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Screening and Evaluation of Biocatalysts from Plant Sources for Trans-esterification Stage of Biodiesel Production

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Abstract: The production of biocatalysts using alternative, cheap and easily accessible plant sources which have the potential of increasing the environmental friendliness of the biodiesel process, was investigated. Four common plant species (*Elaeis guineensis*, *Cocos nucifera*, *Carica papaya* and *Musa paradisiaca*) were investigated. Freshly harvested parts of these species were weighed, dried and burnt to ash. The ash samples were subjected to metal analysis by Atomic Absorption Spectrophotometry (AAS) first as raw ash (5 g of sieved ash for each sample), then as ash leachate (10 mL each). Potash was determined for each sample by evaporating the ash leachate at 60°C with subsequent drying at 110°C. *E. guineensis* fruit bunch recorded the highest ash value of 5.65 kg while the least value of 0.76 kg was observed in *M. paradisiaca.* Potash content increased from 30.67% in *E. guineensis* frond to 53.47% in *M. paradisiaca.* The highest potassium composition in ash of 47650.20 mg kg^{-1} was observed in *M. paradisiaca* while the least value of 4815.2 mg kg^{-1} was recorded in the frond *E. guineensis* (oil palm). The following potassium concentrations were recorded in the leachate in decreasing order: *M. paradisiaca* (4388.37 mg L^{-1}), *C. nucifera* (3662.51 mg L^{-1}), *E. guineensis* bunch (3557.25 mg L^{-1}), *C. papaya* (2781.17 mg L^{-1}) and *E. guineensis* frond (665.56 mg L^{-1}). Pb and Fe were below equipment detection limits in the samples analyzed. The study established that these species are good sources of biocatalysts usable in the trans-esterification stage of biodiesel production. It also provides an alternative platform for the management of plant waste arising from these species.

Key words: Biocatalyst, biodiesel, *Carica papaya*, *Cocos nucifera*, *Elaeis guineensis*, *Musa paradisiaca*, potash, trans-esterification

INTRODUCTION

Trans-esterification of vegetable oils is the most popular method of biodiesel production (Parawira, 2010). It is the reaction of a fat or oil (triglyceride) with an alcohol to form fatty acid alkyl esters, methyl and ethyl esters and glycerol (Demirbas, 2006; Alkabbashi *et al.*, 2009). As an industrial process, trans-esterification is usually carried out by heating an excess of the alcohol with vegetable oils under different reaction conditions in the presence of an inorganic catalyst (Marchetti *et al.*, 2007; Ibeto *et al.*, 2011). The reactions are often catalyzed by an acid, a base or enzyme to improve the reaction rate and yield. Alkali (base) catalyzed transesterification is much faster than acid-catalyzed transesterification and is less corrosive to industrial equipment and therefore, is the most often used commercially (Ranganathan *et al.*, 2008; Agarwal, 2007; Agarwal and Agarwal, 2007; Marchetti *et al.*, 2007; Nahar and Sunny, 2011). The alkali, which are used include sodium hydroxide, potassium hydroxide and carbonates. According to Parawira (2010), catalyst is among the process parameters that affect the yield of biodiesel in the process of transesterification. Apart from recent studies implicating successful transesterification with the direct use of whole cell biocatalyst of intracellular lipases (Kaieda *et al.*, 1999; Matsumoto *et al.*, 2001; Soumanou and Bornscheuer, 2003; Devanesan *et al.*, 2007; Wang *et al.*, 2007), all catalysts used for the process are produced via inorganic synthesis. It is to be noted that the process of catalyzing transesterification using immobilized lipase (enzymatic catalysis) has not been implemented at industrial scale; also as clearly stated by Parawira (2010), the production cost of a lipase catalyst is significantly greater than that of an alkali one. Alkali is produced from potash, which themselves are a fraction of ash (Babayemi *et al.,* 2010a).

Ash is recovered as residue after burning of organic materials (Babayemi *et al.*, 2010a). Wood is a major source of ash and potash from ash of different wood sources has provided means of livelihood and income to both people of old and the present (Campbell, 1990; Taiwo and Osinowo, 2001; Onyegbado *et al.*, 2002; Naik *et al.*, 2003;

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Babayemi and Adewuyi, 2010; Babayemi *et al*., 2010a; Ogundiran *et al*., 2011). Even with the reported uses of potash from wood ash by these authors, most of the reports expressed reservation on the abysmal low conversion of the wood ash to the extractable component alkali, or potash (particularly potassium hydroxide, sodium hydroxide and potassium carbonate), leading to large wood/ash wastes in Nigeria (Babayemi and Dauda, 2009; Babayemi and Adewuyi, 2010).

In this study, the ash and potash yield of different parts of four monocotyledons distributed within three angiosperm families namely *Elaeis guineensis* (Arecaceae), *Carica papaya* (Caricaceae), *Cocos nucifera* (Arecaceae) and *Musa paradisiaca* (Musaceae) were invested. Also investigated are the elements (metals) present in the raw ash for each species. This is a preliminary study towards providing alternative sources of potash (alkali bio-catalyst) for the trans-esterification phase of biodiesel production.

MATERIALS AND METHODS

Plant materials: The plant materials were sourced from Omokiri community in Obio-Akpor Local Government Area of Rivers State, Nigeria (Table 1). The plant materials were harvested in November 2010. The experiments were conducted between November 2010 and May 2011 with facilities in the departments of Plant Science and Biotechnology, Animal and Environmental Biology and Pure and Industrial Chemistry, University of Port Harcourt, Nigeria.

Experimental: Sixty kilogram each (fresh weight) from the different plant parts used for the study were obtained by weighing thrice on a-20 kg capacity weighing scale. The plant materials were subjected to sun drying for 6 to 8 weeks before burning to produce ash. To facilitate drying, the plant materials were chopped into smaller bits. Weights of the different samples were taken after the drying period (dry weight) using the same 20 kg weighing scale. The Moisture Content (MC) for each plant part was deduced from the difference in weights.

Ash content (AC) determination: A known weight (W_1) of each of the samples which has been previously dried to constant weight, was placed in a locally manufactured metal furnace and combusted completely to ashes within 2 h producing mass (W_2) of the ash. The density of the ash was estimated.

Potash content (PC) determination from ash samples: The extraction methods of Kevin (2003) and Adewuyi *et al.* (2008) were adopted with slight modification. In each case, 150 g each of ash was converted to potash (W_3) following the aforementioned methods.

The actual amount of potash from the 150 g of ash was calculated as follows:

- 1.5 L of extract solution contained W_3, then 2 L of extract solution would contain $(W_3{\times}2)/1.5$ g = z (g). Therefore, the percent potash yield is given by $(z/150){\times}100$

Heavy metal (HM_1) determination (ash samples): Five gram of ash from each of the samples was digested with aqua reagents (HCl and HNO_3) in the ratio of 1:2 and heated in a fume hood until transparent solution appeared. At the end of the digestion process, the samples were collected and transferred to the AAS for quantification of each metal.

Heavy metal (HM_2) determination (leachate samples): Five milliliter of the leachate collected from the extraction process of each of the samples was subjected to AAS analysis. The remaining leachate from each of the samples was evaporated at 60°C to remove the water and recover the resulting crystal residue; these were dried at 110°C.

RESULTS AND DISCUSSION

The results obtained for the dry weight, ash and potash contents and other physical characteristics of the different samples are presented in Table 2. From an initial fresh weight of 60 kg each, ash in the range of 0.76 to 5.65 kg was recovered. The significant reduction in weight after burning to ash in all samples implies that controlled wood burning is an efficient management strategy for wood waste. Similar reductions in wood volume and conclusions have been reported Adewuyi *et al.* (2008), Babayemi and Adewuyi (2010), Babayemi *et al.* (2010a) and Ogundiran *et al.* (2011).

Table 1: Plant species used for potash assessment studies

Species name	Common names	Family name	Part(s) used
Elaeis guineensis Jacq.	Oil palm tree	Arecaceae (Palmae)	Frond, fruit bunch, bole
Cocos nucifera L.	Coconut tree	Arecaceae (Palmae)	Frond, bole
Carica papaya L.	Pawpaw	Caricaceae	Stem stump (bole)
Musa paradisiaca L.	Plantain/bananas	Musaceae	Stem stump (bole)

Table 2: Ash and potash contents and other physical characteristics of the plant parts used for the study

Parameters	*E. guineensis* (bunch)	*E. guineensis* (frond)	*C. nucifera* (frond)	*C. papaya*	*M. paradisiaca* (bole)
Dry weight (kg)	23.28±0.330	22.75±0.210	22.05±0.130	8.57±0.020	5.74±0.020
Moisture content (MC)	36.74±0.020	37.12±0.010	37.95±0.020	51.44±0.020	54.32±0.130
Moisture (%)	61.24±0.030	61.86±0.020	63.07±0.380	85.74±0.030	90.53±0.230
Density of samples (kg mL^{-1})	0.63±0.008	0.61±0.005	0.58±0.005	0.17±0.006	0.11±0.005
Weight of ash (kg)	5.65±0.010	1.34±0.020	3.13±0.020	1.15±0.020	0.76±0.010
Ash content (%)	24.16±0.500	5.88±0.110	14.17±0.060	13.43±0.210	13.16±0.240
Weight loss (%)	86.00	87.00	87.00	94.00	76
Weight of potash-W_3 (g)	45.30	34.50	42.75	36.15	60.15
Potash content (%)	40.27	30.67	38.00	32.13	53.47

Table 3: Mean results of metal content of the ash samples

Metal (mg kg^{-1})	*C. nucifera* (frond)	*C. papaya*	*E. guineensis* (frond)	*E. guineensis* (bunch)	*M. paradisiaca*
Ca	10,571.40	7,745.20	21,198.20	11,067.40	7,383.60
K	8,235.80	16,763.60	4,815.20	29,894.00	47,650.20
Na	17,548.00	4,137.80	424.24	530.94	92.16
Mg	6,912.60	3,641.80	7,480.20	7,570.20	309.60
Fe	<0.001	<0.001	<0.001	<0.001	<0.001
Zn	0.09	0.15	0.05	0.14	<0.001
Pb	<0.001	<0.001	<0.001	<0.001	<0.001
Cu	0.36	0.25	0.40	0.33	<0.001

Table 4: Mean results of metal content of the leachate samples

Metal (mg L^{-1})	*C. nucifera* (frond)	*C. papaya*	*E. guineensis* (frond)	*E. guineensis* (bunch)	*M. paradisiaca*
Ca	0.05	0.10	152.58	0.79	0.003
K	10,974.35	6,312.87	359.64	10,350.87	12,945.69
Na	1082.90	30.40	2482.20	1345.30	2607.82
Zn	0.19	0.07	0.12	0.02	0.21
Fe	11.22	0.17	1.56	0.19	3.36
Pb	0.02	0.04	0.02	0.03	0.15
Cu	0.03	0.09	0.05	0.01	<0.001

Thus, this is an effective management strategy for the estimated wood waste of 30, 0643, 230 m^3 generated annually in Nigeria (Babayemi and Dauda, 2009). On the average, ash yield from the samples was in the following decreasing order: 5.65 kg (*E. guineensis* fruit bunch)> 3.13 kg (*C. nucifera*)>1.34 kg (*E. guineensis*)> 1.15 kg (*C. papaya*)> 0.76 kg (*M. paradisiaca*) as shown in Table 2. Low ash yield similar to those obtained in this study have been previously observed for African woody species and their parts (Adewuyi *et al*., 2008; Ogundiran *et al*., 2011). While we observed an average ash content of 13.16% in *M. paradisiaca*, Babayemi *et al.* (2011) specifically reported a range of 6.3 to 12% ash content in some *Musa* species.

Analysis of 150 g ash material for each of the plant samples resulted in relatively good potash yield as shown in Table 2. The decreasing order of potash content in the four species is *M. paradisiaca* (53.47%)>*E. guineensis* fruit bunch (40.27%)>*C. nucifera* frond (38%) > *C. papaya* (32.13%)>*E. guineensis* frond (30.67%). Interestingly *M. paradisiaca* which had the least ash content, possessed the highest concentration of actual potash. This corroborates (Babayemi *et al*., 2010a) which noted that linear relationship between ash and potash contents (i.e., the higher the ash content the more the potash yield) may not always be the case. Comparatively, these results present *M. paradisiaca* as the choice species among the four plants for the purpose of potash production. Babayemi *et al.* (2010b) noted that potash yield is dependent on such factors as type of plant material, the nature of soil that supported the plant and the efficiency of the extraction method used. Differences in results obtained from *E. guineensis* fruit bunch (40.27%) and frond (30.67%) attests to the fact that potash yield/concentration in different plant parts/materials are not the same. Also considering differences in plant material, soil and other environmental variables, the range of 69.0 to 81.9% potash content reported by Babayemi *et al.* (2011) from peels of plantain and banana (both *Musa* species) from western Nigeria is somewhat close to the average potash content of 53.47%, which we observed from the stem of plantain in south-south of Nigeria.

The average concentration of the metal content in ash and leachate from the different samples are presented in Table 3 and 4. The results show that K and Na had the highest values in both the ash and leachate. The highest K values (47,650.20 mg kg^{-1} in ash and 12,945.69 mg L^{-1} in leachate) were both recorded in *M. paradisiaca.* Na in ash was highest in *C. nucifera* frond with an average value of 17,548 mg kg^{-1} and highest in *M. paradisiaca* with 2607.82 mg L^{-1}. Previous studies show that either hydroxides of potassium and sodium (Kuye and Okorie, 1990) or their carbonates (Babayemi *et al*., 2010a) constitute the alkali content of potash. It is however not disputed that potassium and sodium are the main metals that react with carbonates or hydroxides to form potash. Comparing the results obtained from this study with previous studies (Selema and Farago, 1996) recorded 38,600 mg kg^{-1} for K while Babayemi *et al.* (2011) noted high concentrations of K and Na all in *Musa* species, the species we studied are good sources of potash considering the high K and Na values in each case. Ca in ash was highest in *E. guineensis* frond and least in *M. paradisiaca* while Fe, Zn, Pb and Cu were generally low or not detected.

CONCLUSION

The results of this study show that the species (*Elaeis guineensis*, *Cocos nucifera*, *Carica papaya* and *Musa paradisiaca*) are good sources of potash with *M. paradisiaca* topping the list. Controlled burning/incineration of wood wastes from these species is an effective management strategy for part of the estimated wood waste of 30,0643,230 m^3 generated annually in Nigeria; it will also provide the ash convertible to potash needed as biocatalyst in trans-esterification stage of biodiesel production. The environmental friendliness of using potash from renewable sources like those identified in this study outweighs the synthetic or chemically manufactured ones. Potash from these readily available sources also have the potential of reducing the cost of procuring synthetic potash for biodiesel and soap manufacture. Further studies leading to characterizing and determining the purity of the potash arising from this process are ongoing.

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