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Extraction of Biofuels from Empty Fruit Bunches (EFB) Biomass

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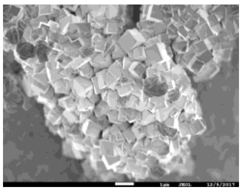
GRAPHICAL ABSTRACT


FESEM image of zeolite A

ABSTRACT

Empty fruit bunches (EFB) is one of oil palm biomass residues which can cause pollution to the environment through its waste treatment process. Thus, in this study, the second generation of biofuels produced by the catalytic conversion of EFB was carried out utilizing zeolite A as a heterogeneous catalyst. The characterization of zeolite A was done using fourier-transformed infrared spectroscopy (FTIR), x-ray diffraction (XRD) and field emission scanning electron microscope (FESEM). An amount of 50 g dried EFB with the aid of zeolite A was catalytically pyrolyzed at different temperatures (320, 350, 370, 400, 420 °C) and catalyst loading (0.3 g, 0.5 g, 1.0 g) to optimize the reaction conditions. Lastly, the liquid biofuels collected from the reaction was characterized using (FTIR) and gas chromatography-mass spectrometry (GC-MS). The diffractogram for zeolite A exhibited narrow and high intense peaks indicating the crystallized properties of zeolite A. Moreover, the FESEM image of zeolite A showed a cubic form with an average size of 100 nm. Experimental results indicated that an optimum biofuels conversion yield of 58.92 % was achieved with optimal conditions temperature of 400 °C, 2 hours and catalyst loading, 0.5 g without solvent. From FTIR spectrum and GC-MS results, there are many types of desired and undesired organic compounds generated from the catalytic pyrolysis reactions. Desired compounds included hydrocarbon, phenol and alcohols while esters, ethers, aldehydes and ketones were catogorized as undesired compounds. The process has successfully converted EFB waste to biofuels with higher efficiency.

Keywords: Empty fruit bunches, zeolite A, pyrolysis, GC-MS.

1. INTRODUCTION

Palm oil manufacturing is one of the industries in Malaysia that have been growing due to the high demands of food, cosmetic, and hygienic product [1]. However, it also produced huge amount of residues which may be harmful and pollute the environment due to the emission of a large amount of white smoke from process of waste treatment. Empty fruit bunch, palm kernel shells, oil palm fronds, oil palm trunks, mesocarp fiber, and palm oil mill effluent are some of residues of palm oil biomass. In order to save the environment, some action should be taken for at least to decrease the amount of residues or recycle it into a good product. Thus, waste to wealth concept can be applied in this case.

Empty fruit bunches (EFB) are part of palm oil biomass residues that produced from fresh fruit bunches. EFB have a great potential to be recycle as it can produce biofuels. Production of biofuels from non-food or abundance of plant waste biomass is called second generation biofuels [2]. These second-generation biofuels is environmentally friendly and in order to reduce the conversion's cost, advance technology still under development. An analytical method is needed to find a way to increase the production of biofuels.

Pyrolysis is the technique that can be used in this case as it can convert palm oil biomass to biofuels. However, it also will produce gas and char as side products of the reaction. In this technique, palm oil biomass thermo chemical decompose with rapid heating and in the absence of oxygen. The lignocellulosic compound in biomass will convert into the biofuels. Hence, dark brown, viscous and corrosive liquid biofuels will be produced. However, with their relatively unstable and chemically very complex compounds, potential to use directly in engines or turbines will be limited [3]. Thus, in order to improve the yield and quality of biofuels, nanocatalyst has been introduced.

The advantages of using a nanocatalyst in this process are because it is 100 % selective, very active and also consume low energy [4]. It can be achieved by controlling the shape, size, electronic structure and surface composition, spatial distribution, and its chemical stability. In this study, zeolite A is used as the catalyst which can improve the yield of biofuels. Hence, the characterization of zeolite A was done using FTIR, XRD and FESEM. Thus, the aim of this study is to extract the biofuels form EFB, characterize the zeolite A and identify the optimize condition for catalytic pyrolysis with the presence of zeolite A. By the end of this study, the biofuels should successfully produce from EFB with higher efficiency.

2. EXPERIMENTAL

Zeolite A was characterized using Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD) analysis and Field Emission Scanning Electron Microscope (FESEM). The particle size and morphology distributions were analyzed using FESEM. The data obtained from the characterization is significant to the effectiveness towards catalytic pyrolysis of EFB in the production of biofuels.

The refined-bleached-deodorized palm oil (12 grades) used was obtained from Bagan Datoh, Perak, Malaysia. The biofuels was prepared in 1L batch reactor together with a mechanical stirrer. Then, the reactor was sealed and filled with nitrogen gas in order to set the temperature and pressure. A tube reactor with an inner diameter of 80 mm and a length of 140 mm was used as the autoclave. An amount of 50 g of dried EFB with aids of 1 g of zeolite A was catalytically pyrolyzed at different temperature (320, 350, 370, 400, 420 °C) and catalyst loading (0.3 g, 0.5 g, 1.0 g) to optimize the reaction conditions. Every hour, the liquid samples of biofuels were extracted then were analyzed using gas chromatography-mass spectrometry (GC-MS).

The dark brown liquid biofuels were analyzed using GC-MS and FTIR. The liquid product sample of biofuels were diluted with 1 : 10 in chloroform and analyzed using the Agilent 6890N GC/5975 B MSD together with the HP-5 capillary column. The injection temperature was set at 280 °C, while GC oven temperature was programmed as follows : 4 minutes hold at 50 °C, 2 °C per minute ramping to 80 °C, a 10 minutes hold at 80 °C, 10 °C per minute ramping at 300 °C, and a 10 minutes hold at 300 °C. The high temperature for the injection was for a reliable and direct quantification of fatty acids and triglycerides without derivatization. The compound distributions of pyrolysis oil were analyzed using GC-MS based on chemical functional groups and was determined via the percentage area of the chromatograph peaks. The percentages of different functional group such as hydrocarbon, phenol, aldehyde, acids and ketone were determined by total ion chromatogram peaks areas using the NIST software.

3. RESULTS AND DISCUSSION

3.1. Characterization of Zeolite A

Zeolite A was characterized with FTIR, XRD and FESEM in order to study the characteristic of zeolite A. Figure 1 showed FTIR results of zeolite A in the range of 400-4000 cm^{-1}. The three bands most common to zeolite can be found in the regions of 1001 cm-1, 666 cm-1 and 553 cm-1. These absorption bands are characteristic of the internal SiO4 tetrahedra vibrations indicating the O-Si-O asymmetrical stretching modes, O-Si-O symmetrical stretching modes and Si-O bending modes respectively. The broad band of weak intensity was observed around 553 cm-1, this peak indicated the presence of zeolite A band assigning the cubic prism. The band at 553 cm-1 represents the beginning of the crystallization of zeolite with double rings. The structure of zeolite A contains 4-membered double rings can be seen in the spectra region of 650 and 500 cm-1. The existence of O-H groups (hydrogen bonded Si-OH groups) represented at the broad band around 3436 cm-1 and the absorption at 1651 cm-1 represents to bending mode of water.

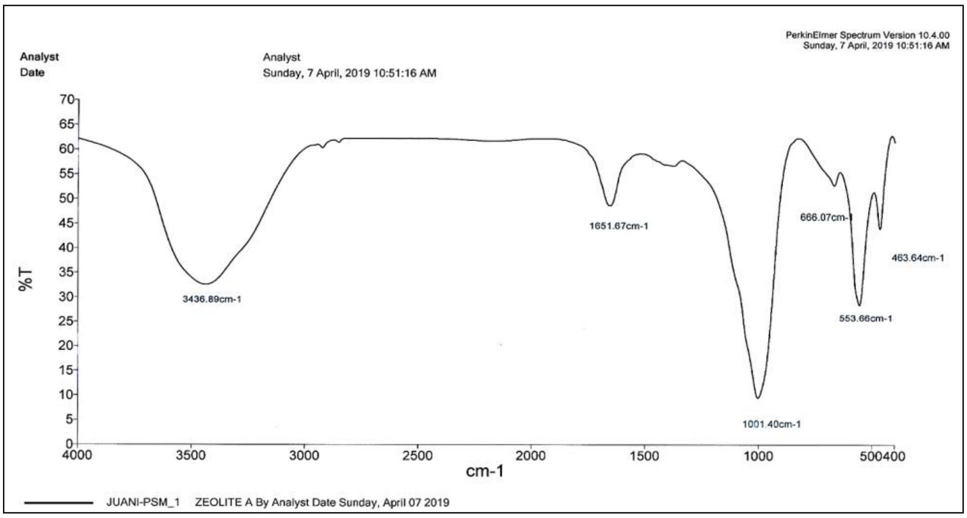


Figure 1. FTIR spectrum of zeolite A

In order to support the FTIR analysis, the characterization of zeolite A was done using X-ray diffraction technique. The XRD pattern of zeolite A was illustrated in Figure 2. The diffractogram for zeolite A exhibited narrow and high intense peaks which indicate the crystallized properties of zeolite A. The synthesis of zeolite A showed the characteristic peak at 7.1°, 10.1°, 12.4°, 16.0°, 20.3°, 21.6°, 23.9°, 26. 0°, 27.0°, 30.8°, 32.5° and 34.1°.

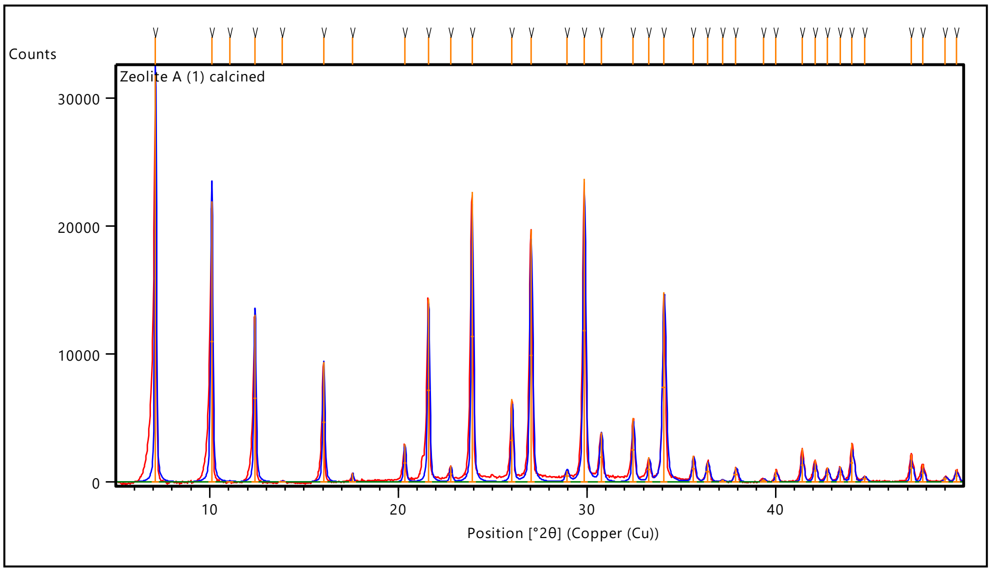


Figure 2. XRD result for zeolite A

The characterization of zeolite A was continued using FESEM in order to identify the morphology and estimate the particle size of zeolite sample. The Figure 3 showed a cubic form with an average size of 0.5–1.0 µm. The image of zeolite A was supported by Ghasemi *et al.* [5] which obtained the same morphology for the zeolite. The nanoparticle size of zeolite A also contained more Na ions which can lead to ion exchange of Na ion in the pyrolysis reaction that helped in increasing liquids biofuels production. In addition, zeolite pore size played an important role in the mass transfer and diffusion of large intermediates into pores along with a variety of reactions for the production of aromatics in catalytic pyrolysis process. However, microporous, mesoporous and macroporous zeolite have been deeply studied where aromatic yield has been reported as a function of pore size [6]. The surface area and pore volume of the catalyst can be increased by chemical treatment such as acid leaching or thermal activation which can enhance its catalytic functions [7]. Higher resolution transmission electron microscopy (HR-TEM) analysis can be used in order to obtain more information on the structural features of zeolite including particle size, clear morphology, crystallographic phases from HR-TEM images, atomic fringes, selected area electron diffraction (SAED) and EDS analysis [8, 9].

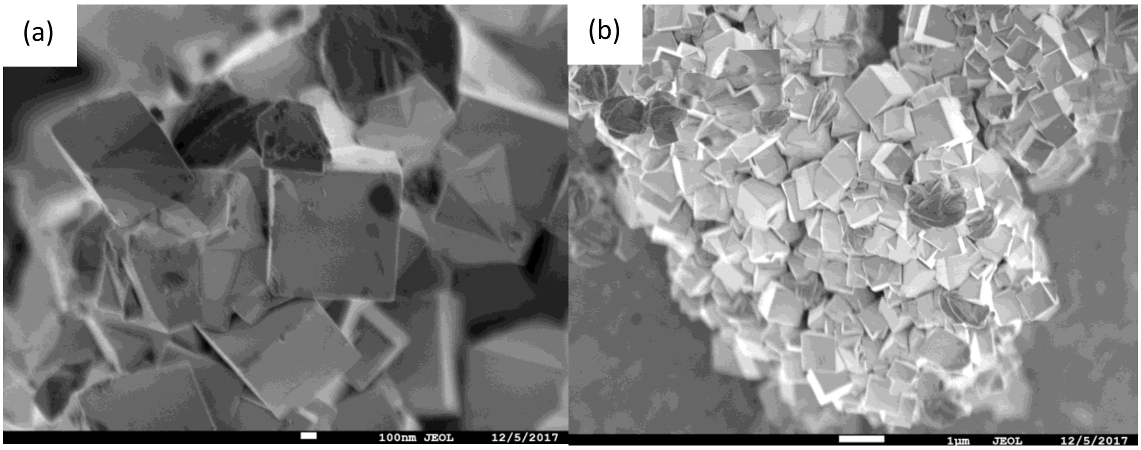


Figure 3. FESEM result for zeolite A

3.2. Effect of Temperature and Catalyst Loading on The Yield of Biofuels

The pyrolysis reaction converted EFB to several products including liquids, gaseous and char. From the catalytic pyrolysis, the color of liquid biofuels produced was dark brown together with char and gaseous as by product. The effect of different temperatures on liquid, char and gas product yields in pyrolysis reaction are depicted in Figure 4.

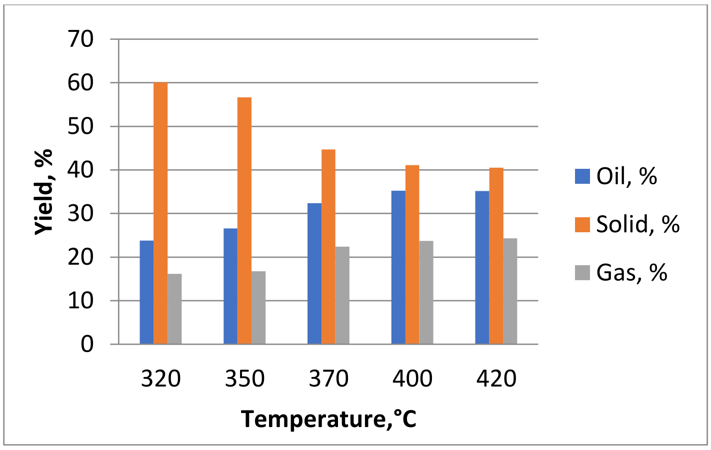


Figure 4. The yield (wt%) of char, liquid and gas products in pyrolysis oil of EFB (1 wt% of zeolite A catalyst, 50 g EFB, pyrolyzed at different temperature for 2 hours)

Figure 4 shows the temperature profile on the pyrolysis products of EFB. Over each temperature used, char yield was obtained the highest product followed by liquid oil and gas from catalytic pyrolysis process. Char yield was obtained highest at lower temperature (320 °C) approximately around 60 wt% and started to decrease when temperature increased. This condition is due to production of partially pyrolyzed raw biomass. The char yield continued decrease from initial weight percentage at the final of terminal temperature used. This reduction is due to the rapid and comprehensive decomposition of lignocelluloses components as the heat increased. Trend of char and liquid pyrolysis product seemed to inverse between each other. The liquid product yielded only around 24 wt% at earlier pyrolysis temperature (320 °C). The yield of pyrolysis liquid was increased to maximum yield percentage around 36 wt% at 400 °C, though the yield was slightly dropped to 35 wt% as temperature increased. This condition is happened due to the small increment of gas yield up to 25 wt% at 420 °C. An increment of gas yield is assured due to the secondary cracking of the pyrolysis vapours and secondary decomposition of the char at higher temperature [10]. The biofuels conversion yield was the total weight percentage of gas and oil yield. Hence, results show that the optimum liquid biofuels conversion yields was 58.92 %, achieved at temperature 400 °C with 0.5 g of catalyst loading.

However, the yield of liquid product for the catalytic pyrolysis process is quite low because the EFB used in this experiment was not treated. The effect of the untreated and treated EFB catalytic pyrolysis on liquids biofuels proved that the liquids products produced increased by 35 wt% for the treated EFB [11]. In order words, yield of liquid product was successfully increased when the EFB was treated. Ideally, the high yield of liquid product for obtained from treated sample was because the cellulose and hemicelluloses structure in biomass easily degraded during pyrolysis. From the results, it is proved that EFB sample need to be treated with NaOH in order to produce high yield of biofuels product.

Next, further study was on the effect of catalyst loading to the biofuels yields. Figure 5 shows the results of pyrolysis products yields with different catalyst loading at temperature 400 °C for 2 hours. Based on Figure 5, oil yield percentage for 0.5 g and 1.0 g catalysts loading were approximately same which is around 35.1 wt%. However, oil yield slightly decreased at 34 wt% with 1.5 g of catalyst loading. This condition could be due to the agglomeration of active CaO phase and the cover of basic sites by excess CaO [12], hence less oil produced.

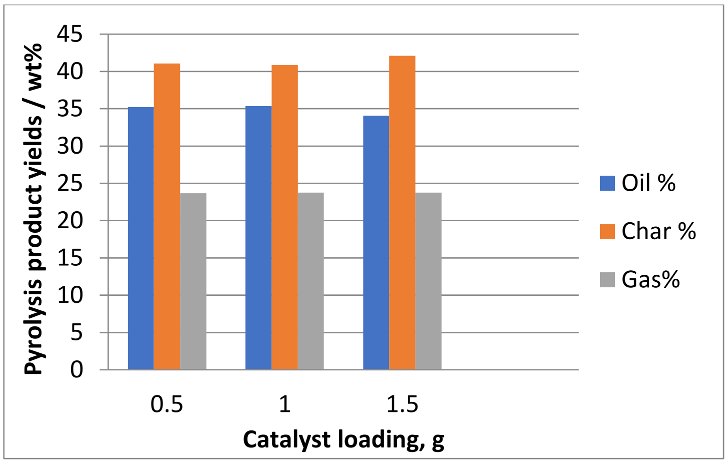


Figure 5. The yield (wt %) of char, liquid and gas products in pyrolysis oil of EFB (different amount of catalyst, zeolite A at 400 °C for 2 hours)

3.3. Characterization of biofuels

The biofuels produced by pyrolysis catalytic process were analyzed with FTIR and GC-MS in order to study the characterization of biofuels. FTIR and GC-MS detected and identified the functional groups of compounds that presence in the biofuels product. The product yield of liquid biofuels from the catalytic pyrolysis was calculated based on weight basis.

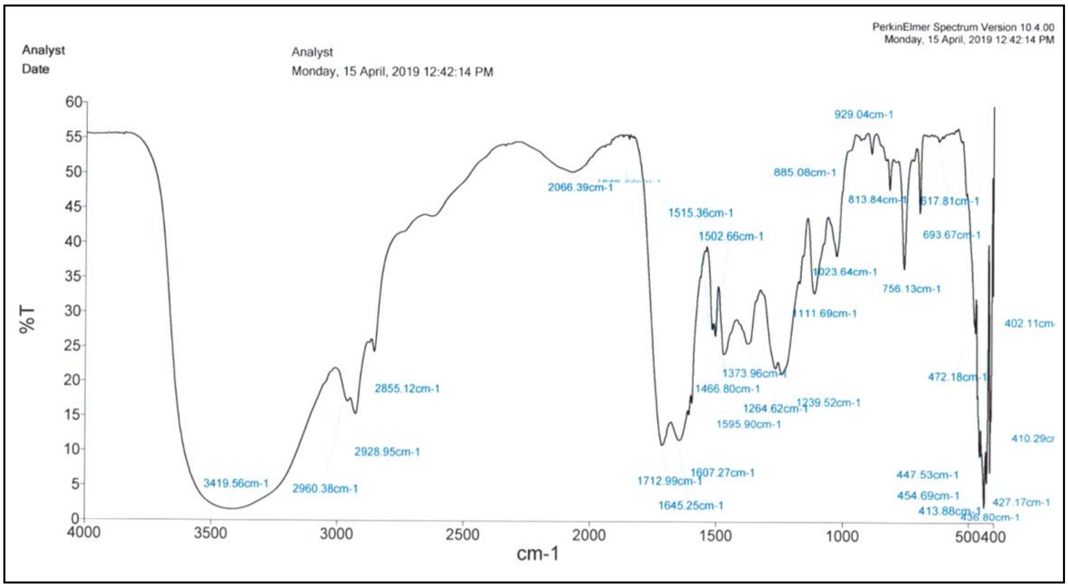


Figure 6. FTIR spectrum for pyrolysis at temperature 400 °C, 0.5 g catalyst loading

There are many types of organic compounds that present in liquids biofuels including hydrocarbons, alcohols, phenols, aromatic compounds, esters, ethers, aldehydes and ketones. These functional groups can be categorized into two groups which were desired and undesired compounds. Hydrocarbons, phenols and alcohols are groups as desired compounds because can be used for fossil fuel or high valued chemicals. Meanwhile, the undesired compounds which included esters, ethers, aldehydes and ketones indicated results in the low heating value and stability of bio-oils. According to previous study [13], the C-H stretching bands at range 2800-300 cm^{-1} (partially also caused by O-H stretching and the bands in the region around 1000-1400 cm^{-1} , caused by combination and overlapping of C-O stretching bands and also by deformations occurred. The intensity of width bands between 1000 - 1100 cm^{-1} was depends on the presence of sugars in the samples. The bands in the region above 3000 cm^{-1} which is for hydroxyl group were due to alcoholic or phenolic components.

The compound distributions of pyrolysis oil were analyzed using GC-MS based on chemical functional groups and was determined via the percentage area of the chromatograph peaks. Figure 7 shows the total ion chromatograph of biofuels pyrolyzed at 400 °C and 0.5 g of zeolite A. Based on the total ion chromatography, there are many compounds detected in the chromatograph including aldehydes, phenolic, hydrocarbons, nitrogenated, ketones, acids and alcohols. The result showed that phenolic appeared as the dominant compound in the biofuels which including phenol, 2,5-dimethoxy, phenol,2,6-dimethoxy-4[2-propenyl], phenol, 2-methoxy-4methyl and others phenolic compounds. The furan derivatives, organic acids, long chain alkanes, ester and alcohol also existed in the EFB. The furan derivatives and the organics acids were formed form the cellulose and hemi-cellulose components of the EFB. Moreover, the presences of phenolic compounds in the EFB were due to the degradation of lignin component in the feedstock.

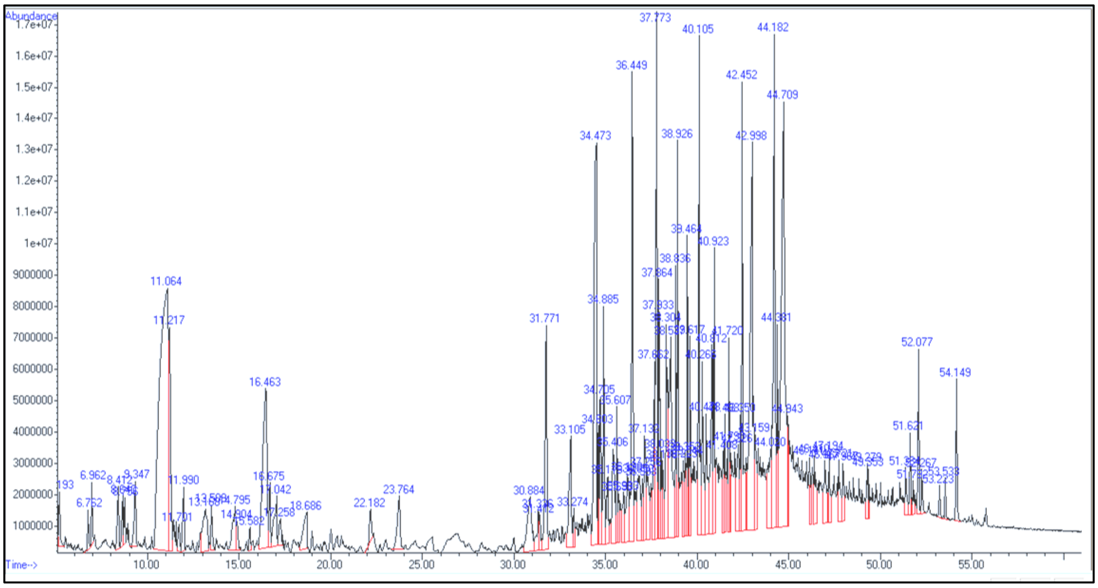


Figure 7. The GC-MS chromatograph of biofuels (50 g EFB pyrolyzed at 400 °C, 0.5 g of zeolite A, for 2 hours)

According to previous reports [14], the multicomponent mixtures are derived primarily from depolymerisation and fragmentation reaction of the three key building blocks of lignocelluloses: cellulose, hemicelluloses and lignin. The phenol-2,6-dimethoxy are formed from the lignin fraction. The basic unit of lignin is phenyl propane that have high source of phenolic compounds in the liquid hydrocarbons. The miscellaneous oxygenates, sugars and furans chemical compounds might form from the cellulose and hemicelluloses of the EFB biomass. Besides, the formation of esters, acids, alcohols, ketones and aldehydes might due to the results of decomposition of miscellaneous oxygenate, sugars and furans. The presence of aromatic and oxygenated compounds is due to their nature biopolymer on earth such as cellulose and hemicellulose. In the future research, the oxygenated organic compounds need to be separated from the aqueous phase and need to be upgraded using hydrotreating-hydrocracking process in order to increase their heating value together with reducing the corrosiveness for potential fuel used [15].

4. CONCLUSION

The production of biofuels was successfully obtained using EFB biomass with the presence of the zeolite A catalyst with biofuels conversion yields of 58.92 %. The optimal conditions for the production of biofuels was achieved at temperature 400 °C, 2 hours and catalyst loading, 0.5 g without solvent. Based on the FTIR spectrum and GC-MS results, there are many types of desired and undesired organic compound generated from catalytic pyrolysis reactions including hydrocarbons, alcohols, phenols, aromatic compound, esters, ethers, aldehydes and ketones. Desired compounds included hydrocarbon, phenol and alcohols while undesired compounds were esters, ethers, aldehydes and ketones. Liquid biofuels from pyrolysis contains high concentration of phenolics and its derivatives compound which confirmed with FTIR and GC-MS analysis. The extraction of EFB waste to biofuels was successfully achieved with higher efficiency.

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