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EFFECT OF TiO_2 AND RED-MUD IMPREGNATION ON PYROLYSIS OF OIL PALM EMPTY FRUIT BUNCH BIOMASS-OPEFB

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ABSTRACT:
The production of Pyrolysis product is known with inherent problem of oil generation. In this research work, oil palm empty fruit bunch (OPEFB) were impregnated with TiO_2 and red-mud to improve the quality of the oil produced. The impregnation was enhanced by drying and calcinations at 105^0C and 550^0C.The study of the effect of TiO_2 was carried out in a carbonate vapor depositor furnace reactor (CVD). The result shows that the pyrolysis of OPEFB impregnated TiO_2 and red-mud increased the bio-oil yield from 28 wt. % for activated TiO_2 to 31 wt. % for activated red-mud at the expense of char and gas yield at 5 wt. % impregnation ratio and 500^0C pyrolysis temperature. This was linked to the ability of the TiO_2 and red-mud to interact with the biomass and retain condensable compounds at temperature between $(300- 350)^0C$. Addition of TiO_2 and red-mud above 10 wt. % was found to reduce the overall liquid yield and promote gasification. The optimum impregnation ratio was found to be 5 wt. %. The oil produced from both OPEFB impregnated with TiO_2 and red-mud were characterized using Fourier transform and infra-red (FT-IR), gas chromatograph-mass spectrometry (GC/MS) and elemental analysis (E.A). The FT-IR results showed that the oil produced from impregnated OPEFB contains less amine functional group which has detrimental effect on the quality of the bio-oil produced. For impregnation of OPEFB, besides enhancing its bio-oil yield, the impregnated TiO_2 selectively produced sugars and O-ring compounds.

Keyword; *Pyrolysis, Biomass, Impregnation.*

1. INTRODUCTION

The shortage of fossil fuels and the emission of greenhouse gases have led to great interest in exploring cleaner, renewable energy resources. It has been reported that natural system such as atmospheric, land and sea as well as plant are clearly being disturbed due to the complete reliance on the combustion of fossil fuel for domestic and industrial consumption [1]. Apart from the health and environmental challenges it constitutes, a steady depletion of the world's limited fuel reservoir is of great concern. Consequently, there is need to urgently develop renewable, eco-friendly energy sources that are more efficient than the conventional fossil resources. Biomass resources have great reserves and has a particular advantage in terms of renewability and carbon dioxide neutral characteristics [2]. Bio-fuels are largely considered to be carbon cycle neutral due to the fact that CO_2 that is released into the atmosphere when burnt is fixed in to the biomass by photosynthetic process. In recent years, effort have been made towards producing bio fuels from many varieties of biomass such oil palm empty fruit bunch (OPEFB) [3]. Biomass of lignocellulosic such as residues of agriculture, municipal and industrial waste is seen as major resources of potential energy in the near future. Reports shows that in palm oil industries residues generated contain calorific value equivalent to over 50 million barrels of oil [4].

Pyrolysis technology is a thermochemical process by which biomass waste is converted into crude liquid bio –oil, gas and char, with high yields, in the absence of oxygen, which the liquid is very rich in oxygenated hydrocarbon [5]. It is considered as one of the very promising conversion technologies in which biomass at moderate temperature is decomposed in the absence of oxygen [6]. Various parameters such as temperatures, particles size, heating rate, gas residence time and biomass constituents are very important. The biomass constituents include cellulose, hemi cellulose, inorganic minerals and lignin [7]. There are three main approaches for evaluation namely: dry mining of the catalyst with the biomass, post treatment by passing pyrolysis vapor through a catalytic bed and also inserting the catalyst in the biomass with impregnation [3]. On the pyrolysis product yield, more effects have been observed with the metal-impregnated biomass as impregnation enables the metal to uniformly dispersed into the biomass matrix to the greater extent and thereby provide high intimate contact with the lignocellulose compound structure [8]. Reported studies on iron catalyst compounds indicated that they have a positive impact on the product yields and bio-oils composition. [9] Have reported that Fe-species show a very promising result in catalyzing the production of anhydrosugars, especially that of the levoglucosan in bio-oils. Similar result which showed that Fe –impregnated wood produced high levoglucosan yield of 27.3 wt. % [10].

Nomenclature

CVD	Carbonate vapor depositor
OPEFB	Oil palm empty fruit bunch
RM	Red mud
TiO_2	Titanium oxide
TiO_2-OPEFB	Titanium oxide impregnated oil palm empty fruit bunch
wt.%	Weight percent

2. MATERIAL AND METHODS

2.1 Materials

The palm oil empty fruit bunch (OPEFB) was supplied by Chatafu farms Gudu –Gbagba via Doko in Lavun Local Government area of Niger State. Fifty kilogram (50 kg) of OPEFB biomass was used for the pyrolysis experiment. The red mud was obtained from red-mud dump site of Rogota village, opposite Federal Polytechnic, Bida. A standard 50kg of red mud is maintained with solid contents of 30 % and average particles size of 5mm. TiO_2 was obtained from panlac chemicals in Ketaren Gwari, Minna. Niger state. Nigeria. Calcination was at a control Temperature of 550 ^{0}C.

2.2 Sample Preparation

Fifty kilogram (50kg) of the biomass procured were prepared as follows. The samples were sun-dried as received prior to utilization in the experiment. Parts of the sample of the biomass (OPEFB) were ground, mill and sieved to the particle size range of between 1.7 – 2mm prior to wet processing. Ultimate analysis was done at National Cereal Research Institute Baddegi via Bida. Them gravimetric analysis was done at Centre for Genetic and Bio engineering, (STEP B Centre), Basso Campus, Federal University of Technology, Minna. The prepared samples were used for pyrolysis experiments.

2.3 Activation of Red Mud by Calcination Method

Red mud as received was activated using calcination method of activation. Thirty gram (30 g) of the Red mud was weighed out of the bulk and deposited into the muffle furnace and dried at 105 ^{0}C for 24hrs. It was calcined at 550 ^{0}C for 6hrs to improve it surface area. The Red mud, prior to calcinations was beneficiated and characterized.

2.4 Activation of TiO_2 by Calcination Method

The Titanium Oxide as received from Panlac Chemicals was used directly and labelled TiO_2. To activate sample by calcination method 30 g each of the sample were weighed and calcined in the muffle furnace at different temperatures according to their melting point temperatures to improve their catalytic capabilities for pyrolysis processes.

2.5 Sample preparations

A laboratory test sieve (model BS410-1:20) with aperture of 1.70mm was used to obtained particle size ranged 1 – 2mm. Paying much attention to mesh size, the sieve fabric was joined into the receiving pan. The OPEFB biomass was placed on the sieve stack and continuously shaken to get the desired particle size into the pan beneath the sieve stack. The procedure was repeated until sufficient quantity was recovered from the bulk OPEFB biomass. These particle sizes were used for pyrolysis experiment that produced the targeted bio-oil and other pyrolysis products. All weighing operations was carried out using a standard Scout Pro Weighing balance with maximum capacity of 400 g. The weighing balance was connected to the power source and then switched on. It was immediately initialized to zero point. The scale pan was placed on the weighing platform and the weight noted. It was then removed and sample placed on it before taken it to the weighing platform. Addition and or subtraction was done to obtain the weight of interest. Machine was switched off and disconnected from the power source at the completion of the weighing process.

2.6 Sample Conditioning

Laboratory environment was ensured to be relatively humid controlled. The biomass was oven dried until constant weight was achieved. Temperature of 105 ^{0}C was strictly adhered to. This high temperature was adopted for short period of time to give way to moisture content. Gallenkamp Muffle furnace model was used for drying and calcinations at 500^{0}C. The weight of samples was periodically measured until constant weight was attained and drying process was stopped with the oven switched off. The sample was withdrawn from the oven for next stage of experiment.

2.8 Carbonate Vapor Depositor (CVD) Pyrolysis

The horizontal furnace reactor for the pyrolysis of oil palm empty fruit bunch impregnated with TiO_2 and Red mud was setup as carbon vapor depositor (CVD). The design was based on the actualization of pyrolysis products. Pyrolyser was designed to the specification of 1010 mm length and diameter of 60 mm, which was constructed at the Scientific Equipment Development Institute, (SEDI) Minna. Niger State. Analytical grade Nitrogen gas was purchased in Lagos prior to the experiment. All pyrolysis experiments were performed at 400 ^{0}C, 450 ^{0}C, 500 ^{0}C with impregnation ratios of 5, 10 and 25 wt. % in a stainless steel tubular carbon vapor depositor (CVD) reactor. A constant stream of nitrogen gas at 1L/min was fed into the reactor for batch withdrawal of the volatile products and maintaining an inert atmosphere during pyrolysis. Pyrolyser was installed inside an electrical heater within the CVD and was insulated to enable the heating of the furnace reactor up to 1000 ^{0}C. The reactor (CVD) was equipped with a biomass holder connected to both vacuum and nitrogen. To record the pyrolysis temperature, a J-type of thermocouple was inserted inside the pyrolyser. The pyrolyser was connected to the ice –trap immersed in ice-water bath to condense the pyrolysis vapors at 0.5 ^{0}C. The inlet of the ice trap was connected with gas sampling bottle to collect the non- condensable gases. The pyrolysis product yield was determined by measuring the weight of the bio-oil in condensing bottle and the bio-char collected using electronic weighing balance model. The gas yield was calculated by difference. The experiments for each sample under 500 ^{0}C temperature condition were run twice and a standard error of ±5 wt. % product yield was established.

3. RESULTS AND DISCUSSION

3.1 Them gravimetric (TG) Analysis of OPEFB

The thermal degradation characteristics of oil palm empty fruit bunch (OPEFB) are presented in TGA curves shown in Fig.1. The TGA curve indicates the fractional weight loss of the oil palm empty fruit bunch samples as a function of temperature. In Fig. 1, the thermal degradation for the feed stock sample is approximately 300 ^{0}C/100 ^{0}C. Below this temperature, the weight loss for oil palm empty fruit bunch OPEFB exhibited no significant changes. This behavior is due to reduction in moisture content of the samples during analysis. Consequently, when the temperature was greater than 200 ^{0}C, the percentage weight decreased by 33.6 wt. %.[11] The weight loss for feedstock samples was most prominent between 230^{0}C – 500^{0}C, possibly due to the thermal degradation of polymer blocks within the biomass [12] such as cellulose, hemicelluloses and lignin, this also is contained in a work by [13]. It was apparent that when the temperature was greater than 350^{0}C, the weight loss is 60.3 wt. %. The degradation rate for OPEFB with a higher ash content of 3.5 wt. % was slower at 450^{0}C.

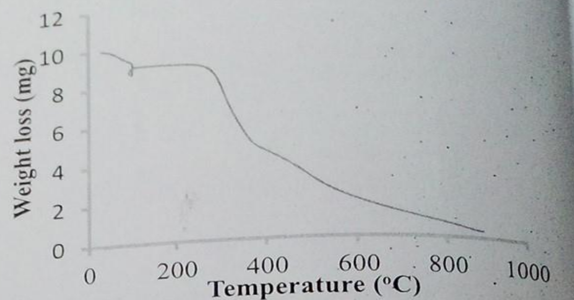

Fig. 1. Them gravimetric (TG) Analysis Curve of OPEFB

Table 1 shows the proximate analysis of OPEFB biomass properties of the raw (OPEFB). The main component properties are given in Table 1, majorly OPEFB. According to [14], the high ash and potassium values present in oil palm empty fruit bunch (OPEFB) are not good enough because potassium and ash content in particular results to reduction in liquid yield pyrolysis. The carbon and hydrogen are comparable to that of pine woody biomass [15]. OPEFB feed stock contain a large percentage of volatile matter, 75 wt. % moderate percentage of ash content at 3.5 wt.% and a small percentage of fixed carbon contents at 17.5 wt. % Thus making OPEFB a suitable feedstock for bio-oi generation. The low percentage of nitrogen an sulphur in OPEFB of less than 1 % is an indication o eco-friendly feedstock material of the bio-oil afte pyrolysis Operations [16].

The percentage of lignocellulose component OPEFB by [17] and [18], was presented in Table for comparison. It was discovered that cellulose w (57.8 %), lignin (22.8 %) and Hemi cellulose (21 %) indicating the eco friendliness of the feedsto material.

Table 1
Proximate and Ultimate Analysis of Raw Sample-OPEFB (wt. %)

Components/properties (%)	OPEFB (wt. %) This work	A	B	C
Proximate analysis				
Moisture content	10.00	1.33	7.95	3.00
Ash content	3.50	5.29	5.36	4.30
Fixed carbon	11.50	17.25	10.78	17.00
Volatile matter	75.00	77.46	83.86	75.70
Ultimate analysis				
Carbon	81.00	47.14	48.90	62.10
Hydrogen	7.56	6.03	6.30	6.90
Nitrogen	9.89	0.10	0.70	1.10
Oxygen	1.35	45.99	36.70	29.90
Sulphur	0.20	0.84	0.20	< 0.1
HHV	36.74			
Fiber analysis				
Cellulose	11.58	57.80	44.20	62.10
Hemicellulose	6.38	21.20	33.50	35.30
Lignin	1.38	22.80	20.40	22.10

Source : a. [3] ; b. [2] ; c. [27].

3.2 Them Gravimetric (TG) Analysis of Red-mud

The TG analysis of red mud in Fig. 2 was obtained by testing the mass loss through the heat treatment of red mud. The red mud shows a continuous weight loss from room temperature at 25 ^{0}C to 700 ^{0}C. The curves consist of three portions of mass loss progressively at different temperature interval. The first one was observed at the heating temperature interval of 25 ^{0}C to 150 ^{0}C. The mass loss of 4.8 % and 26.7 % was mainly caused by the evaporation of free water in the red mud at a low temperature.

The mass of the sample then undertook a low decline between 150 ^{0}C and 625 ^{0}C (50 %). This indicate the existence of hydrous materials in the red-mud. It also indicates that the combination states and boiling strengths of water in the hydrous minerals are not really the same, and water may exist in hydrous minerals with different states and combination strengths such as crystal water and structural water [11].

Above 625^{0}C, the curve decreases further because of the decomposition of CaO then from 625^{0}C to 900^{0}C of the red-mud at 3.2 % of its total mass.

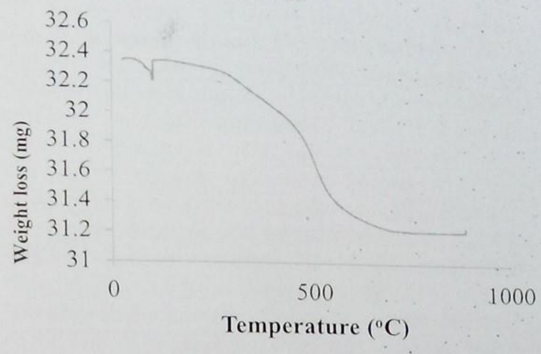

Fig. 2. Them gravimetric Curve (TG) Analysis of Red mud

3.3 Pyrolysis of TiO_2 and Red-mud Impregnated OPEFB in CVD Furnace Reactor

Table 2 shows the pyrolysis product distribution of OPEFB at 500^{0}C on an ash free basis (AF wt. %) at impregnation ratio of 5 wt. %. The uncatalyzed OPEFB gave a liquid yield of only 26 wt. % while the TiO_2 impregnated OPEFB and red-mud increase the liquid yield up to 31 wt. %. This can be supported by [10] and [9], which reported that, the interactions between lignin and metal-ions (Fe) inhibits the scavenging activity of lignin and apparently promotes the liquid or tar formations instead of char or gas. The results clearly suggest that the impregnation of Red mud into biomass (Red mud-OPEFB) do not promotes the oil yield significantly, but the combine effect of TiO_2 and red mud with OPEFB promotes better yield. This result is in line with [3] findings with AWRM-EFB oil yield of 52 wt. %, although higher and which is due to the acid washing which increases its catalytic selectivity.

The TiO_2 impregnated OPEFB shows the highest gas yield of 46.40 % for syngas and 36.95 % for char and moderate Bio oil yield of 29.90 %. Impregnated OPEFB shows a decrease in the char formations below 36 %. This is linked to the high content of iron compound in Fe-ion or Fe_2O_3 form impregnated into OPEFB biomass. Consequently, iron is an efficient catalyst for tar cracking and reforming which reduces the secondary tar formations or yield on char particles.

Table 2
Effect of Metal-ions and Red-mud Impregnation on the Properties of OPEFB

OPEFB	Product (wt. %)			
	Bio-oil	Bio-char	Syngas	Total
OPEFB	26.00	64.20	31.90	122.10
TiO_2-OPEFB	29.90	36.95	46.40	113.25
RM-OPEFB	31.55	43.55	36.15	121.25

The distribution of OPEFB was studied by GC/MS. The compound names identified were classified into five major groups (Table 3) namely: 1. Phenols such as phenols and diamethoxy phenols, 2. Sugars such as levoglucosan, glutaraldehyde and glucopyranose, 3. Linear compounds such as carbonyls which represent pentatonic acid, butanone and mequinol, 4. Cyclic compound such as cyclopentanone and cyclopentene and 5. Oxygen ring (O-ring) such as 5-hydroxymethyl, 2-hydroxy-3-methyl, furans and pyrans. More than 200 compounds were detected whereas 17 most abundant were identified and quantified from the bio-oil analysis. Table 3 shows the most abundant chemical components of the bio-oil samples, phenols and its derivatives. The increase in the amount of phenol, 2-ethoxy was observed for the RM-OPEFB oil samples which were linked to the inhibition of decomposition of methoxy groups in the sample. It is believed that metal-oxides which is renowned to form stable complexes with phenols, could interact with lignin molecules in the biomass and hence decreases the interference of lignin in the conversion of cellulose to glucopyranose and levoglucosan [9]. The OPEFB shows a decrease in the phenol yield as compared to TiO_2-OPEFB and RM-OPEFB which gave 51 % and 54 % phenolic content respectively, where as 61% of the bio-oil comprised of phenol derivative [19]. Substantial decrease in phenolic compound is observed as metal-oxides impregnated into OPEFB biomass to have an ability to form complexes with phenols compound hence the decrease in phenol in the OPEFB when compared with the impregnated titanium and red-mud. The second most abundant compounds is the linear compounds acids and carbonyls of pentatonic acid and butanone.

The cyclopentanones and cyclopentene related derivatives are the main compounds found in the cyclic group, they are about 7 % in the RM-OPEFB oil and typically formed C-C bond breakage which is induced by minerals which have a catalytic effect on dehydration during biomass degradation [20]. The cyclopentene is formed possibly through fragmentation and then cyclic reaction from the pyrolysis of glucose structure [21]. The RM-OPEFB has the highest cyclic yield among other OPEFBs.

The Titanium impregnated OPEFB shows an increase in O-ring compounds particularly the furan derivatives. According to [22], formation of C5 normally involves a single carbon-carbon bond cleavage of the first or last carbon from stable glucose molecule and the balance of fragment can cyclize to form stable furan compounds, whereas smaller fragments leads to formation of formic acid glyceraldehyde and gaseous species. In this study, the TiO_2-OPEFB contained high amount of O-ring as compared to OPEFB and RM-OPEFB.

Besides glucopyranose, the most abundant sugar in the bio-oil is the glutaraldehyde [23]. At temperature above 250^{0}C, depolymerisation of dehydrated cellulose occurs and produces glucopyranose. This compound was not detected in the OPEFB TiO_2 impregnated OPEFB bio-oils indicating pyrolysis environment were in a non-acidic environment hence, the amount of sugar derivative in the oil is as a result of red-mud impregnation effect.

Table 3
Classification and Quantification of Chemical Compounds identified from different Bio-oil produced.

Class	OPEFB (% area)	TiO_2-OPEFB (% area)	RM-OPEFB (% area)
1. Phenols	3.94	51.28	54.32
2. Sugars	62.09	2.93	1.73
3.Linear compound	21.46	26.60	33.29
4.Cyclic compound	3.98	2.41	7.46
5.O-ring compound	8.53	16.78	3.20

The qualitative aspect of infrared spectroscopy is one of the most powerful attribute of this diverse and versatile analytical technique. FT-IR spectra are used to identify functional groups and bonds with the same stretching and bending vibrations in the pyrolysis liquid oil. The position of the carbonyl group in FT-IR is very sensitive to subsequent effects and to the structure of the molecule [13].

Table 4 shows the measured absorption frequency spectra of the combined effect of FT-IR spectrum in

TiO_2 and Red mud impregnation on the pyrolysis of oil palm empty fruit bunch OPEFB biomass. The bio-oil was analyzed using FT-IR spectroscopy to obtain a qualitative impression of the basic functional groups present in the oil. The results shows the presence of amine (N-H) group to be larger in red mud impregnated OPEFB biomass; this is consequence upon the high amount of cyanide that is present in the OPEFB biomass. Diametric (OH) group is also present in the aluminum impregnated OPEFB which is alcoholic base. The other functional group present are in smaller quantity which indicate the presence of multi-functional group. The C-H bending vibrations between 1090- 1020 cm indicates the presence of alkanes. The absorption peak between 1650- 1600 cm represent the C=0 stretching vibrations an indication of the presence of Quinone, carboxylic acids, aldehydes and ketones. The absorbance peaks between 1680- 1640 cm represents C=C stretching vibrations which suggest the presence of alkenes. Absorption peaks between 1350- 1250 cm stretching of P=0 stretching indicates the presence of a simple hetero- oxy compounds and organic sulphates. The C-N stretching vibration from 1090-1020 cm represents the presence of primary amine and cyanide and absorption peaks between 1410-1300 cm of 0- H bending indicates the presence of phenol, aromatic compound or diametric tertiary alcohol.

Table 4

FT-IR Functional Group Composition of Pyrolysis Liquid

Frequency range (cm^{-1})	Group	Class of compounds
1680-1640	C=C stretching	Alkenes
1650-1600	C=O stretching	Quinone or conju gate ketones
1470-1430	C-H bending	C-H bending
1410-1300	O-H bending	Phenols, aromatic compound
1350-1250	P=O stretching	Simple hetero-oxy compound
1090-1020	N-H stretching	primary amine, cyanide

4. CONCLUSION

Pyrolysis of biomass is an important source of renewable energy which produces pyrolysis product (bio-char liquid fuel and syngas) for energy utilization. Them gravimetric analysis (TGA) of OPEFB biomass and red mud shows the removal of moisture contents and volatile matter at 3.5 and 3.2 wt % respectively, and shows the carbon contents of the biomass and red mud. The effect of metal-oxides and red mud was studied in the carbonate vapor depositor furnace reactor of which the presence of calcined red-mud impregnated OPEFB gave the highest target liquid oil of 31 wt. % and the lowest char yield among the calcined and catalyzed OPEFB of 36 wt. % against the uncanalyzed OPEFB liquid of 31 wt. % (which is due to presence of the combine iron and aluminum oxides). The FT-IR results shows the oil produced from impregnated OPEFB contains less amine which has detrimental effect on the quality of the bio-oil produced. The results indicates that the impregnation of metal-ions and Red-mud improve the liquid yield at the expense of gas and char yield at temperature of 500^0C and also favors the formation of gas yield at 53 wt. % for catalyzed and uncanalyzed OPEFB yield of 64 wt. % at the temperature of 500^0C. The TiO_2-OPEFB char, yield 46 wt. %.

The overall influence of TiO_2 and red-mud impregnated OPEFB is presented in Fig. 4 of a combine FT-IR spectrum. Composition of functional groups from metal-ions and Red-mud OPEFB shows that, the RM-OPEFB has higher percentage of amine (N-H). The FT-IR result shows that, the oil produced from impregnated OPEFB contains less amine functional group which has detrimental effect on the quality of the bio-oil produced.

Comparing the bio-oil from OPEFB sample and the samples impregnated with RM and TiO_2 shows that, the addition of RM and TiO_2 to OPEFB increases the Nitrogen and Oxygen content of the resulting oil and decreases the aromatic compounds with Nitrogen functional groups from 7 % to 10 % respectively. This may be due to inhibition in the decomposition of glucose units from the cellulose contents of the original biomass. This signifies that red-mud and titanium oxides can be used to improve the quality of the fuel obtained from the biomass of OPEFB through pyrolysis. These results also suggest that it is possible to increase the yield of desirable chemical compounds of pyrolysis oil by impregnating or amending the biomass of OPEFB with red-mud and titanium oxide for fuel use. The results of GC/MS for TiO_2 and RM impregnated OPEFB on bio-oil compositions shows that the impregnated OPEFB shows an increase in phenols and sugar yields and also O-ring compounds with reduced linear compound group.

The OPEFB shows mainly phenol which was related to the removal of inherent minerals from the biomass.

It is therefore concluded that impregnation of OPEFB with metal-ion and red-mud could produce an heterogeneous catalyst (TiO_2 and red-mud) for the catalytic pyrolysis of empty fruit bunch for the production of bio-oil, that can add value to chemical feedstock and serve as an alternative source to selectively catalyze biomass during pyrolysis process.

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