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INFLUENCE OF IMPREGNATION ... TEMPERATURE ON THE PYROLYSIS OF OIL PALM EMPTY FRUIT BUNCH BIOMASS-OPEFB

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ABSTRACT:

Oil palm empty fruit bunch (OPEFB) were impregnated with metal-oxides and red-mud to improve the quality of the oil produced. The impregnation was enhanced by drying and calcinations at 105°C and 550°C respectively. The study of the effect of each of the metal-oxides was carried out in a carbonate vapour depositor furnace reactor (CVD).The result shows that the pyrolysis of OPEFB impregnated metal-oxides and red-mud increased the bio-oil yield from 28 wt. % for activated metal-oxides to 31 wt. % for activated red-mud at the expense of char and gas yield at 5wt. % impregnation ratio and 500°C pyrolysis temperature. Impregnation ratio of 5, 10 and 25 wt. % was observed. The optimum impregnation ratio was found to be 5wt%. Addition of metal- oxides and red-mud above 10 wt. % was found to reduce the overall liquid yield and promote gasification. The red mud impregnated OPEFB gave the highest yield of oil at 32.10% as against the metal-oxides that gave lower values. This may be due to the fact that the red mud already contained most of these ions which are known to act as catalyst. The highest yield of oil at 550°C is already showing an increase in energy level by 50°C even though the oil yield is higher in TiO_2 impregnation as energy consumption is minimized. The lowest oil yield is 15.55 wt. % at impregnation ratio of 10 wt. %. Ion impregnated OPEFB biomass for gas yield decreased as the temperature increased with impregnation ratio of 10 wt. %. In the case of titanium impregnated OPEFB the gas yield increases with increase in temperature and increase with the impregnation ratio. Aluminum and Red mud impregnated OPEFB decreases in gas with increase in the impregnation ratio and temperatures. The char yield is favored most in titanium impregnated OPEFB biomass with char yield of about 43.85% both, for 500°C and 550°C which increases char formations with increase in temperature at 10wt% impregnation ratio. The lowest char is in ion impregnated OPEFB with 20.30% at 5wt. % impregnation ratio.

Keyword; *pyrolysis, biomass, impregnation, calcination, temperature.*

1. INTRODUCTION

The emission of greenhouse gases have led to great interest in analyzing clean, renewable energy resources. Alternatively, there is need to urgently develop renewable, eco-friendly energy sources that are more efficient than the conventional fossil resources [7]. Biomass resources have great reserves and particular advantages in terms of renewability and carbon dioxide neutral characteristics [16]. Biomass of lignocellulose such as residues of agriculture, municipal and industrial waste is seen as major resources of potential energy sources in the near future [15]. Reports show that in palm oil industries, residues generated contain calorific value equivalent to over 50 million barrels of oil. Bio-fuels are largely considered to be carbon cycle neutral due to the fact thatCO_2 that is released into the atmosphere when burnt is fixed in to the biomass by photosynthesis process. In recent years, effort have been made towards producing bio fuels from many varieties of biomass such as oil palm empty fruit bunch (OPEFB) [22]. Pyrolysis technology is considered as one of the very promising conversion technologies in which biomass at moderate temperature is decomposed in the absence of oxygen [8]. It is a thermo chemical process by which biomass waste is converted into crude liquid bio-oil, gas and char, with high yields, in the absence of oxygen of which the liquid is very rich in oxygenated hydrocarbon [21]. Various parameters such as temperatures, particles size, heating rate, gas residence time and biomass constituents are important. The biomass constituents include cellulose, hemi cellulose, inorganic minerals and lignin which yield products. Many researches have been done on the catalytic activity of transition earth metals, alkali metal and alkaline earth metals on the bio-oils production during biomass pyrolysis. These 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 [22]. 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. Reported studies on iron catalyst compounds indicated that they have a positive impact on the product yields and bio-oils composition. [17] Have reported that Fe-species show a very promising result in catalyzing the production of anhydrosugars, more especially that of the levoglucosan in bio-oils. Similar result showed that Fe –impregnated wood produced high levoglucosan yield of 27.3 wt. % [12].

It is very clear that feedstock for pyrolysis either pre-treated or washed with acid increases the oil yield potentials of any biomass. Pyrolysis can also be view as a promising future technology that will in the near future substitutes fossil fuel in region such as Africa that has a lot of biomass resources [21]. Although the current bio-oil production system from biomass pyrolysis offers a futuristic solution to the major issues of climate change and greenhouse emissions which fossil fuel causes [7]. However, It suffers some draw back due to its high production temperature typically above 500°C and low oil yield. This has hindered its application beyond alternative biofuels [15]. There are some evidences that pyrolysis with addition of metal-ion and red mud will help to solve the issue of greenhouse gas emissions. However the use of metal-ion has not been studied, although bio-oil production from biomass alone has been carried out extensively, hence the need to study the effect of metal-ions and red mud impregnation ratio on the pyrolysis of oil palm empty fruit bunch (OPEFB) biomass.

2. MATERIAL AND METHODS

2.1. Sample Preparation

The procured samples of 50kg of biomass were sun-dried as received prior to utilization in the experiment. Parts of the sample of the biomass (OPEFB) were grinded, milled and sieved to the particle size range of between 1.6 – 2mm prior to wet processing. The prepared samples were used for pyrolysis experiments.

2.2. Carbonate Vapor Depositor (CVD) Pyrolysis

All pyrolysis experiments were performed at 400°C, 450°C, 500°C with impregnation ratios of 5, 10 and 25 wt. % in a stainless steel tubular carbon vapor depositor (CVD). A constant stream of nitrogen gas at 1L/min was fed into the reactor for batch withdrawal of the bio-oil and volatile products and maintaining an inert atmosphere during pyrolysis [6]. Pyrolyzer was installed inside an electrical heater within the CVD and was insulated to enable the heating of the furnace reactor up to 1000°C.

The reactor was equipped with a biomass holder known as cu bet and connected to both vacuum and nitrogen. To record the pyrolysis temperature, a 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°C. The inlet of the ice trap was connected with gas sampling bottle to collect the non- condensable gases. The pyrolysis product yield were 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 the condition of 500°C temperatures were run twice and a standard error of ±5 wt. % in product yields was established at different impregnation ratios of all the metal oxides

3. RESULTS AND DISCUSSION

3.1 Pyrolysis of Metal-oxides and Red-mud Impregnated OPEFB in CVD Furnace Reactor

The pyrolysis product distribution of OPEFB at 500°C on an ash free basis (AF wt. %) of impregnation ratio of 5wt% is shown in Table 1. The uncatalysed OPEFB gave a liquid yield of only 26wt% while the metal-ions impregnated OPEFB and red-mud increase the liquid yield up to 31%. This is supported by [9], which shows 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 Aluminum and Titanium which are metal-ions showed no major changes in the increasing bio-oil yield against [19] which shows significant changes in bio-oil yield. The results clearly suggest that the impregnation of metal-ions into biomass do not promotes significant oil yield but the combine effect of metal-ions and red mud promotes better yield. This result is in line with [22] findings with AWRM-EFB oil yield of 52 wt. %, although higher and which is due to the acid washing which has increase its catalytic selectivity which also in conformity with the report from [20].

Table 1: OPEFB pyrolysis product distribution in a CVD furnace reactor

OPEFB	Product (wt. %)			
	Bio-oil	Bio-char	Syngas	Total
OPEFB	26.00	64.20	31.90	122.10
Al2O3-OPEFB	28.55	45.80	42.90	117.25
Fe2O3-OPEFB	28.30	53.25	30.60	112.15
TiO2-OPEFB	29.90	36.95	46.40	113.25
RM-OPEFB	31.55	43.55	36.15	121.25

3.2. Effect of Metal-ions and Red-mud Impregnation on the Properties of OPEFB

The proximate and ultimate analysis of OPEFB impregnated metal-ions; red-mud and OPEFB raw are shown in Table 2. There is a notable decrease in the volatile matter (VM) of all the impregnated metal-ions which is accompanied by an increase in their fixed carbon (FC) content compared with the uncatalysed OPEFB. This result is not in line with [11] which showed that, the volatilities increased at the expense of char by washing wood biomass with either water or acid. This result suggested that only acid or water treated biomass increases the volatile matter and decreases the fixed carbon. By considering the volatile matter/fixed carbon (VM/FC) ratios in Table 2. The reactivity of the OPEFB feedstock were decreasing in the order of OPEFB (2.56) > TiO_2-OPEFB (1.73) > RM-OPEFB (0.84). This suggests that impregnation ratio of TiO_2-OPEFB only had an impact on the OPEFB thermal behavior as compared to OPEFB and RM-OPEFB. This is due to the material impregnated into the structure. The elemental analysis also showed that there is a drop in nitrogen when compared with the uncatalysed and untreated OPEFB of (8.7). The amount of sulphur content in the catalyzed OPEFB with TiO_2 and RM shows that the metal-ion impregnate well into the biomass as compared with the work of [22] in which the sulphur content is negligible in the acid pre-treated EFBs that showed the sulphate from sulphuric acid or $FeSO_4$ is remained in the treated solution and does not impregnated into the biomass unlike the metal-ions.

Table 2: OPEFB feed stock characterization on the proximate and Elemental analysis bio char

Biomass	Proximate Analysis wt. %				
	MC	FC	VM	ASH	
OPEFB	0.98	20.30	51.80	8.21	
Ti02-OPEFB	0.53	15.10	63.30	2.10	
RM-OPEFB	0.56	17.00	71.20	2.90	
OPEFB-CHAR	0.48	8.02	79.70	9.90	
Biomass	**Elemental Analysis wt. %**				
	N	C	H	O	S
OPEFB	8.71	77.98	11.08	1.19	0.20
Ti02-OPEFB	8.54	78.10	10.72	1.51	0.21
RM-OPEFB	7.24	79.02	10.83	2.63	0.21
OPEFB-CHAR	77.98	11.90	0.21	8.71	1.19

3.3. Effect of Impregnation Ratio on Metal-oxides, Red mud and OPEFB yield

3.3.1. Effect of Impregnation Ratio on Metal-oxide and Red mud-OPEFB Oil Yield

Pyrolysis was carried out using the optimum temperature of 500°C, while 450°C and 550°C was also investigated. Figure 1 contains oil yield with impregnation ratio of 5, 10 and 25 wt. %. The highest oil yield of 32.10% was obtained with impregnation ratio of 5wt. % of which there is no any significant increase above this ratio. This result is in conformity with 5wt. % reported by [18]. The impregnation ratio at 0% is non-catalytic with oil yield of 51.50 %. This means that the oil contains a lot of water content hence its lower quality. The higher the bio-oil yields the lower the quality of the oil and vice versa [3], these results suggest that the impregnation of metal-ions into OPEFB biomass promotes the liquid yield while demineralization effect of water or acid which shows no significant contribution in increasing liquid oil yield [22].

Figure 2 shows that, the pyrolysis temperatures are almost the same with increase in temperature and impregnation ratio. In Figure 3, the highest oil yields at different temperatures and impregnation ratio is 29.70% at 5wt% impregnation ratio for 500°C, and the lowest yield of 24.90% at 550°C for 10wt. % impregnation ratio. Red mud impregnated OPEFB give the highest oil yield at 550°C with impregnation ratio of 5wt. % and the lowest oil yield at 21.10% at 10wt. %, this is contrary to the optimum condition of temperature of 500°C as established in the non-catalytic process, this is for the fact that ordinarily transition earth metals are catalyst on their own capacity and red mud contains most this metal-oxides [5].The red mud impregnated OPEFB give the highest yield of oil 32.10% as against the metal-oxides that gave lower values [1]. This may be due to the fact that the red mud already contained most of these ions which are known to act as catalyst. The highest yield of oil at 550°C is already showing an increase in energy level by 50°C even though the oil yield is higher in TiO_2 impregnation as energy consumption is minimized. The lowest oil yield had been 15.55 wt. % at impregnation ratio of 10 wt. %.

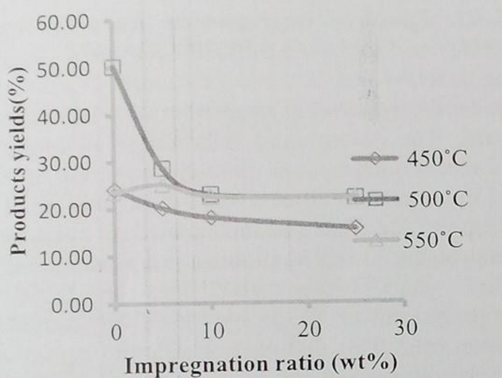

Figure 1. Oil Yield from Al_2O_3-OPEFB

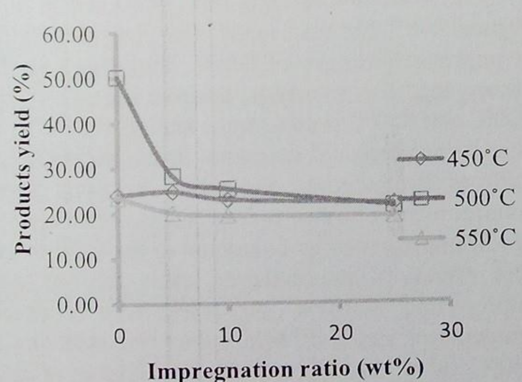

Figure 2. Oil Yield from Fe_2O_3-OPEFB

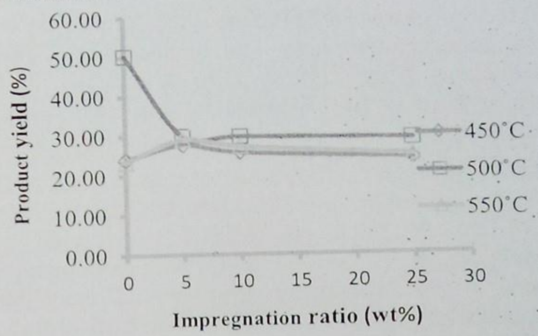

Figure 3. Oil Yield from TiO_2-OPEFB

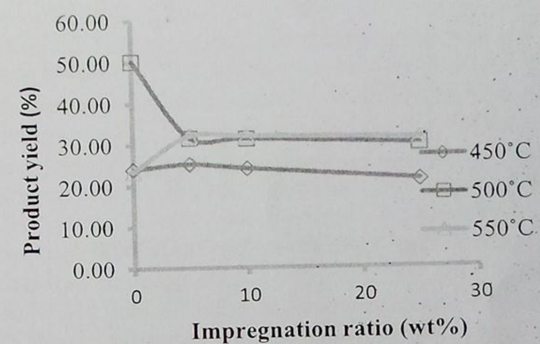

Figure 4. Oil Yield from Red mud-OPEFB

3.3.2. Effect of Impregnation Ratio on Metal-oxide and Red mud-OPEFB Gas yield

Figure 5 shows gas yield with various impregnation ratios. At maximum temperature, pyrolysis favors gas yield as increase in temperature favors gas/volatile matter yield. The Fe_2O_3-OPEFB gave a higher gas yield of 51.40%. Al_2O_3-OPEFB, TiO_2-OPEFB, and red mud gave yield of gas at 45.10, 27.70 and 40.10% respectively. This is supported by [23]. Figure 8 favors gas yield for 51.40 wt. % at 500°C for 5wt. % impregnation ratios as the temperatures are favorable. Titanium impregnated OPEFB gas yield in Figure 8 shows a parallel effect of impregnation effect. The formation of char shows an order of increment in a way that the highest yield of char is below the optimum temperature of 500°C with char yield of 35.95%. The gas yield in figure 6 Iron impregnated OPEFB biomass shows a compressing nature as all the yield at different temperature falls almost on the same axis. The highest yield of gas was at 550°C for impregnation ratio of 10wt. %. In the case of titanium impregnated OPEFB in Figure 7, the gas yield increases with increase in temperature and with increase in the impregnation ratio. However Aluminum and Red mud impregnated OPEFB increased with increase in the impregnation ratio and temperatures. The deductions from Figures 5 to 8 are the Iron impregnated OPEFB biomass for gas yield which decreased as the temperature increased with impregnation ratio of 10 wt. %.

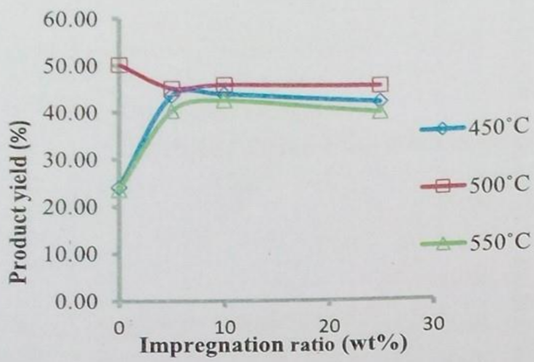

Figure 5. Gas Yield from Al_2O_3-OPEFB

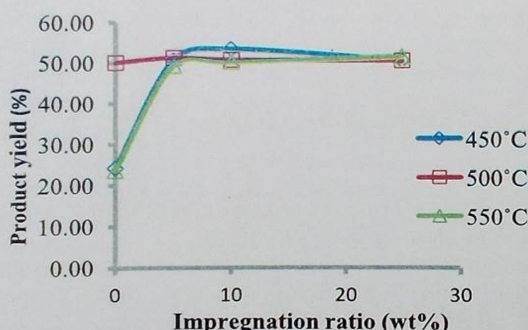

Figure 6. Gas Yield for Fe_2O_3-OPEFB

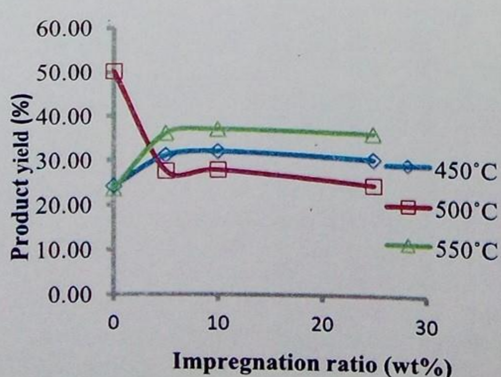

Figure 7. Gas Yield from TiO_2-OPEFB

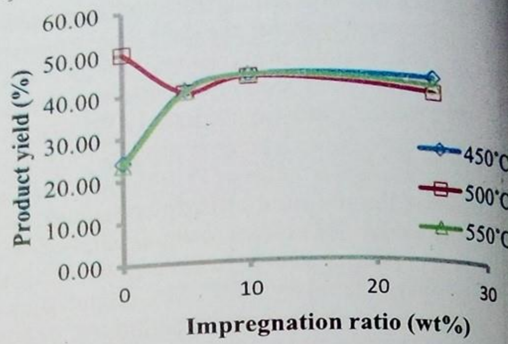

Figure 8. Gas Yield for Red mud-OPEFB

3.3.3. Effect of Impregnation Ratio on Metal-oxides and Red mud-OPEFB Char yield

Figures 9-12 shows the behaviors of char yield under the influence of temperature and impregnation ratio. The pattern and behavior of all the char increases with increase in temperature and addition of impregnation ratio favored char yield in all the Figures [23]. The ion impregnated oil palm empty fruit bunch (OPEFB) shows a sharp decrease in the char yield below 20.30wt% at 500°C of impregnation ratio of 5wt% in all the Figure formations. This may be linked to the high content of ion compound either in Fe-ion or Fe_2O_3 form impregnated into OPEFB samples [13]. The highest char yield is produced at 500°C at impregnation ratio of 25% for 46.40% in TiO_2 impregnated OPEFB for Figures 9-12, and the lowest char yield is at 500°C at impregnation ratio of 5wt%. This result clearly shows that the pyrolysis temperature of 450°C, 500°C and 550°C is considered and adhered to as all char formation/yield increases in the impregnation ratio as compared to the report by [11]. These conditions may be due to low content of compound of ion impregnated as contained in the catalyst [4]. The effect of impregnation ratio on red mud impregnated OPEFB decreases with optimum temperature and increases below the optimum at 450°C in all the Figures (9-12). This is a clear indication that red mud impregnated catalyst does not really favors the formation of char [2]. The char yield is favored most in titanium impregnated OPEFB biomass with char yield of about 43.85% both for 500°C and 550°C meaning that the char formations will increase with increase in temperature at 10wt% impregnation ratio in Figure 11. The lowest char is in ion impregnated OPEFB of 20.30% at 5wt. % impregnation ratio in all the char formation as depicted in Figures 9-12 respectively.

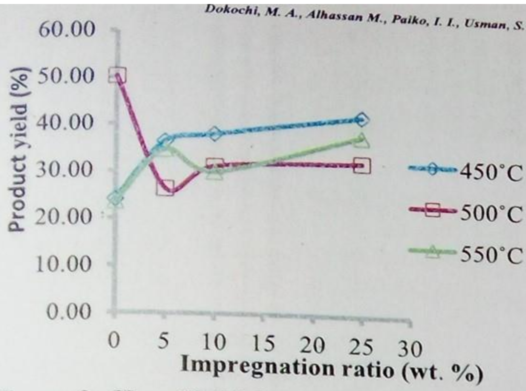

Figure 9. Char Yield for Al_2O_3-OPEFB

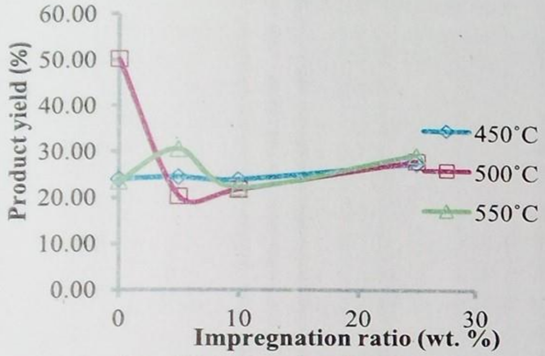

Figure 10. Char Yield for Fe_2O_3-OPEFB

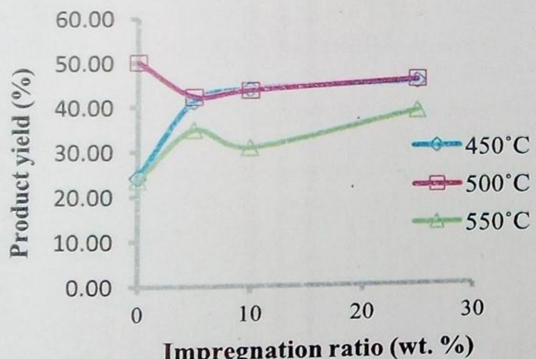

Figure 11. Char Yield for TiO_2-OPEFB

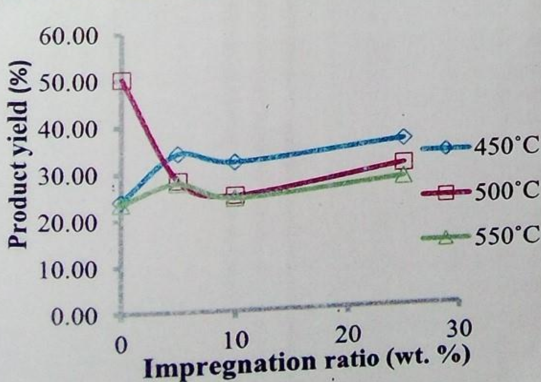

Figure 12. Char Yield from Red mud-OPEFB

4. CONCLUSION

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 31wt. % and the lowest char yield among the calcined and catalyzed OPEFB of 36 wt. % against the uncatalysed OPEFB liquid of 31 wt. %. Impregnation ratio of 5, 10 and 25 wt. % was employed. The optimum impregnation ratio was found to be 5wt%. Addition of metal- oxides and red-mud above 10 wt. % was found to reduce the overall liquid yield and promote gasification. The red mud impregnated OPEFB gave the highest yield of oil 32.10% as against the metal-oxides that gave lower values. The highest yield of oil at 550°C shows an increase in energy level by 50°C even though the oil yield is higher in TiO_2 impregnation as energy consumption is minimized. Ion impregnated OPEFB biomass for gas yield decreased as the temperature increased with impregnation ratio of 10 wt. %. In the case of titanium impregnated OPEFB the gas yield increases with increase in temperature and increase in the impregnation ratio. The ion impregnated oil palm empty fruit bunch (OPEFB) showed a decrease in the char yield below 20.30wt% at 500°C of impregnation ratio of 5wt%. However Aluminum and Red mud impregnated OPEFB increased with increase in the impregnation ratio and temperatures. The char yield is favored in titanium impregnated OPEFB biomass with char yield of about 43.85% both, for 500°C and 550°C which increases char formations with increase in temperature at 10wt% impregnation ratio. The lowest char is in ion impregnated OPEFB at 20.30% at 5wt. % impregnation ratio, the lowest oil yield had been 15.55 wt. % at impregnation ratio of 10 wt. %. It is therefore concluded that impregnation of OPEFB with metal-ion and red-mud impregnation ratio could produce a good quality bio-oil free from amine which can add value to chemical feedstock and serve as an alternative source to selectively catalyze biomass in pyrolysis processes.

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