Journal of Energy Research and Reviews

9(1): 43-50, 2021; Article no.JENRR.76284 ISSN: 2581-8368

Characterization of Coconut Shell Activated Carbon Catalyst for the Pyrolysis of Waste Sac Bags into Liquid Hydrocarbon Fuels

Kelechi Angelina Iheonye1,2*, Ifeanyichukwu Edeh² ,Ibrahim Kolawole Muritala³ and Ayoade Kuye1,2

¹World Bank African Centre of Excellence for Oil Field Chemicals Research, University of Port Harcourt, Port Harcourt, Nigeria.

²Department of Chemical Engineering, University of Port Harcourt, Port Harcourt, Nigeria. ³Department of Low Carbon Reducing Agents, Institute of Low-Carbon Industrial Processes, Deutsches Zentrumfür Lüft- Und Raumfahrt (DLR) / German Aerospace Center, 02763 Zittau, Germany.

Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/JENRR/2021/v9i130224 *Editor(s):* (1) Sreekanth. K. J., Kuwait Institute for Scientific Research, Kuwait. *Reviewers:* (1) Deacha Chatsiriwech, Chulalongkorn University, Thailand. (2) Moises Meza Pariona, State University of Ponta Grossa, Brazil. Complete Peer review History: https://www.sdiarticle4.com/review-history/76284

Original Research Article

Received 14 August 2021 Accepted 28 October 2021 Published 28 October 2021

ABSTRACT

Aim: The use of synthetic catalysts in pyrolysis of waste plastics into hydrocarbon fuels is the common practice, these synthetic/ commercial catalysts are not readily available in Nigeria. The aim of this research paper is to prepare and characterize and test the catalytic performance of a locally made catalyst for waste plastic to hydrocarbon fuel pyrolysis.

Study Design: locally made catalyst was prepared from coconut shells, its elemental composition, structural morphology and pore properties investigated using appropriate instruments and methods. **Place and Duration:** The experiments were carried out at the Petroleum Development Laboratory, situated at the Gas Engineering building, University of Port-Harcourt Nigeria. It took about 18 months to complete this study.

___ **Methodology:** Thermal and chemical activation methods were used to prepare the local catalyst from coconut shells. Scanning electron microscopy method was used to investigate the morphology

and texture of the coconut shell activated carbon catalyst. Response Surface Method (RSM) in design expert software 12.0 was used to design the experiment, and investigate the effect of operating parameters on the response variable.

Results: The assessment of coconut shell activated carbon shows it can be used as an alternate to synthetic catalysts. This is because more than 60 % fuel oil was recovered when it was used in the pyrolysis of waste sac bags

Conclusion: Coconut shell activated carbon is effective in the conversion of waste sac bags high purity hydrocarbon fuels such as aviation kerosene.

Keywords: Catalysts; coconut shells; activated carbons; pyrolysis; liquid fuels.

1. INTRODUCTION

Researchers are making efforts towards managing the negative impact of waste plastics to the environment. One of such is the conversion of waste plastics into transportation fuels and other chemicals, which are used as feedstock in the industries. Among various technologies that have been used catalytic pyrolysis stands out because it gives rise to lighter hydrocarbons, which can serve as transportation fuels. Treaties like the Kyoto Protocol and Agenda 21, encourage the use of climate friendly solutions [1]. In the absence of oxygen, complex polymer organic molecules can be degraded into smaller short-chain molecules via thermal pyrolysis and catalytic pyrolysis in the presence of a catalyst. The reaction mechanism for the conversion of waste plastic is complex, but discussed it in four steps- initiation, transfer, decomposition and termination [2]. Temperature, residence time, heating rates, feedstock composition, presence of a catalyst, catalyst to feed ratios, and type of reactor employed, e.g. fixed bed reactor, tubular reactor, batch, and semi-batch reactor, are all elements that affect thermal and catalytic pyrolysis [3]. A lot of work has been carried out on catalytic pyrolysis but there is little knowledge on the production and characterization of low-cost catalysts. To obtain high value products and selectively produce high purity fuels such as aviation kerosene from the pyrolysis of waste plastics, there is a need to develop a sustainable catalyst for the process. A sustainable catalyst is one in which its catalyst material can be easily found and prepared with low-cost materials especially, agricultural waste. In this paper a local catalyst was prepared with agro waste material, the properties of the local catalysts were characterized to know its catalytic properties before it was tested in the pyrolysis of waste sac bags.This paper is driven by the quest to have a circular economy, which is based on the principle of designing out waste.

1.1 Catalytic Pyrolysis

The mechanism involved in catalytic pyrolysis involves three steps: initiation, propagation and termination [4]. In the pyrolysis process, catalysts are used to improve both the process and the products. They can be classified as homogeneous catalyst (involving a single phase, usually liquid) and heterogeneous catalyst (solid phase). Heterogeneous catalyst is common because they can easily be separated from the fluid product, they can also be easily regenerated and reused in pyrolysis [5]. The type of catalyst to use is determined by the desired end product: gas, liquid, or solid [6]. Catalysts have been utilized to improve pyrolysis processes in order to obtain energy and other value-added products, this can be seen in the following studies: [7- 9,3,10]. Despite the recent breakthroughs in catalytic pyrolysis technology, there are still some challenges. The use of synthetic catalysts in pyrolysis technology is one such example, which makes the overall process more energyintensive and economically costly [11]. Different types of synthetic catalyst are used in pyrolysis of waste plastics to hydrocarbon fuels (Table 1), the most commonly used are the different types of zeolites. The catalytic activity and selectivity are strongly affected by the several physiochemical features such as total surface area, total pore volume and metal distribution. Thermal treatment and wet impregnation are used to improve the structural and textural properties of catalysts [12]. Wet impregnation method is mostly used to modify and generate heterogeneous catalysts [13].

1.2 Catalyst Material

Activated carbon is a porous carbonaceous material with a large surface area and numerous surface groups that is widely used for adsorption, catalyst support, gas separation and storage, solvent recovery and decolorization, super capacitors, and electrodes [14]. Internal porosity,

surface area, pore volume, and pore size, as well as the presence and distribution of functional groups on pore surfaces, all have a significant impact on activated carbon performance. The textural and chemical features of activated carbons are affected by elements such as the nature of the raw materials, the activation, activating agent, and the conditions of the activation process. Physical activation can be accomplished by carbonizing the precursor in an inert atmosphere. The generated char is activated using an activation source such as steam, CO2, or air at temperatures between 400 and 500 °C. The carbonization process involves a pyrolysis procedure in which volatile compounds are formed as a result of several complex, competing, and sequential processes that end in the creation of fixed carbon in an inert atmosphere. In the second step of the physical activation process, the precursor is heat treated at high temperatures ranging from 700 to 1100 °C in the presence of an oxidizing agent [15]. During chemical activation, the precursor is mixed with KOH [16-22] to form porous structures in the material. In the present study, coconut shells were prepared by physical and chemical activation as catalysts for the pyrolysis of waste sac bags to aviation range hydrocarbons. The impact of the catalyst on the yield of fuel oil produced at different ratios and temperature was also investigated.

Table 1. List of some synthetic catalysts used in pyrolysis

There is no waste to energy facility in Rivers state, Nigeria that converts waste polypropylene plastics into hydrocarbon fuels like aircraft range kerosene using locally available catalysts. Coconut shell activated carbon catalysts have yet to be described or tested as possible catalysts for this application. This research seeks to make activated carbon catalysts from coconut shells and assess their impact on the pyrolysis of waste polyethylene sac bags in a batch reactor. The activated carbon catalysts produced were

characterized to know more about their properties.

2. MATERIALS AND METHODS

[Coconut shells were obtained from the Bio resource Institute in Okigwe, Imo State. The institute generates large quantities of coconut shell (waste) from the processing of coconut into coconut oil. About 100 kg of coconut shell was collected, bagged and transported to Port Harcourt by road. 50 kg of sac bags were obtained from rice traders in Oroigwe, Port Harcourt. Sulphuric acid used was produced by Fisher Scientific International Company and is 98.0% pure, distilled water and the acids were purchased from Emma continental Chemicals co ltd Aba, Abia State.

2.1 Catalyst Preparation

2.1.1 Procedure for preparing activated carbon catalyst from coconut shell

The coconut shell was activated with Sulphuric acid solution according to the method reported by [22] to enhance the porosity and surface area of carbon generated from coconut shells. The Normality equation was used to make a 5N sulphuric acid solution in distilled water.

Normality of $H_2SO_4 = 2 \times \text{molarity}$ [1]

A 500 mL beaker was filled with 135 mL sulphuric acid, and a conical flask was filled with 500 mL distilled water. The acid was poured into the distilled water, and the solution was produced up to 1000 mL. The coconut shells were cut to small sizes of not more than 10 cm. Wet impregnation method was used, at an impregnation ratio of 10:1. The mixture was allowed for 12-18 hours before the coconut shells were separated from the acid solution by pouring it out [21]. The coconut shells were dried overnight in a muffle furnace at 110 °C, and the masses were monitored until a constant mass was achieved. The coconut shells were then thermally activated for 10 minutes at 600 °C. The dry mass of coconut shells was ground to a particle size of sizes 1 mm and stored in an airtight plastic bag

2.2 Grinding of Activated Carbon Catalysts

The activated carbons catalyst sample obtained was ground to particle sizes of 1 mm using an Electric Blender (Original Millennium Nakai blender, model 333 special, power 220V/50Hz 350W) to reduce the particle size and stored in an airtight plastic bag.

2.3 Characterization of Activated Carbon Catalyst

2.3.1 Scanning electron microscopy

Scanning electron microscope JEOL JSM-7600F was used to produce images of the activated carbon catalysts at various magnifications to explore the surface morphology, which indicates the texture and porosity of the activated carbon catalyst. The platinum coating was applied to 2g of each activated carbon catalyst and placed on the specimen stub. At a voltage of 15 KV, a working distance of 10.0 mm, and a pressure of 70 Pa, the sample was observed.

2.3.2 Surface area and pore volume of coconut shell activated carbon catalyst

Nitrogen adsorption/desorption isotherms at - 198.250 °C were performed utilizing a Particulate Systems High-Pressure Volumetric Analyzer to evaluate the surface area and pore properties of activated carbon catalysts. The samples were degassed automatically, which is required to remove moisture and contaminants from the samples. The Brunauer-Emmett Teller theory was used to compute the specific surface area (BET). The exterior surface area, micropore volume, and micropore area were calculated using a T-plot.

2.3.3 Elemental composition of coconut shell activated carbon catalyst

GeniusIF X- ray fluorescence spectrometer was used to determine the element composition of the manufactured activated carbon catalyst samples. To assure the smoothness of the thin film surface, the sample cup was constructed with polypropylene thin film. The pulverized sample was poured into a thin film-covered cup, filling it up to a third of the way (approximately 5 g). The sample cup's lid was covered, and it was checked for leaks or loose particles on the thin film layer, as well as tightening the lids. The sample was then placed in the Genius -IF XRF sample turret. On the RUN tab, the X-ray lamp was powered on and allowed to stable for two minutes. The voltage and emission current values were chosen to achieve a dead time of 35-40 kv. After that, the analysis was RUN in

order to collect spectrum data. The Master elements were then opened in the XRS-FP software. After uploading the tfr file, the sample's spectra file was analyzed and stored.

2.4 Catalytic Pyrolysis of Waste Sac Bags over Coconut Shell Activated Carbon Catalyst

Fig. 1 displays the experiment set up; it consists of a stainless-steel batch reactor placed into a muffle furnace (JP Selecta, 582543 S/N, 230 VAC, 00-C/2000367, Spain). The reactor consists of two openings, one at the top connected directly to a pipe which collects the vapor coming out from the reactor to the reflux condenser where it is condensed. The condensate is collected in an oil collector having an opening by the side through which the uncondensed gases exit. The other opening at the side supplies nitrogen gas which is used to purge out oxygen from the reactor. 50 g of waste sac bags and activated carbon from coconut shells (5 g or 15 g) were fed into the reactor per run of experiment, it was tightly closed before it was put into the muffle furnace. The muffle furnace has a PID temperature regulator, this was used to set and monitor the temperature per run of experiment. Table 2 shows the design parameters in generating the design matrix for the experiment using central composite design in Design expert 12.0 software. A total of 9 runs of experiment was conducted, the 9th run was done without coconut shell activated carbon.

Nitrogen gas bottle, 2. Furnace, 3. Stainless steel reactor, 4.Vapour outlet, 5. Reflux condenser, 6. Tap water, 7. Cooling water outlet, 8.Ice bath, 9. Bio-oil collector, 10. Uncondensed gas outlet, 11. Tap water sink outlet.

3. RESULTS AND DISCUSSION

3.1 Characteristics of Coconut Shell Activated Carbon as Catalyst in Pyrolysis

To have a deep knowledge of the catalyst produced, it was characterized. The result from the scanning electron microscopy revealed that the texture of the coconut shell activated carbon seems to be rough, with different sizes of pores on the catalyst surface, and the pores were seen as hollows without a defined shape. The appearance of pores on the surface of the catalyst is as a result of the carbonization process [21]. These pores are very significant during pyrolysis of waste sac bags, because they act like oil traps where secondary cracking of the plastic material occurs.

Table 3 shows the pore characteristics of coconut shell activated carbon catalyst, BET surface area of coconut shell activated carbon 1820.40 m^2/g is higher than the 891.12 m^2/g and 1266.68 m² /g, for CAC2 and CAC5 in Zhang et al., [23]. A high BET surface area favors the catalytic performance of a catalyst, the reason for this is due to the formation of more active sites on the surface of the catalyst, the more active sites available on the surface of the catalyst for activity, the better the performance of the catalyst. Whereas the micropore surface area of coconut shell activated carbon catalyst (1.252 m^2 /g) is lower than the values obtained for CAC2. Total pore volume in the coconut shell catalyst is $3.280 \, \text{cm}^3$. These properties indicate that coconut shell activated carbon can be effective in the pyrolysis of waste sac bags.

Table 4 shows the elemental composition of coconut shell activated carbon catalysts. 25 out of 28 elements investigated were identified to be present in the coconut shell activated carbon catalyst. Elemental oxygen had the highest concentration in the sample. There is therefore a need to purge out this oxygen, since pyrolysis takes place in the absence of oxygen. Nitrogen gas was used to do this. Aluminum and silica were also present in significant quantities. The presence of phosphorus in the sample is good for the aromatization of the liquid fuel such as aviation range hydrocarbons [23].

Table 2. Design parameters

Factor	Unit	Type	low	High	Response
Temperature	$\rm ^{o}C$	numeric	600	640	% yield
Catalyst to feed		numeric	0.1	0.3	% yield
尣 1				8	10

Fig. 1. Pyrolysis experiment set up

Fig. 2. Surface morphology of coconut shell activated carbon catalyst at 8000, 9000, 1000 mag

Table 3. Pore characteristics of coconut shell activated carbon catalyst

Table 4. Elemental composition of coconut shell activated carbon catalyst

3.2 Catalytic Performance of Coconut Shell Activated Carbon in Sac Bags Pyrolysis into Fuel Oil

To investigate the performance of the catalyst prepared, it was employed in the pyrolysis sac bags. Table 5, shows the yield of fuel oil obtained from the pyrolysis waste sac bags with coconut

shell activated carbon catalyst. It consists of 8 runs of experiments carried out by varying temperature and catalyst to feed ratio, with the response being yield of fuel oil. The 9th run of the experiment was performed without coconut shell activated carbon catalyst. The highest yield of fuel oil was obtained in 7, while the 9th run had the lowest yield. This can be attributed to the fact that it was done in the absence of a catalyst.

3.3 Effect of Temperature and Catalyst to Feed Ratio on the Yield of Fuel Oil Produced

To investigate the impact of the process factors varied on the yield of fuel oil produced per run of experiment, it became necessary to statistically study the result by carrying out analysis of variance (Anova) on the yield of fuel obtained. The various values obtained per run of experiment for the yield of fuel oil were inputted into the design matrix obtained by Design expert software for analysis. The *p-*values obtained from analysis of variance in Table 6, show that the model, temperature, catalyst to feed ratio were all significant (*P*<.05), this means that they have an impact on the yield of fuel oil. The *P*-value for the interaction between temperature and catalyst to feed ratio shows that it had no impact on the yield of fuel oil. Fig. 3 shows a three dimensional view of the yield of fuel oil produced as a function of temperature and catalyst to feed ratio. It shows that at the temperature of 600 \degree C and catalyst to feed ratio of 0.1 the maximum yield of 61.64 % fuel oil was obtained. The yield of fuel oil was reduced with an increase in temperature and catalyst to feed ratio. Increasing the temperature above 600 °C decreased the yield of fuel oil obtained, also catalyst to feed ratio greater than 0.1, gave a lower yield of fuel oil.

Fig. 3. Yield of fuel oil as a function of temperature and catalyst to feed ratio

4. CONCLUSION

In order not to rely on synthetic catalysts, a lowcost catalyst for the catalytic pyrolysis of waste plastics has been developed. Findings from the characterization and testing of coconut shell activated carbon catalyst in pyrolysis in the present study proves that it can be applied in converting waste plastics into hydrocarbon fuels. The paper also highlighted that the yield of fuel oil was favored at the temperature of 600°C and catalyst to feed ratio of 0.1.

DISCLAIMER

The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

- 1. Rehan M, Miandad R, Barakat MA, Ismail IM, Almeelbi T, Gardy J, et al. Effect of zeolite catalysts on pyrolysis liquid oil. International Biodeterioration & Biodegradation. 2017;119:162-75.
- 2. Faravelli T, Pinciroli M, Pisano F, Bozzano G, Dente M, Ranzi E. Thermal degradation of polystyrene. Journal of Analytical and Applied Pyrolysis. 2001;60(1):103-21.
- 3. Syamsiro M, Saptoadi H, Norsujianto T, Noviasri P, Cheng S, Alimuddin Z, Yoshikawa K. Fuel oil production from municipal plastic wastes in sequential pyrolysis and catalytic reforming reactors. Energy Procedia. 2014;47:180-8.
- 4. Patni N, Shah P, Agarwal S, Singhal P. Alternate strategies for conversion of waste plastic to fuels. International Scholarly Research Notices. 2013;2013.
- 5. Westerhout RW, Waanders J, Kuipers JA, van Swaaij WP. Kinetics of the lowtemperature pyrolysis of polyethene, polypropene, and polystyrene modeling, experimental determination, and comparison with literature models and data. Industrial & Engineering Chemistry Research. 1997;36(6):1955-64.
- 6. Walendziewski J, Steininger, M. Thermal and catalytic conversion of waste polyolefins. Catal. Today. 200165:323-330.
- 7. Marcilla A, Beltrán MI, Navarro R. Thermal and catalytic pyrolysis of polyethylene over HZSM5 and HUSY zeolites in a batch reactor under dynamic conditions. Applied Catalysis B: Environmental. 2009;86(1- 2):78-86.
- 8. Butler E, Devlin G, Meier D, McDonnell K. A review of recent laboratory research and commercial developments in fast pyrolysis and upgrading. Renewable and Sustainable Energy Reviews. 2011;15(8): 4171-86.
- 9. Ateş F, Miskolczi N, Borsodi N. Comparision of real waste (MSW and MPW) pyrolysis in batch reactor over different catalysts. Part I: Product yields,
gas and pyrolysis oil properties. gas and pyrolysis oil properties. Bioresource Technology. 2013;133:443- 54.
- 10. Donaj PJ, Kaminsky W, Buzeto F, Yang W. Pyrolysis of polyolefins for increasing the yield of monomers' recovery. Waste Management. 2012;32(5):840-6.
- 11. Miandad R, Barakat MA, Aburiazaiza AS, Rehan M, Nizami AS. Catalytic pyrolysis of plastic waste: A review. Process Safety and Environmental Protection. 2016;102:822-38.
- 12. Shah J, Jan MR. Polystyrene degradation studies using Cu supported catalysts. Journal of Analytical and Applied Pyrolysis. 2014;109:196-204.
- 13. Nizami AS, Ouda OK, Rehan M, El-Maghraby AM, Gardy J, Hassanpour A, Kumar S, Ismail IM. The potential of Saudi Arabian natural zeolites in energy recovery technologies. Energy. 2016;108:162-71.
- 14. Yorgun S, Yıldız D. Preparation and characterization of activated carbons from Paulownia wood by chemical activation with H₃PO₄. Journal of the Taiwan Institute of Chemical Engineers. 2015;53:122-31
- 15. Kumar A, Jena HM. High surface area microporous activated carbons prepared from Fox nut (Euryale ferox) shell by zinc

chloride activation. Applied Surface Science. 2015 Nov 30; 356:753-61.

- 16. Ji Y, Li T, Zhu L, Wang X, Lin Q. Preparation of activated carbons by microwave heating KOH activation. Applied Surface Science. 2007;254(2):506- 12
- 17. Wu FC, Tseng RL, Juang RS. Preparation of highly microporous carbons from fir wood by KOH activation for adsorption of dyes and phenols from water. Separation and Purification Technology. 2005;47(1- 2):10-9.
- 18. Cazetta AL, Vargas AM, Nogami EM, Kunita MH, Guilherme MR, Martins AC, Silva TL, Moraes JC, Almeida VC. NaOHactivated carbon of high surface area produced from coconut shell: Kinetics and equilibrium studies from the methylene blue adsorption. Chemical Engineering Journal. 2011;174(1):117-25.
- 19. Xu J, Chen L, Qu H, Jiao Y, Xie J, Xing G. Preparation and characterization of activated carbon from reedy grass leaves by chemical activation with H3PO4. Applied Surface Science. 2014;320:674- 80.
- 20. Liu H, Zhang J, Zhang C, Bao N, Cheng C. Activated carbons with well-developed microporosity and high surface acidity prepared from lotus stalks by organophosphorus compounds activations. Carbon. 2013;60:289-91
- 21. Kumar A, Jena HM. Preparation and characterization of high surface area activated carbon from Fox nut (*Euryale ferox*) shell by chemical activation with H3PO4. Results in Physics. 2016;6:651-8.
- 22. Gawande PR, Kaware J. Characterization and activation of coconut shell activated carbon Research Paper. International Journal of Engineering Science Invention. 2017;6(11):43-9.
- 23. Zhang Y, Duan D, Lei H, Villota E, Ruan R. Jet fuel production from waste plastics via catalytic pyrolysis with activated carbons. Applied Energy. 2019;251:113337.

___ *© 2021 Iheonye et al.; This is an Open Access article distributed under the terms of the Creative Commons Attribution License [\(http://creativecommons.org/licenses/by/4.0\)](http://creativecommons.org/licenses/by/4.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.*

> *Peer-review history: The peer review history for this paper can be accessed here: https://www.sdiarticle4.com/review-history/76284*