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ANALYSIS AND COMPARISON OF THE FUEL PROPERTIES OF BIO-OILS PRODUCED BY CATALYTIC FAST PYROLYSIS OF *Tectona grandis*

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Abstract: This study analyzed the fuel properties of bio-oils produced by catalytic fast pyrolysis of *Tectona grandis* in a fixed bed reactor at different temperatures (400 – 600 °C) and biomass to catalyst (b/c) weight ratios (90/10 – 60/40). Magnesium oxide (MgO) was used as catalyst. The product yields were determined. Bio-oils were characterized with their elemental composition and their Higher Heating Values (HHVs) as well as their basic fuel properties at maximum bio-oil yields conditions, including viscosity, flash point, moisture content, pH value and Conradson Carbon Residue (CCR), were determined and compared with those of non-catalytic pyrolysis bio-oils. The maximum yields of bio-oil at 400, 500 and 600 °C were 31.53, 40.87 and 29.30 wt.%, respectively, obtained at b/c ratios of 70/30, 80/20 and 70/30. Catalytic pyrolysis bio-oils possessed higher carbon and hydrogen but lower oxygen and sulphur contents than non-catalytic pyrolysis bio-oils. The HHVs of catalytic pyrolysis bio-oils (40.31 – 42.08 MJ/kg) were higher than those of non-catalytic bio-oils (36.47 – 36.76 MJ/kg). Catalyst reduced the viscosity (at 400 and 500 °C), moisture content and CCR (at 400 and 600 °C), and increased the pH value of bio-oils (at 400 and 600 °C). Catalytic pyrolysis deoxygenates and enhances the fuel properties of bio-oils.

Keywords: Characterization, Catalyst, Fast pyrolysis, *Tectona grandis*, Bio-oil, Fuel properties

Tectona grandis' in Katalitik Hızlı Piroliziyle Üretilen Biyo-Yağların Yakıt Özelliklerinin Analizi ve Karşılaştırılması

Öz: Bu çalışmada, farklı sıcaklıklarda (400 – 600 °C'de) ve farklı biyokütle/katalizör (b/c) ağırlık oranlarında (90/10 – 60/40) sabit yataklı bir reaktörde Tectona grandis'in katalitik hızlı pirolizi ile üretilen biyo-yağların yakıt özellikleri incelenmiştir. Katalizör olarak magnezyum oksit (MgO) kullanılmıştır ve ürün verimleri belirlenmiştir. Biyo-yağlar karakterize edilmiştir ve element bileşimleri, yüksek ısıtma değerleri, maksimum biyo-yağ verimi koşullarındaki temel yakıt özellikleri, viskozite, parlama noktası, nem içeriği, pH değeri ve Conradson karbon kalıntısı (CCR) değerleri incelenmiştir ve katalitik olmayan piroliz biyo-yağların değerleri ile karşılaştırılmıştır. 400, 500 ve 600 °C'de ve 70/30, 80/20 ve 70/30 b/c oranlarında elde edilen ağırlıkça maksimum biyo-yağ verimleri sırasıyla, %31,53, % 40,87 ve % 29,30 olarak bulunmuştur. Katalitik piroliz biyo-yağları, katalitik olmayan piroliz biyo-yağlarından daha yüksek karbon ve hidrojene ancak daha düşük oksijen ve kükürt içeriğine sahip bulunmuştur. Katalitik piroliz biyo-yağlarının Yüksek Isıtma Değerleri (HHV) (40,31 – 42,08 MJ/kg), katalitik olmayan biyo-yağlardan (36,47 – 36,76 MJ/kg) daha yüksek belirlenmiştir. Katalizör, viskoziteyi (400 ve 500 °C'de), nem içeriğini ve CCR'yi (400 ve 600 °C'de) azaltmıştır ve biyo-yağların pH değerini (400 ve 600 °C'de) artırmıştır. Katalitik piroliz, biyo-yağların yakıt özelliklerini geliştirmektedir.

Anahtar Kelimeler: Karakterizasyon, Katalizör, Hızlı piroliz, *Tectona grandis*, Biyo-yağ, Yakıt özellikleri

1. INTRODUCTION

Advances in global economy and sustainable development have necessitated the need to make energy readily available in the most environmentally friendly way. Energy generation from fossil fuels is no longer business as usual as humans are now well aware of its various consequences on the environment (Thangalazhy-Gopakumar et al., 2010), humans and aquatic lives (Latake et al., 2015). These include acid rain, depletion of the ozone layer, global warming (Zabeti et al., 2012) and destruction of microalgae, to mention a few. Sequel to these, regulations on carbon emissions into the atmosphere have become more stringent than ever. Besides, the depletion of fossil fuel resources suggests that fossils will not be able to meet the ever increasing energy demand in the future (Kraiem et al., 2014).

Renewable energy resources are now being considered as substitutes for fossils. Amongst the promising renewable resources, biomass is seen as a viable option. Although there are thermochemical and biochemical technologies for biomass conversion to energy fuels, thermochemical processes are often preferred. Pyrolysis, one of the thermochemical processes, has been shown to be a viable means for production of solid, liquid and gaseous biofuels, with the liquid fuel accounting for about 70% of the energy content of the feedstock (Bridgwater and Peacocke, 2000).

However, the liquid fuels (bio-oils) from pyrolysis have high moisture, oxygenated compounds, acidity and viscosity. Besides, they are unstable during storage and are characterized with low H/C ratios (Pütün, 2010). These shortcomings have brought about the use of catalysts in upgrading bio-oils from biomass pyrolysis (Samolada, 2000). Zhou et al. (2013) studied the effect of zinc oxide on the characteristics bio-oil derived from pyrolysis of rice husk in a fixed bed reactor. Pütün et al. (2008) investigated the effect of alumina on the product yields from pyrolysis of *Euphorbia rigida* biomass sample in inert and steam atmospheres and analysed the compositions of the bio-oil yields. French and Czernik (2010) evaluated the performance of commercial and laboratory-synthesized catalysts on hydrocarbon production during pyrolysis of aspen wood, Avicel PH-105 cellulose and straw lignin. Pütün (2010) studied the effect of magnesium oxide on pyrolysis of cotton seed and compared the yields of asphaltenes, n-pentane solubles, aliphatic sub-fraction, aromatic sub-fraction and polar sub-fraction from non-catalytic and MgO catalyst-assisted pyrolysis. Güllü (2003) studied the effect of sodium and pottasium carbonate on the yield of liquid products from pyrolysis of hazelnut, tea factory waste, tobacco stalk and yellow pine wood. Onay (2014) studied the effect of Ni-Mo/$\gamma -$ alumina catalyst on pyrolysis of Laurel (*Laurus nobilis L.*) seed in a fixed bed tubular reactor. Samolada et al. (2000) presented an evaluation of some catalysts commonly used for catalytic pyrolysis of biomass. In many of the studies discussed above, the basic fuel properties of the derived bio-oil were not determined.

Qiang et al. (2008) analysed the chemical and physical properties of bio-oil from fast pyrolysis of rice husk and determined the basic fuel properties of the bio-oil. However, the effect of catalyst on these properties was not considered. Mythili et al. (2017) studied the effect of pyrolysis temperature on physicochemical properties of *Prosopis juliflora* bio-oil but did not also consider the effect of catalyst on these properties. Shah et al. (2012) analysed the physicochemical properties of the bio-oil produced by fast pyrolysis of corn stover and cobs and only reported the proximate and ultimate analyses with modified acid number without considering the effect of catalyst. Lyu et al. (2015) estimated and compared the components of bio-oils from different pyrolysis conditions but did not determine the basic fuel properties, neither was the effect of catalyst considered. Yu et al. (2007) analysed the physical and chemical properties of bio-oil from microwave pyrolysis of corn stover but did not also consider the effect of catalyst on these properties. Several other researchers studied the properties of bio-oils from various biomass materials under different pyrolysis conditions without considering the effect of catalysts (Nanda et al., 2014; Weerachanchai et al., 2007; Garcia-Perez et al., 2007; Chukwuneke et al., 2019;

Garcìa-Pèrez et al., 2002; Kato et al., 2016). Besides, studies have shown that different feedstocks give different yield patterns and properties of pyrolysis-derived bio-oil (Chukwuneke et al., 2019). Therefore, in this study, the effect of magnesium oxide catalyst on the physicochemical properties of bio-oil from *Tectona grandis* pyrolysis was studied. The basic fuel properties, including density, viscosity, pH value, flash point, pour point and Conradson carbon residue of the bio-oil were also determined and compared with those of the bio-oil from non-catalytic experiments.

2. MATERIALS AND METHODS

2.1. Materials

Tectona grandis sawdust was procured from a sawmill in Ogbomoso, South-Western Nigeria. Magnesium oxide (MgO) catalyst (having 5% loss on ignition at 1000 °C) was procured from a chemical vendor in Ogbomoso, Nigeria.

2.2. Methods

2.2.1. Feedstock Processing

The procured sawdust sample was sundried for three days in order to reduce its moisture content. After sun drying, it was weighed and bagged in a cellophane bag for it to maintain its moisture content and it was kept at room temperature till when it was used for the experiments.

2.2.2. Feedstock Characterization

The biomass sample was characterized with its fixed carbon, volatile mater, moisture and ash by proximate analysis using a thermogravimetric analyzer (TGA) (Model 5E-MAC 6710, Changsha Kaiyuan Instruments Co. Ltd, China). The elemental analysis of the raw sample was done in a CHN analyzer (Leco CHN 2000 elemental analyzer). Sulphur content was determined by a sulphur analyzer (TSHR TS 6000 Total Sulphur Analyzer). The Higher Heating Value (HHV) of the raw sample was estimated by equation 1, according to Sheng and Azevedo (2005), given as

$$HHV_{raw}(MJ/kg) = -1.3675 + 0.3137 \times wt.\%C + 0.7009 \times wt.\%H + 0.0318 \times wt.\%O \quad (1)$$

2.2.3. Experimental Setup and Procedure

Figure 1 shows the exploded view of the pyrolysis unit used for the experiments. The detailed description of this setup has been given elsewhere (Okekunle et al., 2016). Samples with different biomass/catalyst weight ratio (b/c ratio) of 90/10, 80/20, 70/30 and 60/40, thoroughly mixed together, were fed into the crucible, one at a time, and the crucible was covered and fastened with bolts and nuts in preparation for a run. The furnace was then plugged to the mains, pre-set and heated with the aid of an electric heating element to a temperature 50 °C higher than the desired temperature for pyrolysis in order to compensate for the heat loss during the insertion of the crucible. When the furnace attained the pre-set temperature, it was opened and the crucible was inserted into it. The furnace was covered again and reset to the actual pyrolysis temperature.

This procedure was followed for the pyrolysis temperatures of 400, 500 and 600 °C and a residence time of 15 min. After each run, the liquid and char yields were weighed and expressed in percentages of the weight of the initial sample while gas yield was obtained by mass balance.

2.3. Bio-oil Characterization

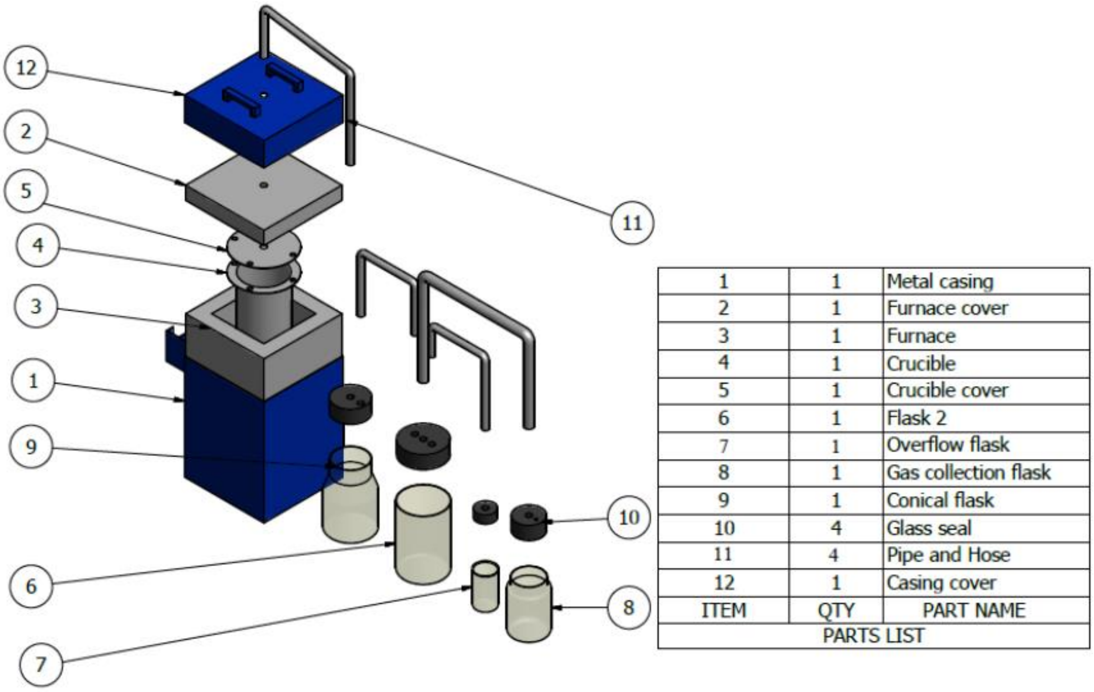
2.3.1. Ultimate Analysis

The elemental analysis of the bio-oils was done with the same equipment used for the feedstock. The sulphur content of the bio-oils was also determined by a Sulphur analyzer (TSHR TS 6000 Total Sulphur Analyzer). The Higher Heating Values (HHVs) of the bio-oils were determined using modified Dulong's formula according to Theegala and Midgett (2012), given by equation 2.

$$HHV_{bio-oil}(MJ/kg) = \frac{33.5 \times wt.\ \%C}{100} + \frac{142.3 \times wt.\ \%H}{100} - \frac{15.4 \times wt.\ \%O}{100} \tag{2}$$

2.3.2. Fuel Characterization of Bio-oils

The fuel properties of the bio-oils were determined in accordance with standard methods. Viscosity was determined according to ASTM D 445. The flash point was determined according to ASTM D 1310. The pour point and Conradson Carbon Residue (CCR) were determined according to ASTM D 5853 and ASTM D 189, respectively. The pH value was determined with the aid of a pH meter (Hanna Model HI 8424). Moisture content was determined according to ASTM E 203. Ash content was estimated according to ASTM D 482.



1	1	Metal casing
2	1	Furnace cover
3	1	Furnace
4	1	Crucible
5	1	Crucible cover
6	1	Flask 2
7	1	Overflow flask
8	1	Gas collection flask
9	1	Conical flask
10	4	Glass seal
11	4	Pipe and Hose
12	1	Casing cover
ITEM	QTY	PART NAME
PARTS LIST		

Figure 1:
The exploded view of the pyrolysis unit

3. RESULTS AND DISCUSSION

3.1. Physicochemical Properties of *Tectona grandis*

The physicochemical properties of the feedstock are presented in Table 1. Proximate analysis showed a high percentage of volatile matter (78.42%), low moisture content (9.00%) and ash (0.58). Elemental analysis revealed the percentage of carbon (50.82%), hydrogen (5.88%) and oxygen (42.80%). The detailed analysis of the physicochemical properties of the feedstock has been given elsewhere (Okekunle et al., 2021).

3.2. Products Yields

Table 2 shows the yields of char, bio-oil and gas from the catalytic pyrolysis at different b/c ratios and temperatures. From the table, the highest yields of char (52.45%), bio-oil (40.87%) and gas (46.95%) were obtained at 400 °C (60/40 b/c ratio), 500 °C (80/20 b/c ratio) and 400 °C (80/20 b/c ratio), respectively, while the lowest yields of char (25.65%), bio-oil (10.27%) and gas (21.83%) were respectively obtained at 600 °C (90/10 b/c ratio), 500 °C (60/40 b/c ratio) and 400 °C (60/40 b/c ratio).

Table 1: Physicochemical properties of *Tectona grandis*

Proximate analysis (wt.%)	Elemental analysis (wt.%)	Atomic ratio (-)
Moisture content 9.00	Carbon 50.82	H/C 1.3787
Ash content 0.58	Hydrogen 5.88	O/C 0.6322
Volatile matter 78.42	Nitrogen 0.28	N/C 0.0047
Fixed carbon 12.00	Oxygen 42.80	
	Sulphur 0.01	
	HHV (MJ/kg) - 20.1	

Source: Okekunle et al. (2021)

Table 2: Char, bio-oil and gas yields from catalytic pyrolysis of *Tectona grandis*

B/C ratio	Char yield (wt.%)			Bio-oil yield (wt.%)			Gas yield (wt.%)		
	400 °C	500 °C	600 °C	400 °C	500 °C	600 °C	400 °C	500 °C	600 °C
90/10	36.29	32.30	25.69	26.13	28.89	28.58	37.58	38.81	45.73
80/20	28.29	32.89	33.49	24.76	40.87	27.36	46.95	26.24	39.15
70/30	35.49	37.35	39.52	31.53	29.61	29.35	32.98	33.04	31.13
60/40	52.45	42.63	42.49	25.72	10.27	17.05	21.83	47.10	40.46

3.3. Elemental Analysis of Bio-oils

Table 3 shows the elemental composition of the bio-oils from catalytic pyrolysis at different temperatures and b/c ratios compared with those of the bio-oils from non-catalytic experiments. As shown in the table, the bio-oils derived from catalytic pyrolysis are richer in carbon and hydrogen but leaner in oxygen than those obtained from non-catalytic (NC) runs at the same temperatures.These results are in agreement with the findings of Pütün (2010), who reported higher percentages of carbon (77.62 wt.%) and hydrogen (12.15 wt.%) but a lower oxygen percentage (4.9 wt.%) for catalytic pyrolysis bio-oil compared to the values obtained for non-catalytic pyrolysis bio-oil (C - 74.24 wt.%, H - 11.39 wt.% and O - 9.56 wt.%). Zhou et al. (2013) also reported higher percentages of carbon (49.73 wt.%) and hydrogen (12.57 wt.%) with a lower oxygen percentage (35.62 wt.%) for bio-oil from catalytic pyrolysis than the values obtained for non-catalytic pyrolysis bio-oil (C - 49.20 wt.%, H - 11.65 wt.%, O - 36.78 wt.%). Carbon and hydrogen enrichment with reduction in oxygen in the bio-oils from catalytic pyrolysis suggests they have better calorific values than those from non-catalytic experiments. This fact is substantiated by the HHVs presented in Table 3. These results have also shown that catalysts help in deoxygenating bio-oils (Pütün, 2010). Oxygen reduction in catalytic pyrolysis bio-oils will improve their stability and enhance their upgrading to hydrocarbons (Shah et al., 2012). This is because oxygen in bio-oil has been identified as a source of bio-oil instability (Bardalai and Mahanta, 2015) and also, bio-oil upgrading to hydrocarbons will require oxygen removal (Shah et al., 2012).

Moreover, Table 3 also shows that the presence of MgO catalyst reduced the percentage of sulphur in catalytic pyrolysis bio-oils (0.05 – 0.07%) compared to the values for bio-oils from non-catalytic experiments (0.11 – 0.21%). This implies that Sox emissions from the combustion of catalytic pyrolysis bio-oils will be much lower than those from non-catalytic pyrolysis bio-oils. Therefore, bio-oils from catalytic pyrolysis could be more environmentally friendly. H/C and O/C ratios for bio-oils from catalytic pyrolysis are respectively higher and lower than those for non-catalytic pyrolysis bio-oils. These results are in agreement with the findings of Pütün (2010) and Zhou et al. (2013), who reported higher H/C and lower O/C ratios for bio-oils from catalytic pyrolysis compared to the values obtained for bio-oils derived from non-catalytic pyrolysis.

Table 3: Elemental composition and HHVof bio-oils obtained at different temperatures and b/c ratios

T (ºC)	B/C ratio (-)	Element (wt.%)					Atomic ratio (-)			HHV (MJ/kg)
		C	H	N	O	S	H/C	O/C	N/C	
400	90/10	81.36	10.90	3.24	4.52	0.07	1.596	0.042	0.034	42.07
	80/20	81.10	10.98	3.26	4.60	0.06	1.613	0.043	0.034	42.08
	70/30	80.02	10.88	4.48	4.80	0.06	1.620	0.045	0.048	41.55
	60/40	80.26	10.90	4.24	4.55	0.07	1.618	0.043	0.045	41.70
	NC*	75.82	8.98	4.29	10.80	0.11	1.410	0.110	0.049	36.52
500	90/10	80.30	9.98	5.27	4.60	0.05	1.481	0.043	0.056	40.39
	80/20	80.22	9.96	5.30	4.57	0.05	1.479	0.043	0.057	40.34
	70/30	80.22	9.98	4.29	4.88	0.07	1.482	0.046	0.046	40.32
	60/40	80.46	9.96	5.24	4.50	0.06	1.475	0.042	0.056	40.43
	NC*	76.50	8.96	4.24	10.50	0.11	1.400	0.100	0.048	36.76
600	90/10	80.40	9.93	4.26	4.60	0.06	1.472	0.043	0.045	40.36
	80/20	80.52	9.98	4.28	4.65	0.07	1.477	0.043	0.046	40.46
	70/30	80.36	9.90	4.24	4.52	0.05	1.468	0.042	0.045	40.31
	60/40	81.20	9.94	4.26	4.60	0.05	1.459	0.043	0.045	40.64
	NC*	75.80	8.93	4.46	10.60	0.21	1.400	0.110	0.050	36.47

NC - Non-catalytic pyrolysis, * Data for NC were obtained from Okekunle et al. (2021).

3.4. Basic Fuel Properties of Bio-oil

The basic fuel properties of the bio-oils from catalytic pyrolysis at the b/c ratios where maximum yields were obtained for all the considered temperatures are compared with those of the bio-oils from non-catalytic experiments at the same temperatures. The maximum bio-oil yields from catalytic pyrolysis at 400 (31.53 wt.%), 500 (40.87 wt.%) and 600 ^{o}C (29.35 wt.%) were obtained at b/c ratios of 70/30, 80/20, and 70/30, respectively.

3.4.1. pH Value

Figure 2 shows the pH values of the bio-oils from catalytic pyrolysis at optimum b/c ratio for bio-oil yield at 400, 500 and 600 ^{o}C compared with those of the bio-oils from non-catalytic experiments at the same temperatures. As shown in the figure, MgO catalyst increased the pH values of the bio-oils at 400 and 600 ^{o}C. These results are in agreement with the findings of Shadangi and Mohanty (2014 a&b), who reported increase in pH values of the bio-oils from catalytic pyrolysis of Karanja and Niger seed as compared to those of bio-oils from non-catalytic pyrolysis of the same biomass materials. At 500 ^{o}C, however, the pH value of the bio-oil from catalytic pyrolysis was lower than that of the bio-oil from non-catalytic experiment. This may be linked to the difference in b/c ratio that gave the optimum yield of bio-oil at this temperature. Lower pH values make bio-oils acidic, causing damages to internal combustion engines when such bio-oils are used. The pH values of the catalytic pyrolysis bio-oils are within the range (2.0 – 3.8) reported for other bio-oils (Garcìa–Pèrez et al., 2002). Catalytic esterification can be used to further increase the pH values of the bio-oils (Wang, 2013).

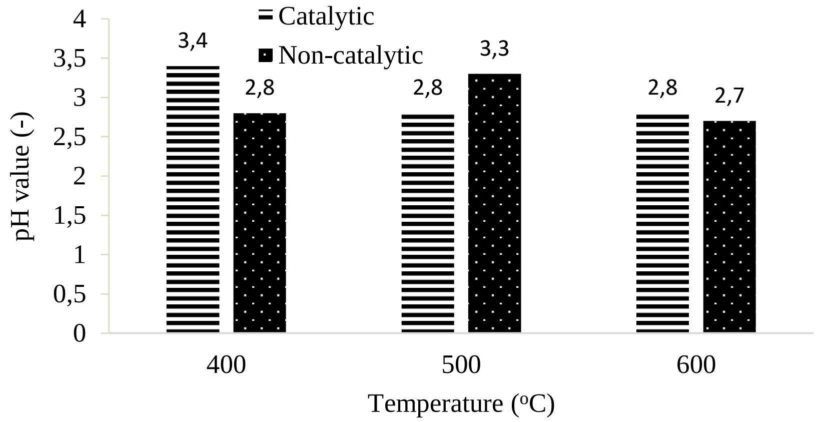


Figure 2:
Comparison of pH values of bio-oils from catalytic and non-catalytic pyrolysis

3.4.2. Viscosity

Figure 3 shows the viscosities of the bio-oils from catalytic pyrolysis at optimum b/c ratio for bio-oil yield at 400, 500 and 600 ^{o}C compared with those of the bio-oils from non-catalytic experiments at the same temperatures. As shown in the figure, the presence of catalyst reduced the viscosity of bio-oil at 400 and 500 ^{o}C. Shadangi and Mohanty (2014 a&b) have also reported reduction in viscosity of bio-oils obtained from catalytic pyrolysis compared to the values obtained for bio-oils from non-catalytic pyrolysis of the same feedstock. One of the main concerns in the use of bio-oil as fuel in diesel engines is high viscosity, which poses a challenge during atomization (Shadangi, 2014a). Catalytic pyrolysis, with the right process conditions and b/c ratio, can help address this concern. At 600 ^{o}C, however, the viscosity of catalytic pyrolysis bio-oil was higher than that of non-catalytic by 1 mPa.s. This may be attributed to repolymerization of lighter organics at this temperature. The viscosities of the catalytic pyrolysis bio-oils obtained in this study are much lower than those reported by Yu et al. (2007), and Oyebanji and Ololade (2017), which were 185 and 53.25 mPa.s, respectively.

3.4.3. Flash Point

Figure 4 shows the comparison of the flash points of the bio-oils obtained from catalytic pyrolysis with those of the bio-oils from non-catalytic experiments. As shown in the figure, catalytic pyrolysis bio-oils have lower flash points than those from non-catalytic experiments, and are also lower than that of petroleum diesel (58.5 ºC) (Khan et al., 2016). This implies that the catalytic pyrolysis bio-oils obtained in this study are more flammable than petroleum diesel. Therefore, for safety in handling and transportation, increasing the flash points of the bio-oils by removing lighter organic compounds may be necessary.

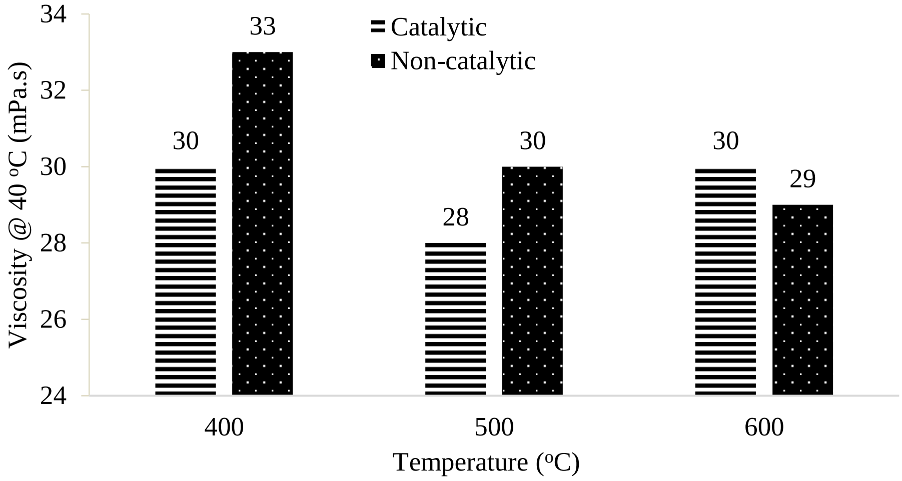


Figure 3:
Comparison of viscosities of bio-oils from catalytic and non-catalytic pyrolysis

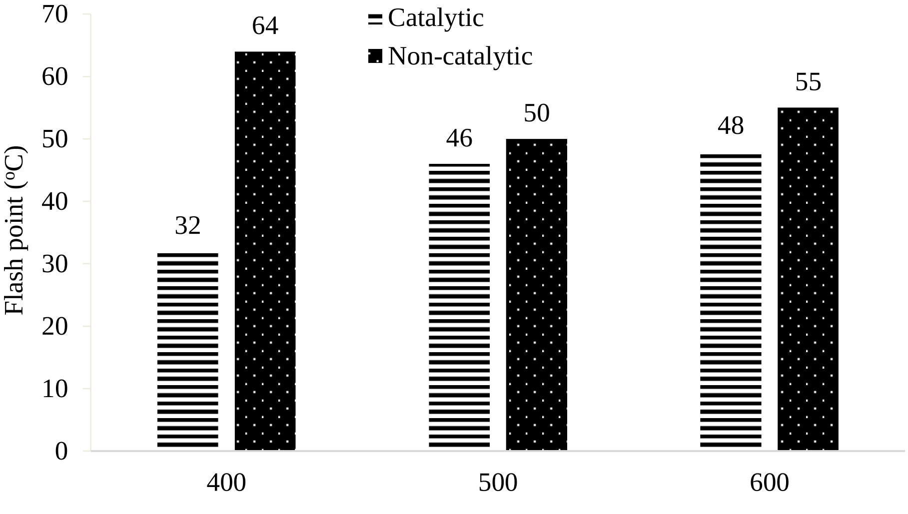


Figure 4:
Comparison of flash points of bio-oils from catalytic and non-catalytic pyrolysis

3.4.4. Pour Point

Figure 5 shows the pour points of catalytic pyrolysis bio-oils compared with those of the non-catalytic pyrolysis bio-oils. As shown in the figure, the presence of catalyst has no effect on the pour point at pyrolysis temperatures of 400 and 600 ºC. At 500 ºC, however, the use of catalyst reduced the pour point of bio-oil from − 25 to − 28 ºC. The pour points of bio-oils from catalytic pyrolysis obtained in this study are lower than those reported by Weerachanchai et al. (2007) (−17 to 1 ºC) and Chukwuneke et al. (2019) (13.5 ºC). Since pour point is the temperature below which a liquid loses its flow characteristics, the bio-oils obtained in this study, therefore, are not suitable for use in extremely cold countries.

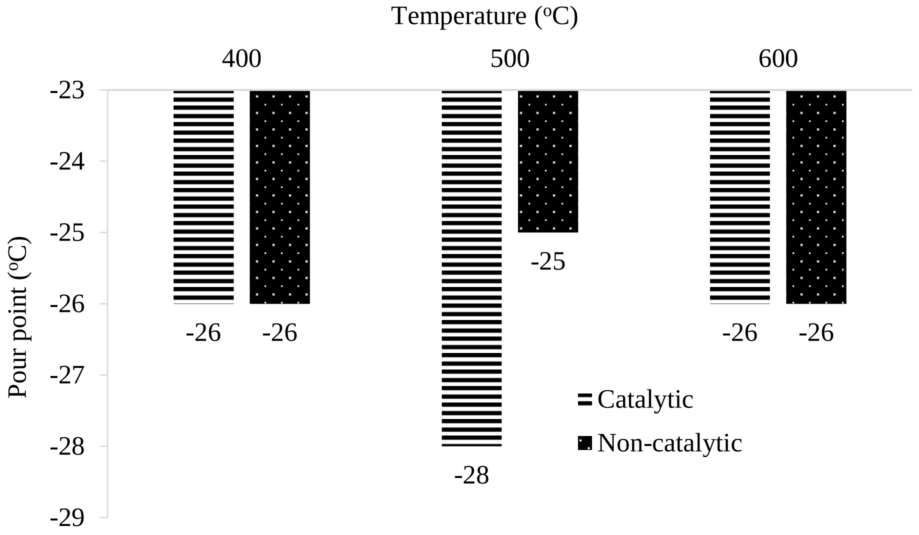


Figure 5:
Comparison of pour points of bio-oils from catalytic and non-catalytic pyrolysis

3.4.5. Moisture Content

Figure 6 shows the comparison of the moisture content of the bio-oils produced by catalytic and non-catalytic pyrolysis. As shown in the figure, the moisture content in catalytic pyrolysis bio-oils was higher at 500 ºC but lower at 400 and 600 ºC than in non-catalytic pyrolysis bio-oils. Shadangi and Mohanty (2014 a & b) reported a higher moisture content in catalytic pyrolysis bio-oils while Zhou et al. (2013) reported a lower value than in non-catalytic pyrolysis bio-oils. Many factors can be responsible for these different observations, including the type of feedstock, the catalyst used, the temperature of pyrolysis as well as the feed to catalyst ratio. In this study, the moisture content of the bio-oils from catalytic and non-catalytic experiments were not significantly different at 400 and 500 ºC. At 600 ºC, however, there was a reduction from 15.8% to 13% with the use of MgO catalyst (b/c ratio of 70/30).

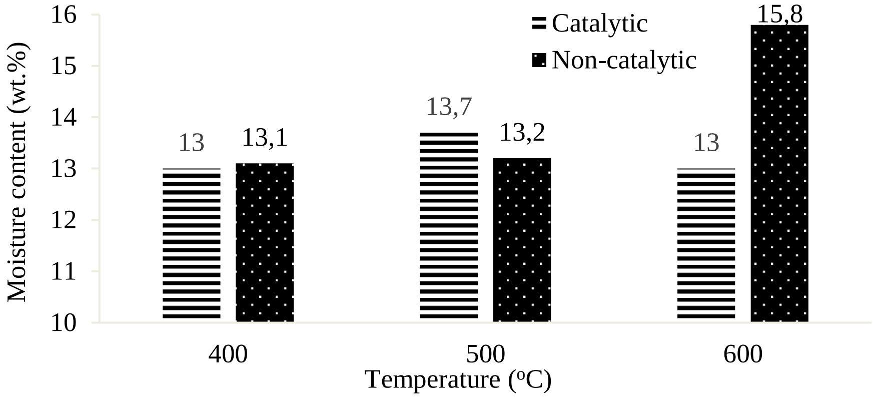


Figure 6:
Comparison of moisture content of bio-oils from catalytic and non-catalytic pyrolysis

3.4.6. Conradson Carbon Residue (CCR)

Figure 7 shows the comparison of the CCR of the bio-oils from catalytic and non-catalytic pyrolysis. Carbon residue is a measure of the coke-forming tendencies of fuel oils. From Figure 7, it is interesting to note that the CCR is the same for all the catalytic pyrolysis bio-oils at all temperatures. This may be due to the fact that the data presented are for the b/c ratios yielding maximum bio-oil at all the temperatures considered. Beisdes, the figure also shows that the CCR for the catalytic pyrolysis bio-oils is lower than the values obtained for non-catalytic pyrolysis bio-oils at 400 and 600 °C. This implies that at these temperatures and b/c ratios for maximum yield of bio-oil, the formation of heavy structures that are difficult to evaporate was reduced. The values of CCR for both catalytic and non-catalytic bio-oils are lower than those reported for other bio-oils (18 – 23 wt.%) (Garcìa-Pèrez et al., 2002) but higher than the values specified for gasoline (≤ 0.2 wt.%) and diesel ((≤ 0.3 wt.%) according to NF EN 590 and NF EN 228, respectively (Anouti et al., 2016). The use of polar solvents can be helpful in extracting complex polar heavy structures, thereby reducing the CCR values of the bio-oils (Anouti et al., 2016).

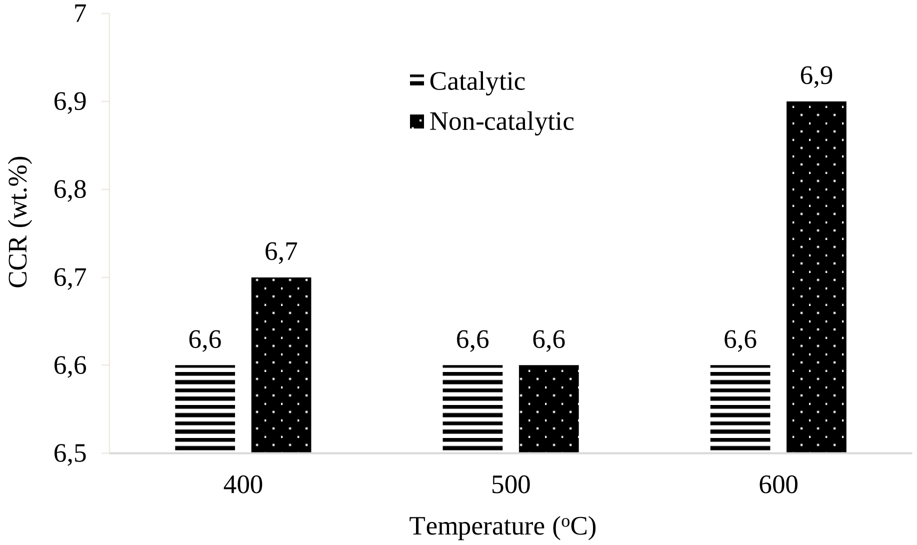


Figure 7:
Comparison of carbon residue of bio-oils from catalytic and non-catalytic pyrolysis

4. CONCLUSION

The fuel properties of bio-oils from catalytic pyrolysis (with MgO as catalyst) of *Tectona grandis* at different temperatures and b/c ratios have been analyzed and compared with those of non-catalytic pyrolysis bio-oils. The maximum yield of bio-oil at 400 (31.53 wt.%), 500 (40.87 wt.%) and 600 ºC (29.30 wt.%) were obtained at b/c ratios of 70/30, 80/20 and 70/30, respectively. Elemental analysis showed that catalytic pyrolysis bio-oils are richer in carbon and hydrogen but leaner in oxygen and sulphur than non-catalytic bio-oils. The calorific values of catalytic pyrolysis bio-oils are therefore higher than those of non-catalytic. The use of MgO as catalyst in pyrolysis improved the fuel properties of bio-oils by reducing their viscosity (at 400 and 500 ºC), carbon residue and moisture content (at 400 and 600 ºC), and increasing pH values (at 400 and 600 ºC) as well as their HHV at all the temperatures considered.

CONFLICT OF INTEREST

Authors approve that to the best of their knowledge, there is not any conflict of interest or common interest with an institution/organization or a person that may affect the review process of the paper

AUTHOR CONTRIBUTION

Pious O. Okekunle determined the concept and/or design the process of the research. Pious O. Okekunle and Oluwapelumi A. Babayemi managed the concept and design process of the research. Emmanuel D. Abodunrin and Olanrewaju M. Daramola handled data collection. Pious O. Okekunle and Akinola D. Ogunsola were responsible for data analysis and interpretation of the results. Pious O. Okekunle, Akinola D. Ogunsola, Oluwapelumi A. Babayemi, Emmanuel D. Abodunrin and Olanrewaju M. Daramola worked on preparation of the manuscript. Pious O. Okekunle handled critical analysis of the intellectual content. Pious O. Okekunle, Akinola D. Ogunsola, Oluwapelumi A. Babayemi, Emmanuel D. Abodunrin and Olanrewaju M. Daramola are responsible for the final approval and full responsibility.

REFERENCES

1. Anouti, S., Haarlemmer, G., Déniel, M. and Roubaud, A. (2016) Analysis of physicochemical properties of bio-oil from hydrothermal liquefaction of blackcurrant pomace, *Energy & Fuels*, 30(1), 398 – 406.

2. Bardalai, M. and Mahanta, D.K. (2015) A review of physical properties of biomass pyrolysis oil, *International Journal of Renewable Energy Research*, 5(1), 277 – 286.

3. Bridgwater, A.V. and Peacocke, G.V.C. (2000) Fast pyrolysis process for biomass, *Renewable and Sustainable Energy Reviews*, 4, 1 – 73.

4. Chukwuneke, J.L., Ewulonu, M.C., Chukwujike, I.C. and Okolie, P.C. (2019) Physico-chemical analysis of pyrolyzed bio-oil from *swietenia macrophylla* (mahogany) wood, *Heliyon*, 5(6), 2019, accessed May 21, 2020, from https://doi.org/10.1016/j.heliyon.2019.e01790.

5. French, R. and Czernik, S. (2010) Catalytic pyrolysis of biomass for biofuels production, *Fuel Processing Technology*, 91, 25 – 32.

6. Garcia-Perez, M., Adams, T.T., Goodrum, J.W., Geller, D.P. and Das, K.C. (2007). Production and fuel properties of pine chip bio-oil/biodiesel blends, *Energy & Fuels*, 21, 2363 – 2372.

7. Garcìa–Pèrez, M., Chaala, A. and Roy, C. (2002) Vacuum pyrolysis of sugarcane bagasse, *Journal of Analytical and Applied Pyrolysis,* (65), 111 – 136.

8. Güllü D. (2003) Effect of catalyst on yield of liquid products from biomass via pyrolysis, *Energy Sources*, 25(8), 753 – 765.

9. Kato, Y. Enomoto, R., Akazawa, M. and Kojima, Y. (2016) Characterization of Japanese cedar bio-oil produced using a bench-scale auger pyrolyzer, *Springer Plus*, 5, 1 – 11.

10. Khan, M.Z.H., Sultana, M., Al-Mamum, M.R. and Hasan, M.R., Pyrolytic waste oil and its diesel blend: fuel characterization, *Journal of Environmental and Public Health*, 2016, accessed May 10, 2020, from https://doi.org/10.1155/2016/7869080.

11. Kraiem, T., Hassen-Trabelsi, A. B., Naoui, S. and Belayouni, H. (2014). Characterization of syngas and bio-char: co-products from pyrolysis of waste fish fats, *The Fifth International Renewable Energy Congress, IREC 2014,* March 25 – 27, Hammamet, Tunisia.

12. Latake, P.T., Pawar, P. and Ranveer, A.C. (2015) The greenhouse effect and its impacts on environment, *International Journal of Innovative Research and Creative Technology*, 1(3), 333 – 337.

13. Lyu, G., Wu, S. and Zhang, H. (2015) Estimation and comparison of bio-oil components from different pyrolysis conditions, *Frontiers in Energy Research*, 3(28), 1 – 11.

14. Mythili, R., Subramanian, P. and Uma, D. (2017) Physicochemical properties of the bio-oil from *Prosopis juliflora* in fluidized-bed reactor, *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 39(8), 843 – 849.

15. Nanda, S., Mohanty, P., Kozinski, J.A. and Dalai, A.K. (2014) Physico-chemical properties of bio-oils from pyrolysis of lignocellulosic biomass with high and slow heating rate, *Energy and Environment Research*, 4(3), 21 – 32.

16. Okekunle, P.O., Itabiyi, O.E., Adetola, S.O., Alayande, I.O., Ogundiran, H.O. and Odeh, K.G. (2016) Biofuel production by pyrolysis of cassava peel in a fixed bed reactor, *International Journal of Energy for a Clean Environment*, 17(1), 57 – 65.

17. Okekunle, P.O., Ogunsola, A.D., Babayemi, O.A., Abodunrin, E.D. and Daramola, O.M. (2021). Fuel characterization of bio-oil from fast pyrolysis of *Tectona grandis* in a fixed bed reactor at different temperatures (400 – 700 ºC), *International Journal of Energy for a Clean Environment*, 22(3), 1 – 14.

18. Onay, Ö. (2014) Effects of catalyst on pyrolysis of Laurel (*Laurus Nobilis L.*) seed in a fixed bed tubular reactor, *Chemical Engineering Transactions*, 37, 127 – 132.

19. Oyebanji, J.A. and Ololade, Z.S. (2017) Fast Pyrolysis of *Tectona grandis* Wood for Bio-oil: Characterization and Bactericidal Potentials, *Global Journal of Researches in Engineering: A Mechanical and Mechanics Engineering*, 17(1), 31 – 37.

20. Pütün, E.(2010) Catalytic pyrolysis of biomass: Effects of pyrolysis temperature, sweeping gas flow rate and MgO catalyst, *Energy*, 35, 2761 – 2766.

21. Pütün, E., Ateş, F. and Pütün, A.E. (2008) Catalytic pyrolysis of biomass in inert and steam atmospheres, *Fuel*, 87, 815 – 824.

22. Qiang, L., Xu-lai, Y. and Xi-feng, Z. (2008) Analysis on chemical and physical properties of bio-oil pyrolyzed from rice husk, *Journal of Analytical and Applied Pyrolysis*, 82, 191 – 198.

23. Samolada, M.C., Papafotica, A. and Vasalos, I.A. (2000) Catalyst evaluation for catalytic biomass pyrolysis, *Energy & Fuels*, 14, 1161 – 1167.

24. Shadangi, K.P. and Mohanty, K. (2014a) Thermal and catalytic pyrolysis of Karanja Seed to produce liquid fuel, *Fuel*, 115, 434 – 442.

25. Shadangi, K.P. and Mohanty, K. (2014b) Production and characterization of pyrolytic oil by catalytic pyrolysis of Niger seed, *Fuel*, 126, 109 – 115.

26. Shah, A., Darr, M.J., Dalluge, D., Medic, D. Webster, K. and Brown, R.C. (2012) Physicochemical properties of bio-oil and biochar produced by fast pyrolysis of stored single-pass corn stover and cobs, *Bioresource Technology*, 125, 348 – 352.

27. Thangalazhy-Gopakumar, S., Adhikari, S., Ravindran, H., Gupta, R.B., Fasina, O., Tu, M. and Fernando, S.D. (2010) Physiochemical properties of bio-oil produced at various temperatures from pine wood using an auger reactor, *Bioresource Technology*, 101, 8389 – 8395.

28. Wang S. (2013) High Efficiency Separation of Bio-oil. In M.D. Matovic (Ed.), *Biomass Now – Sustainable Growth and Use* (pp. 401-418). London: IntechOpen. https://doi.org/10.5772/51423.

29. Weerachanchai, P., Tangsathitkulchai, C. and Tangsathitkulchai, M. (2007) Fuel properties and chemical compositions of bio-oils from biomass pyrolysis, SAE Technical Paper 2001-01-2024, 2007, https://doi.org/10.4271/2007-01-2024.

30. Yu, F., Deng, S., Chen, P., Liu, Y., Wan, Y., Olson, A., Kittleson, D. and Ruan, R. (2007) Physical and chemical properties of bio-oils from microwave pyrolysis of corn stover, *Applied Biochemistry and Biotechnology*, 136 – 140, 957 – 970.

31. Zabeti, M., Nguyen, T.S., Lefferts, L., Heeres, H.J. and Seshan, K. (2012) *In situ* catalytic pyrolysis of lignocellulose using alkali-modified amorphous silica alumina, *Bioresource Technology*, 118, 374 – 381.

32. Zhou, L., Yang, H., Wu, H., Wang, M. and Cheng, D. (2013) Catalytic pyrolysis of rice husk by mixing with zinc oxide: Characterization of bio-oil and its rheological behaviour, *Fuel Processing Technology*, 106, 385 – 391.