3.40	9.25	nd

Continued on next page

Chemical component	Catalyst				
	Na-Y	H-Y1	H-Y2	H-Y3	H-Y4
3-Hexadecene	nd	nd	nd	nd	0.28
Heptadec-8-ene	1.10	nd	nd	2.06	1.64
Heptadecane	2.49	21.70	8.29	23.5	1.59
Heptadec-1-ene	nd	nd	nd	0.89	nd
9-Octadecene	1.06	1.80	0.96	2.67	nd
5-Octadecene	nd	0.99	2.21	1.12	nd
Dodecane, 2-cyclohexyl	nd	nd	0.77	nd	nd
3-Octadecene	nd	1.22	nd	nd	nd
Octadecane	nd	2.63	nd	nd	3.10
1-Nonadecene	nd	nd	2.30	1.33	nd
3-Eicosene	nd	nd	1.16	nd	nd
9-Eicosene	nd	nd	1.26	1.46	nd
Eicosane	nd	nd	2.69	3.141	nd
Heptyl methyl ketone	nd	nd	nd	1.51	nd
2-Heptadecanone	0.60	nd	nd	0.77	0.83
9-Heptadecanone	nd	0.61	nd	nd	nd
Hydroxymethyl ethyl ester	0.88	nd	nd	nd	nd
Nonadecane, 1,2-epoxi	0.61	nd	nd	nd	nd

As displayed by the experimental results in Table 4, the samples are characterized by the existence of some common compounds, while some others are found only in certain samples indicating that some compositional differences between the samples should also be acknowledged. These compositional similarities and differences between the samples are related to the complexity of the reactions during the catalytic upgrading process applied. To make the comparison between the samples easier, the components of the samples were grouped into more general categories as indicated in Table 5.

Table 5. Relative composition of BCO and upgraded oils produced using original and protonated zeolite-Y as catalysts.

Catalyst	Relative composition (%)				
	Hydrocarbon	Acid	Ketone	Ester	Ether
-	80.23	18.93	0.84	-	-
Na-Y	90.46	-	0.60	8.33	0.61
H-Y1	99.39	-	0.61	-	-
H-Y2	100.00	-	-	-	-
H-Y3	97.72	-	2.28	-	-
H-Y4	99.17	-	0.83	-	-

The results in Table 5 displays several interesting features of the relative compositions of the samples. First is the presence of hydrocarbon as the component with the highest relative percentage in all samples, including the BCO, which was produced without the use of a catalyst. With respect to hydrocarbon content, it was also observed that the percentage of this category is significantly lower

than those found for the upgraded fuels. In addition to significant increases in hydrocarbon contents as a result of upgrading treatment, another interesting result is that in the upgraded oils, no acid was found, suggesting that the acid was completely deoxygenated during the upgrading process. Comparing the composition of upgraded oils, it can be seen that the hydrocarbon contents of the upgraded oils using H-Y catalysts are significantly higher than that of the upgraded oil using Na-Y as a catalyst. This trend implies that the increased acidity of H-Y, as compared to that of Na-Y, strengthens the performance of the catalysts for deoxygenation process. In addition to lower hydrocarbon content, the upgraded oil using Na-Y is characterized by the presence of ketone, ester, and ether, while in the upgraded oils using H-Y catalysts, only ketone was detected in addition to hydrocarbons, with the exception of the upgraded fuel using the H-Y2 catalyst, which is practically pure hydrocarbon. Overall, the results presented in Table 5 demonstrate that protonation extent has a significant effect on the hydrocarbon contents of the upgraded oil, which signify the appreciable performance of the protonated zeolites to enhance deoxygenation process, leading to hydrocarbon enrichment as expected. It is acknowledged that biomass pyrolysis involves complex and random non-stoichiometric reactions. Despite basic reaction features, several catalytic upgrading reactions leading to deoxygenation and hydrocarbon formation have been suggested, including cracking of long chain hydrocarbons, decarbonylation to remove oxygen as carbon monoxide, decarboxylation to remove oxygen as carbon dioxide, and hydrodeoxygenation to remove oxygen as water [21].

To provide more insight on the profile of hydrocarbon content in the BCO and upgraded oils, the hydrocarbons were distributed into biogasoline range (C_5-C_{12}), bioavture range (C_{13}-C_{17}), and biodiesel range (C_{18}-C_{28}) as shown in Table 6.

Table 6. Distribution of hydrocarbons in BCO and upgraded oils produced using original and protonated zeolite-Y as catalysts.

Catalyst	Hydrocarbon distribution (%)		
	C_5-C_{12}	C_{13}-C_{17}	C_{18}-C_{28}
-	43.33	36.89	nd
Na-Y	48.06	41.34	1.06
H-Y1	42.30	50.45	6.64
H-Y2	44.75	43.90	11.35
H-Y3	24.23	63.77	9.72
H-Y4	36.33	59.74	3.10

As displayed by the data in Table 6, no biodiesel range hydrocarbon was found in BCO, which is in agreement with the results obtained for this particular sample, in which two C_{18} compounds detected are acids (Table 3). In all upgraded oils, the three hydrocarbon categories were found; however, no evident trend to draw the relation between the extent of protonation of the zeolite-Y and the distribution of the hydrocarbon in the oils. Regardless of this lack of evident relation, the results obtained displayed that Na-Y has the highest tendency to enhance the formation of biogasoline, while the H-Y3 is the catalyst with the highest tendency to promote the formation of bioavture. In all samples, it can be seen that biodiesel is the category with the lowest percentage.

The appearance of hydrocarbon compounds belonging to the biodiesel category (C_{18}-C_{28}) in the samples resulting from upgrading, while they are not detected in the BCO samples, is most likely due to deoxygenation of the acids contained in the BCO with the use of catalyst. This assumption is

based on the characteristic of zeolite which has been acknowledged to have the ability to promote deoxygenation of oxygen-containing components of the BCO during the upgrading process [21].

Catalytic upgrading of BCO using zeolites as catalyst has also been reported in several literatures. As an example, Chen and Yoshikawa [9] conducted bio-oil upgrading using ZSM-5 as catalyst and reported that upgrading treatment resulted in a reduction of oxygen up to 16%. The same catalyst was used in the study by Pattiya et al. [22] to upgrade bio-oil produced from cassava rhizome and reported enhanced production of aromatic hydrocarbon. In another study [23], catalytic upgrading of volatiles obtained by pyrolysis of lignite sample using H-Y zeolite was reported and the results obtained indicate that upgrading process resulted in increased content of naphthalene and methylnaphthalene up to 8.9 and 6.8 times, respectively, compared to the contents in the original sample. With respect to increased hydrocarbon contents of upgraded bio-oil, the results obtained in this present study are in agreement with the findings reported by others, although some differences in the types of hydrocarbons obtained should be acknowledged.

4. Conclusions

The results of this investigation demonstrated that zeolite-Y was successfully prepared from rice husk and food grade aluminium as raw materials, as confirmed by the results of XRD which show the existence of faujasite phase, and SEM which displays the existence of octahedral structure. The zeolite was then successfully converted into protonated zeolite with varied protonation extents depending on the concentration of the ammonium nitrate solution used, where the highest Na content reduction up to 89.948% was achieved according to XRF results. The results of catalytic upgrading experiments demonstrate that H-Y zeolites functioned to increase the bio-hydrocarbon content from 80.23% in the BCO to practically 100% in the upgraded oil. In addition, no acids were identified in the upgraded fuels, implying that H-Y zeolite is a promising catalyst for BCO upgrading for bio-hydrocarbon enrichment of the oil.

Use of AI tools declaration

The authors declare that they have not used Artificial Intelligence (AI) tools in the creation of this article.

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Conflict of interest

The authors declare no conflicts of interest in this paper.

Author contributions

Conceptualization, W.S. and K.D.P.; Methodology, W.S. and K.D.P.; Software, K.D.P. and I.I.; Validation, W.S.; K.D.P.; and I.I.; Formal Analysis, K.D.P and I.I.; Investigation, T.D.F. and A.P.I.; Resources, K.D.P. and W.S.; Data Curation, K.D.P. and I.I.; Visualization, T.D.F. and A.P.I.; Project Administration, K.D.P. and I.I.; Writing—Original Draft Preparation, W.S.; K.D.P. and S.H.; Writing—Review & Editing, W.S.; K.D.P. and S.H.; All authors have read and agreed to the published version of the manuscript.

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