Effect of Thermal Power Plant Fly Ash Reinforced with Silica Oxide as Catalyst for Hydrogenation#

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ABSTRACT

The high cost of commercial catalysts has hampered the commercialization and cost-effective production of renewable diesel in recent times. This research investigates the effect of silica (SiO_2) reinforcement on bio-based thermal power plant fly ash (BBTPPFS) for hydrogenation. The BBTPPFS and the SIO_2 were pulverized, calcinated, and subjected to various characterization processes. The value of micropore volume, surface area, and external surface area of sample due to the reinforcement by SiO_2. These results show that the addition of SiO_2 to BBTPPFS improved the potential of the BBTPPFS as a heterogeneous catalyst for hydrogenation.

Keywords: BBTPPFS, HDRD, renewable energy, silica Oxide, hydrogenation.

1. INTRODUCTION

The demand for energy supply can be traced to the ever-increasing global population, industrialization, modernization, urbanization, and social-economic activities [1]. The massive sectorial consumption of energy was estimated to be over 230 exajoules in 2018 [2]. However, the consumption rate per annum, which is about 3.8 percent is higher than the supply (34 %) documented per year. Manufacturing industries consumer the largest energy, whereas the residential sector has about 6.9% per annual consumption growth in 2018 (Figure 1) [3].
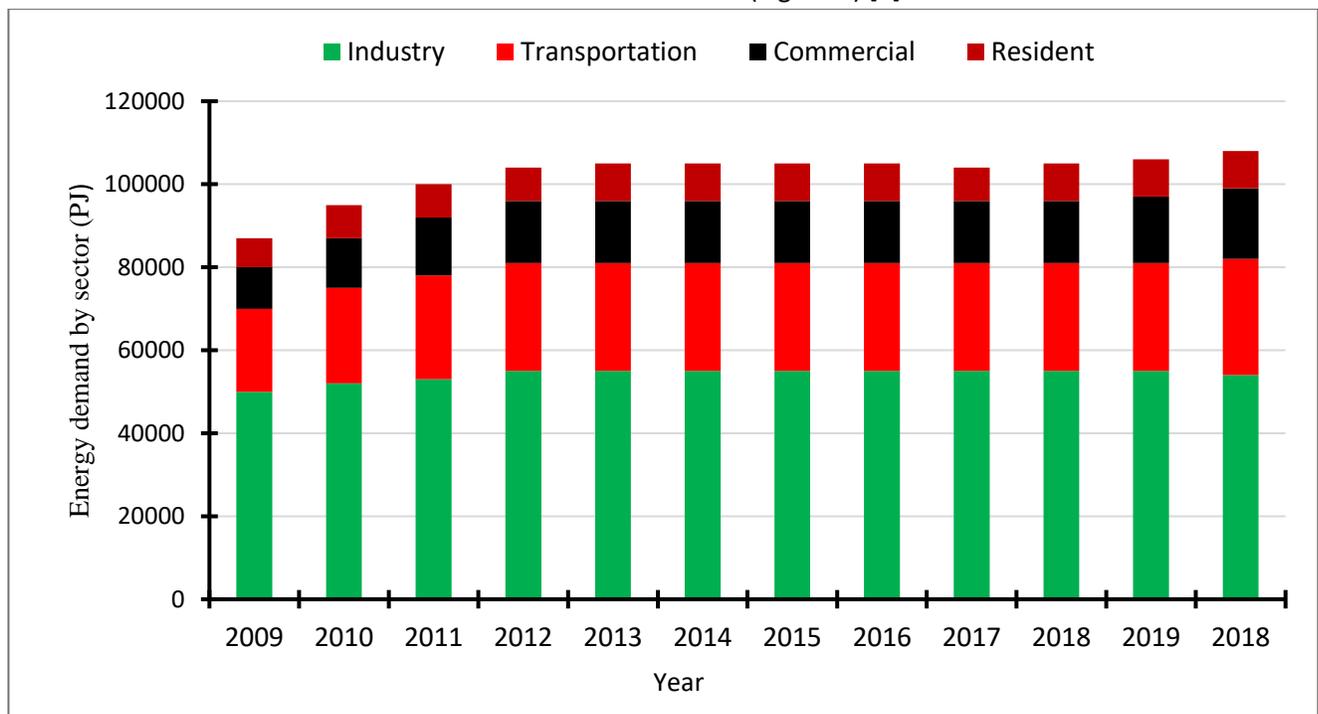
Fig. 1 Energy consumption per sector

Global economic growth which is the driver of energy demand has attracted growing attention from scholars [4]. Sorrell [5], reported a 2.5 % annual increase in the global energy demand since the 1850s. Being one of the core economic development, institutions and the energy sector decided to use energy with zero carbon emission, while maintaining a steady industrial performance [6]. These have stimulated the interest of the energy sector to search for renewable energy to replace depleting fossil fuels.

The application of biowaste heterogeneous catalyst for the production hydrogenation derived renewable diesel (HDRD) has gained the attention of various researchers in recent times. The varying outcome has been reported by quite a lot of scholars who have explored the use of biowaste catalysts sourced from the shell of an egg, and snail shell as a reliable catalyst for hydrogenation [7]. Scholars have used a variety of catalysts for hydro-processing purposes, eg CoMo/C [8], NiMo/-Al$_2$O$_3$ or CoMo/-Al$_2$O$_3$ [9], and CoMo/Si [10], Galadima and Muraza [11], Yusup et al. [12], have reported production processes, limitations, and benefit of biowaste as a locally sourced catalyst for hydrogenation.

Bio-based thermal fly ash (BBTPPFS) is a waste generated when coal is burned for energy production in thermal power plants. The product obtained is BBTPPFS The elemental properties of these waste materials can be processed and developed as heterogeneous catalysts for the hydrogenation of UCO into hydrocarbon. BBTPFS heterogeneous catalyst was considered highly effective for hydrogenation to obtain 97.0 vol% and 68.2 vol.% of crude and organic liquid fraction (OLF) [13]. Table 1 shows the chemical elemental composition of fly ash.

The addition of SiO$_2$ to BBTPPFS to obtain optimal catalytic properties that are capable of mild cracking feedstock resources into the green diesel range form the motivation of this research. This research work aims to investigate the effect of silica oxide reinforced into BBTPPFS heterogeneous catalyst for hydroprocessing purposes. The objective of these research is to investigate the catalytic activity of a calcinated catalysts mixed with BBTPPFS heterogeneous catalysts properly prepared. The scope of this study is to reinforce 40 % SiO$_2$ to 60 % BBTPPFS heterogeneous catalyst, calcinate, and characterize the effect on hydrogenation.

Table 1 Elemental composition of bio-based thermal power plant fly ash (BBTPPFS)

Element	CaO	SiO$_2$	MgO	K$_2$O	Fe$_2$O$_3$	Al$_2$O$_3$	SO$_3$	P$_2$O$_5$	Cl	Na$_2$O
Composition (Wt%)	30.74	27.87	6.67	13.96	2.36	2.83	4.83	1.35	3.36	1.14

2. MATERIALS AND METHODS

2.1 Materials Collection

The bio-based thermal power plant (BBTPPFS) sourced from ESKOM, Lethado power generation plant, South Africa was used for this research. The BBTPPFS was processed to ensure a micro seize particle with the aid of a laboratory mechanical grinder and a sieve of < 50 μm mesh. The uniform particle was stored in a well-prepared, moisture-free, and airtight glass vial marked as sample A. The analytical grade of silica oxide was purchased from Lichro Chemical and Laboratory Supplies, South Africa. The Silica oxide was milled to powder form using a laboratory mortal to grind then filtered it by using a < 50 μm mesh. The sample (SiO$_2$) powder was kept in a clean, dry, and airtight glass vial, and designated as sample B. 60 % of samples A and 4 0% of sample B were thoroughly mixed, and stored in a clean, dry, and airtight glass vial, and labeled as sample C. Table 2 and Figure 2 shows the sample preparation.

Table 2 Sample Preparation

Sample Notation	Catalyst Samples	
	SiO$_2$	BBTPPFS
A	1	-
B	-	1
C	1	1

2.2 Catalyst characterization

Experimental investigation and analysis were carried out by various techniques, including SEM-EDX, XRD, and BET.

2.2.1 XRD analysis

X-ray diffractometer, a multipurpose D8-Advance laboratory equipment was used to perform the measurement. This is operated in a continuous ϑ-ϑ scan in locked coupled mode with Cu-K$_\alpha$ radiation. The holder

was held at the middle of a glass slide and ensured accurate height. The range of 2ϑ measurements was taken as prescribed by the user with the size of 0.034° in 2ϑ. The diffraction data were recorded using a Lyn-Eye, at a speed of 0.5 sec/step which is the same as an effective time of 92 sec/step for a scintillation counter.

The identified phases of the computed peaks were compared with the measured phases, this is repeated until all peak were identified within the limits of the resolution of the outcome. The result of the XRD analysis shows the properties of the samples and their potential for conversion of UCO int hydrocarbon.

2.2.2   SEM analysis

Phenom ProX Desktop SEM was used for the SEM analysis. Desktop SEM with EDS has the capability of robust, effortless, and versatile elemental and SEM analysis.
SEM was performed by loading the sample in a vacuum with holder of about 25 mm diameter (optional 32 mm) at 15 kV and room temperature. The results of the SEM analysis showed the sample images and the EDXS, the elemental composition of the sample supports its viability as a potential catalyst for hydro processing of used cooking oil into HDRD.

2.2.3   BET characterization

Micromeritics ASAP 2460 instrument was used to perform the nitrogen sorption analysis. The sample of about 0.25 g was kept in a vacuum to degassed at 100 °C under the influence of nitrogen gas till next day. The sample is kept in the oven and allow to cool, this will prepare its surfaces and pores ready for analysis. Both surface area (m^2/g), total pore volume (cm3/g at STP), pore size distributions, and average pore radius (Å) of the sample was calculated by the BET and the Barrett-Joyner-Halenda (BJH) method respectively. The outcome of the BET analysis shows the properties as a viable biowaste heterogeneous catalyst for the production of hydrogenation derived renewable diesel.
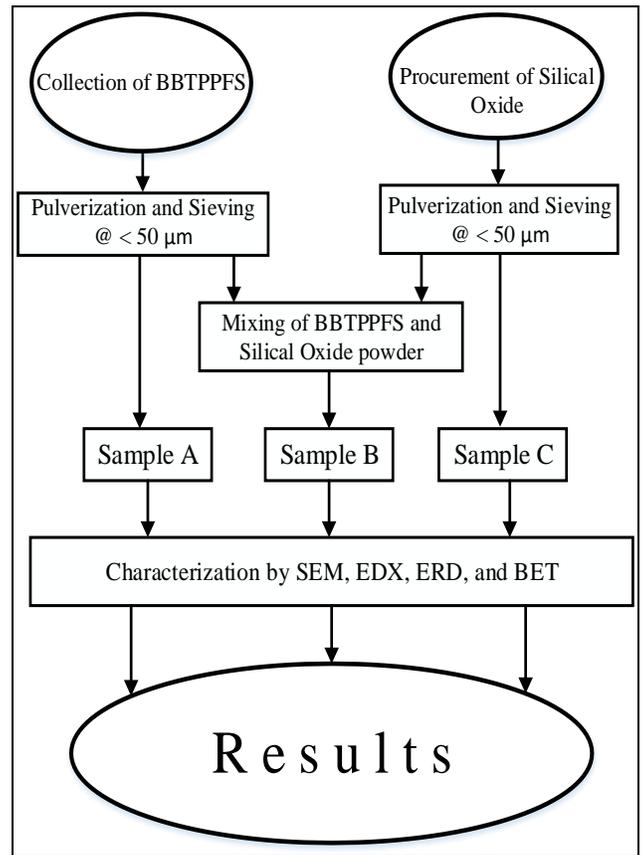
Fig. 2 Flow chart of samples preparation

3.   RESULT AND DISCUSSIONS

3.1 XRD Analysis

Figure 3 and Table 3 show the XRD spectrometry plot for the samples and the major constituents of the samples. The quartz, mullite, calcite increased from 33 percent to 88 percent, 12 percent to 39 percent, and 2 percent to 5 percent in sample A to sample C respectively. This can be mirrored to the mixture in the prescribe proportion of SiO_2 to BBTPPFS. The composition in the structure reveals that freshly prepared BBTPPFS contain the highest quantity of quartz (SiO_2) and mullite (Al4.4Si1.2O9.6) minerals. The value of quartz's and diffraction peak is identified at $2\theta = 27^\circ$, 22°, 51°, 67° and 17°, 25°, 42°, and 62° respectively.

The result of XRD diffraction analysis of sample B shows no peak, however, the significant changes in elemental composition of sample C can be trace to the addition of sample B to sample A. Sample B has no peaks due to the amorphous nature of the biomass[14, 15]. In the calcite the peak was noticed at 29.3°. Sharma et al.[16],Ho et al. [17], Bhandari et al. [18], and Maneerung et al. [19] reported similar result. The outcomes are evidence of the viability of adopting sample C as a suitable green catalyst for hydrogenation [20, 21].
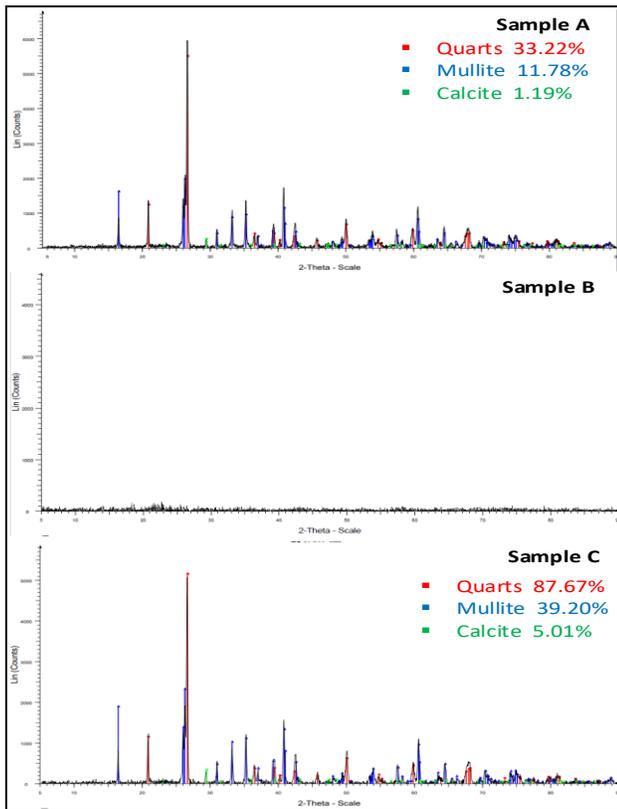
Fig. 3 XRD spectrometry for (A) BBTPPFS, (B), SiO₂ and (C) BBTPPFS +SiO₂ biomass

Table 3 Composition of samples A, B, and C

Compound name	Chemical formula	Lattice	Molecular weight	Volume	Sample Composition (%)		
					A	B	C
Quarts	SiO_2	Hexagonal	60.08	113.59	33.	N/A	88.
Mullite	Al_4Si	Hexagonal	132.02	49.71	12	N/A	39.
Calcite	$CaCO_3$	Rhombohedral	100.09	367.78	2.	N/A	5.

3.2 SEM analysis

The sample's surface morphology was investigated using Scanning electron microscope (SEM) analysis. The three samples have similar morphologies. Figure 4 shows an image of the samples which has large and asymmetrical particle. The picture of dry fly ash (sample A) reflects round shape with a uniform surface, sample B admixture with sample A showed a large surface and pores in sample C, which was confirmed by X-ray diffraction analysis. The increase in the value of SiO_2 from 19 percent to 26 percent shows the great potentials and capability of mild cracking of feedstock to obtain higher yield. SiO2 reinforced with thermal power plant fly ash can withstand high temperatures above 998 °C, this is an evidence that sample C possess a high catalytic activity than sample A and sample C.

Figure 1 Image Sample A, B, C

3.3 BET analysis

The properties and the value of samples A, B, and C are shown in Table 4. From the table, the value of the surface area, external surface area, and pore volume increase when 40% SiO_2 added to 60% thermal power plant fly ash the changes were due to the mixture of SiO_2 from 0.60 m^2/g to 0.86 m^2/g, and 0.01 cm^3/g to 35.1 m^2/g, 33.0 m^2/g, and 0.13 cm^3/g respectively. The total pore volume of 0.13 cm^3/g was found within the range of 0.1 cm^3/g to 0.30 cm^3/g when fly ash was processed and transformed to zeolites by double-stage fusion–hydrothermal [22]. The value of average pore volume decreases in sample A from 179.70 Å to 73 Å in sample C due to the impurities contained in sample B. This is an evidence that the mixture of Silica Oxide (SiO_2) with fly ash caused a reduction in the mesoporous range due to the impurities. Hence, the significant increase in sample A from -0.0001 cm^3/g to 0.0006 cm^3/g in sample C. The value of surface area in sample C were higher than the 17.5 m^2/g and 32.6 Å reported when raw thermal fly ash was impregnated with calcium metal and calcinated at a temperature of 550 °C for 4 hours as reported by Arif et al. [23]. BET surface area and pore volume of 9.0 m2/g and 0.01 cm^3/g respectively were reported for thermal plant fly ash by Vargas et al. [24].

BET surface area with the value of 35.1 m^2/g will promote the catalytic activities of SiO_2 and BBTPPFSs for the desorption and adsorption of molecules such as vegetable oil, and glycerin [24, 25]. The results of the BET analysis of the samples showed the suitability as a cheap and sustainable green catalyst for green diesel production by hydrogenation [26, 27].

Table 4 Properties of samples A, B, and C

Properties	Unit	Sample A	Sample B	Sample C
BET surface area	m^2/g	0.60	317.2404	35.1
External surface area	m^2/g	0.86	279.1870	33.0
Average pore radius	Å	179.68	70.72	73.0
Pore volume	cm^3/g	0.005426	1.1218	0.13
Micropore volume	cm^3/g	-0.000121	0.014827	0.00082
Micropore area	m^2/g	*NR	38.0533	2.53

NR = Not Reported

4. CONCLUSION

BBTPPFS heterogeneous catalyst is a waste generated from Thermal power plants. Commercialization of HDRD or green diesel can be achieved if BBTPPFS heterogeneous catalyst is adopted as a replacement for high cost of commercial catalysts. This research has critically investigated the effect of 40% SiO_2 as a support heterogeneous catalyst to 60% BBTPPFS collected from South Africa's Eskom power plant. Samples A, B, and C were characterized by BET, XRD, and SEM-EDX analyses. The following outcome were obtained.

A significant increase was obtained on the quartz, mullite, calcite from 33 % to 88 %, 12 % to 39 %, and 2 % to 5 % in sample A to sample C respectively.

SiO_2 reinforced with thermal power plant fly ash in the proportion of 40 % to 60 % can withstand high temperatures above 998 °C, hence sample C is considered as a potential catalyst for hydrogenation.

The properties of BBTPPFS were significantly increased due to the addition of SiO_2 from 0.60 m^2/g to 0.86 m^2/g, and 0.0054 cm^3/g 6 to 35.12 m^2/g, 32.58 m^2/g, and 0.12 cm^3/g. Application of green catalyst and used cooking oil will make the value chain completely green.

The outcome of characterization shows the percentage increment in quartz, mullite, and calcite in sample A increased from 33 %, 11.78 %, and 1 % to 87 %, 39 %, and 5 % respectively in sample C, due to the addition of SiO_2. The application of a calcinated 40 g silica oxide admixture with 60 g BBTPPFS will make the value chain completely green. This will address the challenge caused by fossil fuels.

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