International Journal of Innovation Scientific Research and Review
Vol. 02, Issue, 11, pp.504-507, November, 2020
Available online at http://www.journalijisr.com

IJISRR

Research Article

ISSN: 2582-6131

CHARACTERIZATION STUDY ON THERMAL ACTIVATION OF PETROLEUM COKE (PETCOKE) & OIL PALM SHELL (OPS)

***Alia Khalid,Nurida Mohd Yusop, Hazratul Mumtaz Lahuri, Syarifah Nur Faizah and Yi Herng Chan**

Petronas Research Sdn. Bhd. (PRSB), Lot 3288 & 3289, Off Jalan Ayer Itam, Kawasan Perindustrian Bangi, 43000 Kajang Selangor Malaysia

Received 14th September 2020; Accepted 20th October 2020; Published online 23rd November 2020

ABSTRACT

Waste materials can be used as feedstock for gasification process due to its high heating value. Petroleum Coke (PETCOKE) and Oil Palm Shell (OPS) are among the waste materials that can be used as feedstock in the gasification process. The characterization and properties of the untreated and treated (activated) PETCOKE and OPS through pyrolysis (thermal) were investigated to determine the suitability as feedstock for the gasification process The chemical properties were investigated using the Elemental Analyzer, SEM-EDX , XRF, RAMAN and the physical properties such as surface area, pore volume and pore size were determined using the Brunauer-Emmett-Teller (BET). It was found that there are changes in its elemental constituent as well as its morphological structure and surface area after activation at 900oC were performed. In overall, there is significance improvement observed physically and chemically for OPS compared to PETCOKE in terms of its organic constituent, inorganic constituent, as well as the chemical structure.

Keywords: Petroleum coke, Oil Palm Shell, Gasification, Characterization

INTRODUCTION

Waste materials such as PETCOKE, biomass, plastic, municipal sewage sludge and any other types of waste can be used as alternative conversion into fuel gas or chemical because of its high heating value. Gasification process is one of the process that can be considered as a way to recover energy from low grade fuels, biomass, waste or their mixtures. An Integrated gasification combined cycle (IGCC) is believed highly efficient and has great potential for reducing the amount of man-made CO2 emission and these waste materials have been used as a feedstock for IGCC (Fernando *et al.,* 2011). There are two (2) types of waste have been selected in this study. PETCOKE is a carbonaceous solid material by product with less commercial value where it is generated at Delay Coker Unit (DCU) in Refinery Sungai Udang, Melaka. Generally, there are at least four (4) types of petroleum coke namely sponge coke, needle coke, sponge coke and shot coke (Hassan A. I 1990). Despite of continuing delayed coking process due to continuous supply of heavy crude, it is crucial to pay attention on the economic value of every refinery processes and safe environmentally utilization. Oil Palm Shell or OPS which were collected from one of the palm oil mill in Nilai were largely produced during refinery process and had caused storage problems within the vicinity of factories. It is estimated over 4.6 million of OPS is produced annually as waste in Malaysia (Teo *et al.,* 2006). Hence, utilization of this waste in the gasification process as performance comparison with PETCOKE is an opportunity to convert those low grades by product or waste to produce syngas or other high grade products in the future. Study showed that physical and chemical characterization of PETCOKE had influenced its behavior and application depending on the feedstock properties, coking condition and type of cooking process (i.e. delayed versus fluid coking). In general, PETCOKE consist mostly of carbon with range of75-90%, hydrogen content range of 2-4%, nitrogen content range of 1-2%, oxygen content range of 4-5% and impurities such as sulphur range of 1-8% and 0.05 wt% heavy metals content (Bontu et. al 2013) as well as few traces elements (Hill et. al 2014).

***Corresponding Author: Alia Khalid,**
Petronas Research Sdn. Bhd. (PRSB), Lot 3288 & 3289, Off Jalan Ayer Itam, Kawasan Perindustrian Bangi, 43000 Kajang Selangor Malaysia.

The elemental constituent for OPS indicates element that mostly biomass has such as carbon with range of 40-60%, hydrogen content 1-6%, nitrogen content 0.1-0.5%, oxygen content 8-45% with very low impurities sulphur content <0.02% and very rich of mineral or various type of trace elements (Wiebren de Jong 2014) Activation of PETCOKE and OPS is required to enhance and upgrade low quality petroleum coke to a valuable product adsorbing agent such as treatment of natural gas, polluted water and more interestingly in Reversed Boudouard process. Activation process can be either physical or chemical. However, physical activation is more favorable compare to chemical activation process due to economical reasons with the fact no involvement of chemical such as catalyst throughout the process (Finqueneisel et. al., 1997). The reaction that takes place during activation of PETCOKE is as follows where it is the disproportionation of carbon monoxide into carbon dioxide and graphite or its reverse at known temperatures : $2CO \rightleftharpoons CO2 + C$

Activation through physical process may require a steam or carbon dioxide or subjected to oxidation in air at high temperature (1100K) and atmospheric pressure. This activation whereby will improve the overall porosity, enlarged and improved the surface area of carbonaceous material. In general, the surface area of PETCOKE is classified as non-porous type with very low range which is below than 10 m2/g. (Hill J.M. 2016) Conversion of carbonaceous materials through gasification process into a valued mixture gas such as hydrogen, carbon monoxide and/or methane and not only carbon dioxide and water. Studies have shown the gaseous product can be converted to synthesis gas instead of being used for power generation (Hill et. al., 2014). Production of syngas from raw material such as PETCOKE are not prevalent in Malaysia. However, raw materials with high carbon such as biomass and organic waste are dominant for the study of gasification and syngas production as an alternative source of energy (Luis Puigjaner, 2011).This paper investigates the characterization of PETCOKE and Oil Palm Shell (OPS) that have been activated or heated at 900 oC and its gasification reactivity efficiency. Studies of changes in elemental or mineral contents i.e. inorganic and organic, morphological structure, surface area, pore volume and pore size, carbon structure of raw PETCOKE and OPS were compared to the PETCOKE and OPS that been activated or treated at 900oC.

METHODOLOGY

Raw Material Preparation

Petroleum coke was collected at Delay Coker Unit (DCU) in Refinery Sungai Udang, Melaka while oil palm shell (OPS) was obtained from local palm oil mill at Nilai. The sample was dried in oven at 100oC for 90 minutes, crushed, grinded and passed through a sieved at 62-212 µm size.

Thermal Activation Procedure

Thermal activation on PETCOKE & OPS was carried out by setting up the carbonization in a horizontal tubular furnace size. The experiment was carried out by loading 100 g of untreated PETCOKE and OPS through pyrolysis process under a nitrogen at atmospheric pressure. The sample was heat up by increase at a rate of 21oC/min until reach the carbonization temperature of 900oC and was kept for 90 mins. The carbonized sample was cooled down to room temperature under N2 flow and stored at ambient for further testing.

Analysis of Characterization

Elemental constituent analysis

Both samples i.e. raw PETCOKE, raw OPS, charred PETCOKE & OPS at 900oC was examined for elemental analysis to study the organic constituents through CHNS elemental analyzer (Elementar Vario MICRO Cube) and inorganic constituent compound through X-ray Fluorescence (XRF) (Panalytical Axios Max) and Energy Dispersive X-Ray (EDX) spectroscopy (Hitachi TM 3000) which provide information's on various metals compound such as sodium, potassium, magnesium and etc.

Morphological structure

a) Morphological structure: To investigate morphological microstructure of the sample, Scanning Electron Microscopy (SEM) (Hitachi TM 3000) was used.

b) Surface area, pore size and pore volume through Brunauer-Emmett-Teller (BET): The study on the surface area and its comparison between raw and charred sample was carried out using Brunauer-Emmett-Teller (BET) (Micromeritics ASAP). The sample was measured by 2 stages of degassing under nitrogen adsorption at Stage 1 : 90oC for 1hours followed by Stage 2 : 180oC x 5 hrs and analysis BET adsorption isotherm under liquid N2 at 77K was carried out to study surface area, pore size and pore volume.

Chemical structure

For the investigation of carbon structure, a Raman spectrometer (DXR2xi, Thermo Scientific) was used. Raman spectra was recorded in the range of 50-3400cm-1to study the structure of carbon changes after went through thermal activation process at 900oC.

RESULTS

Comparison of Element Constituents of untreated and treated (activated) PETCOKE and OPS

Element Constituents by X-ray Fluorescence (XRF)

Result of organic and elemental constituents of untreated and after activation by heating at 900oC for PETCOKE and OPS was shown in Table 1 and Table 2. The temperature at 900oC was selected based on recommended activation temperature for PETCOKE (Chao et. al., 2015) and OPS (Pooya *et al.,* 2012). It was observed that majority of elemental constituent in OPS was increased significantly after activation through heat or pyrolysis activity at 900oC. This has shown the increasing of important elements such as Mg, P, Si, Al, Fe, Na and Mn with ranged of 0.03-6.75 wt% in OPS which is believed can enhance the gasification process especially with presence of Ca and K with ranged of 0.96-6.75 wt% (Toshimitsu *et al.,* 2010). However, these elements in PETCOKE were very low detected even after activation with ranged of 0.01-0.11 wt%for Al, Si and Fe and only 0.04-1.01 wt% for Ca and K while not detected for Na, Mg, P and Mn. Hence, the PETCOKE needs catalyst to improve the gasification process due to low detection of these compounds.

Table 1. Elemental constituent of PETCOKE and OPS untreated and treated(activated) at 900oC

Sample	Element (wt%)_XRF								
	Na	Mg	K	Ca	P	Si	Al	Fe	Mn
Treated OPS 900	0.03	0.26	0.96	6.75	0.14	2.50	0.11	0.68	0.03
Untreated OPS	0.05	0.06	0.28	1.56	0.04	1.14	0.10	0.82	N.D
Treated PETCOKE 900	N.D	N.D	1.01	0.04	N.D	0.03	0.01	0.01	N.D
Untreated PETCOKE	N.D	N.D	N.D	0.03	N.D	0.04	N.D	0.08	N.D

Element Constituent through EDX spectroscopy

Presence of organic and inorganic constituents in OPS and PETCOKE through EDX spectroscopy analysis had supported and in agreement with the findings in Table 1 and 2 above. The results tabulated in Figure 2 indicates that the organic and inorganic constituent was detected and increased in amount when the sample went through the pyrolysis treatment. The elements detected in OPS such as Al, Si, K, Ca, C and O are among of the component formed in the OPS sample but very limited element with only C, O and S was detected in PETCOKE (Figure 1).

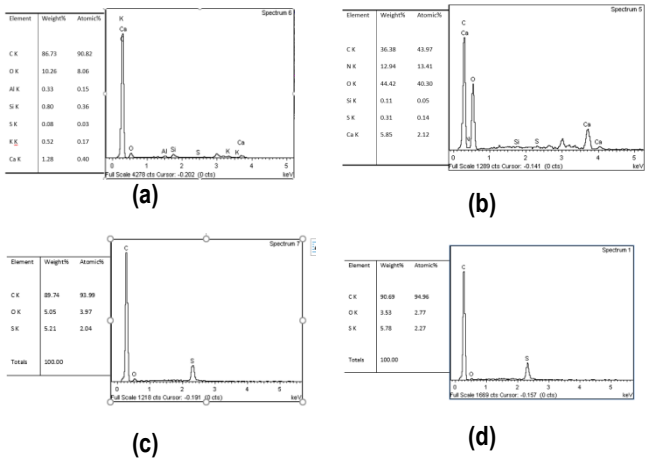

Figure 1. Detection of organic and inorganic constituent by SEM-EDX for untreated and treated at 900oC of OPS and PETCOKE (a) OPS 900 (b) Raw OPS (c) PETCOKE 900 (d) Raw PETCOKE

Organic Constituent by Elemental analyzer

In contrary, most organic constituent had shown opposite trending either in PETCOKE and OPS except element of carbon for both of samples after activation. Carbon compound was seen increase tremendously in OPS from (48.32 to 80.61 wt%) but not significance for PETCOKE (78.80 to 80.65 wt%) after treated (activation) was

performed. Sulphur content was shown detected in PETCOKE sample which support the study that this compound normally presence in PETCOKE 6-8% rather than in OPS. The presence of sulphur compound in PETCOKE will limit the application of this material. The treatment through pyrolysis at 900°C to PETCOKE showed the amount of this compound was 6.24 (wt%) (J.M Hill 2017).

Table 2. Organic constituents of PETCOKE and OPS untreated and treated (activated) at 900°C

Sample	Element (wt%)_CHNS				
	C	H	N	S	O
Treated OPS 900	80.61	1.74	0.45	0.01	17.19
Untreated OPS	48.32	6.17	0.09	0.02	45.40
Treated PETCOKE 900	80.65	1.19	0.76	6.24	11.20
Untreated PETCOKE	78.80	3.80	0.91	6.79	9.71

Comparison of surface area and morphological structure of untreated and treated (activated) PETCOKE and OPS

According to the International Union of Pure and Applied Chemistry (IUPAC), microspores are defined as pores smaller than 2 nm, whereas mesopores are in the range of 2-50 nm and macropores are wider than 50 nm. Table 3 shows BET surface area obtained for untreated and treated (activated) at 900oC for OPS and PETCOKE. It was observed that BET surface area for OPS had improved after activation at 900oC and the surface area of OPS was known as mesoporous. From the analysis, it has been observed that the surface area has been increased from 0.92 m2/g to 89.88 m2/g, unlike PETCOKE, the surface area of this sample had not shown significance improvement from 0.96 m2/g to 1.38 m2/g even after activation process at 900oC. This result has supported the finding from Zamaloa and Utigard 1996 that the specific surface area improved at only certain temperature but at high temperature above than 900oC to 1200oC the pore walls was further collapse due to the melting of the material. From the analysis, it is concluded that PETCOKE is non-porous type, as is evident from the relatively low surface area, low pore size and low pore volumes as reported in Table 3 for both conditions. It has been recommended standard analysis techniques are not necessarily applicable to the pore structures of all materials. Other common technique used such as mercury intrusion porosimetry has been used to quantify porosity (Josephine et. al., 2014). However, for improvement of measurement of surface area and pore size as well as pore volume through BET large volume of sample (near to 1g) instead of 0.3 g sample will be used in future. (Chan C.M. (2020)).

Table 3. Surface areas and pore size for PETCOKE and OPS untreated and treated (activated) at 900°C

BET analysis			
	Surface area (m2/g)	Pore volume N2, BJH (cm^3/g)	Pore size, N2 BJH (nm)
Treated OPS 900	89.88	0.0602	18.33
Untreated OPS	0.92	0.0003	0.09
Treated PETCOKE 900	1.38	0.0010	0.03
Untreated PETCOKE	0.96	0.0011	0.03

The changes of microstructure through SEM is depicted in the Figure 2 below. There is correlation between these two results in BET and SEM. Figure 1 illustrates that there is development of char N2 specific surface area on OPS microstructure compare to PETCOKE before and after the sample was treated. The activation at 900oC for PETCOKE seems gave no effect and improvement on its pore size, pore volume and its surface area. PETCOKE morphologies had shown the treated (activated) petroleum cokes were more rough with more folded structure compare to the untreated PETCOKE. In contrast, the treated OPS microstructure showed more pores were develop with more smooth and dense texture compare to the untreated OPS.

Scanning Electron Microscopy Energy Dispersive X-Ray (SEM-EDX)

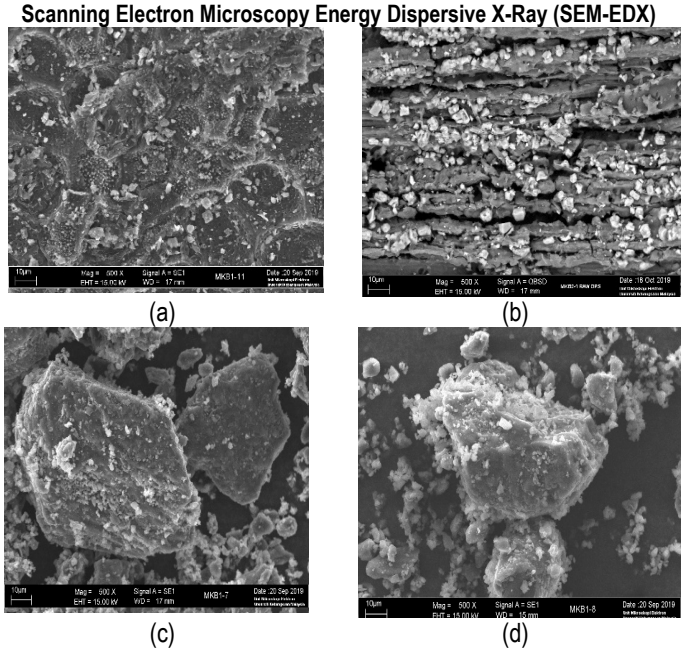

Figure 2. Microstructure analysis by SEM-EDX for untreated and treated at 900oC of OPS and PETCOKE (a) treated OPS 900 (b) untreated OPS (c) treated PETCOKE 900 (d) untreated PETCOKE

RAMAN Spectrometer for untreated and treated (activated) PETCOKE and OPS

The RAMAN spectra for two (2) sets of samples OPS & PETCOKE i.e. untreated and treated at carbonization temperature of 900oC are represented in Figure 3. There are 2 peaks correspond to D and G band were appeared at approximately 1300nm-1and 1600nm-1, respectively. Untreated PETCOKE sample had shown that D and G band intensity was lower compare to the treated (activated) PETCOKE. The decrease intensity of D-Band (ID) which referring to the amorphous carbon and G-Band (IG) representing graphite crystal when the sample treated at carbonization temperature of 900oC. The ratio of defect or graphitic order (ID/IG) for untreated and treated (activated) PETCOKE was decreased from 0.871 to 0.567 indicating the breakdown of atom symmetrical and increase the share of disordered carbon when the sample was pyrolyzed. Since untreated OPS has very low carbon around 48.3% as reported in CHNS, RAMAN result was not shown and compared with the treated (activated OPS). However, the D-band and G-band of treated OPS 900 was lower than treated PC 900. This indicates that the graphite character, its defect, curved graphite sheets and lattice distortion are difference between biomass sample (OPS) and PC.

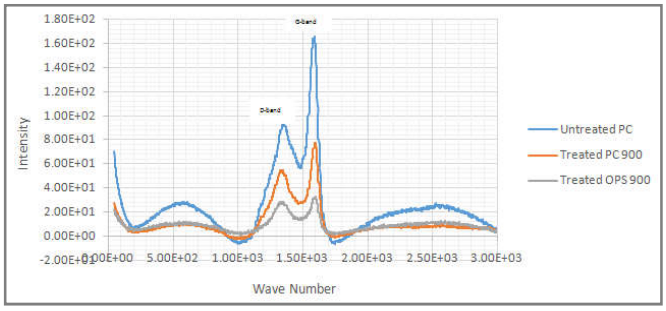

Figure 3. RAMAN spectra for untreated and treated at 900°C for OPS and PETCOKE

CONCLUSION

The physical and chemical properties of petroleum cokes (PETCOKE) and oil palm shell (OPS) have been examined. For elemental constituent analysis, OPS showed more minerals were detected such as Mg, P, Si, Al, Fe, Na, Mn, Ca and Kwhich minerals Ca and K are highly valuable for the improvement of the gasification process. As for PETCOKE, only minerals such as Si, Al, Fe, Ca and K were detected at very low concentration. PETCOKE may need catalyst to improve further its gasification process. Most inorganic element in OPS was increased significantly after treatment (activation) of OPS through thermal at 900^{o}C. Nevertheless, this was not happened to PETCOKE. There is no significant enhancement of these element after pyrolysis treatment (activated) at 900^{o}C. EDX spectroscopy and CHNS elemental analysis for both samples had indicated the presence of sulphur in PETCOKE but very low in OPS. Presence of this impurities will give effect or inhibit the gasification process where sulphur may release H_2S when hydrogen is combined during Syngas production. The release of H_2S level need proper monitoring during small scale reactor experiment for way forward. Study on the surface area, pore size, pore volume by BET versus SEM need further study as these analyses has correlations. However, only OPS had shown significant improvement during BET analysis but not for PETCOKE. The OPS showed it is mesoporous and PETCOKE is non-porous type where further improvement is required for non-porous type sample during BET study. This had supported findings through SEM where more pores were developed in OPS while PETCOKE only showed it's deformed surface after the treatment. The result for chemical structures through RAMAN indicates D-band and G-band of treated OPS 900 (biomass) was difference from PETCOKE. This study also indicates the distortion and defect of graphite structure had happened between untreated PETCOKE and treated (activated) PETCOKE.

REFERENCES

Al-Haj Ibrahim 1990. Desulfurization of petroleum coke, Research report, University of Pittsburgh, Pittsburgh.

Al-Haj I.H. 2019. Activation of Petroleum Coke. Petroleum & Petrochemical Engineering Journal).

Chan C.M. (2020) Effective Solution for Material Characterization Training Module 2020. Micromeritics™

Fernando Rubiera, José Juan Pis and Covadonga Pevida. 2011. Syngas from Waste, Green Energy and Technology, DOI: 10.1007/978-0-85729-540-8_2, _ Springer-Verlag London Limited 201. pp 11-12.

Finqueneisel G, Zimny T, Albiniak A, Siemieniewska T and Vogt D (1997) Improvement of the adsorptive properties of active cokes by mild oxidation in air. American Carbon Soc. Proceedings, pp: 90-91.

Hill J.M., A. Karimi, M. Malekshahian 2014.Characterization, Gasification, Activation and Potential uses for the Millions of Tonnes of Petroleum Coke Produced in Canada Each year. Can. J. Chem. Eng. 92:1618–1626.

Josephine M. Hill 2016. Sustainable and/or Waste Sources for Catalysts : Porous Carbon development and Significant. Elsevier. Catalysis Today 285 (2017) pp: 204-210.

Manuel Zamalloa and Utigard T.A. (1995). Characterization of Industrial Coke Structures. ISIK International 35(5):449-457. DOI: 10.2355/isijinternational. 35.449.

Teo D.C.L, Mannan M. A., Kurian V. J., and Zakaria I, 2006 "Flexural behaviour of reinforced lightweight OPS concrete beams," in Proceedings of the 9th International Conference on Concrete Engineering and Technology, pp. 244–252, Kuala Lumpur, Malaysia.

Toshimitsu Suzuki, Hiroshi Nakajima, Na-oki Ikenaga, Hirokazu Oda and Takanori Miyake (2011). Effect of Mineral Matters in Biomass on the Gasification Rate of their Chars. Biomass Conv. Bioref 1:17-28. DOI 10.1007/s13399-011-0006-2.

Wiebren De Jong 2014. Biomass Composition, Properties and Characterization. Chapter 2. Citation 2. American Institute of Chemical Engineers. Inc

****