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Turning *Leucaena leucocephala* bark to biochar for soil application via statistical modelling and optimization technique

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ABSTRACT

Soil applicable biochar has been prepared from bark of *Leucaena leucocephala* wood which is a waste generated during its pulping and papermaking process. The slow pyrolysis process adopted for this purpose has been modelled and optimized employing central composite design and desirability function under response surface methodology taking temperature (308–592 °C) and time (35–205 min) as independent variable while yield, loss on ignition, stable organic matter, oxidisable carbon and carbon liability index as dependent variable. *L. leucocephala* bark was characterized in terms of proximate analysis (moisture 4.90%, ash 7.20%, fixed carbon 18.10%, volatile matter 69.80%), elemental analysis (carbon 45.78%, hydrogen 10.67%, nitrogen 1.77%, oxygen 32.08%, sulphur 0.09%), lignocellulosic composition (holocellulose 45.86%, hemicellulose 15.01%, lignin 34.75%) and compared with a wide range of feedstocks to find its suitability towards biochar production. The optimum pyrolysis temperature and residence time were found to be 350 °C and 60 min respectively which gave biochar yield 53.16%, loss on ignition 88.17%, oxidisable carbon 28.82%, stable organic matter 38.48%, and carbon liability index 0.32. The biochar produced at optimum conditions were characterized by proximate analysis (moisture 0.65%, ash 11.83%, fixed carbon 40.2%, volatile matter 47.57%) and elemental analysis (carbon 62.91%, hydrogen 3.12%, nitrogen 2.65%, oxygen 20.74%, sulphur 0.05%). The O/C ratio of 0.25 and H/C ratio of 0.60 confirmed its life between 100–1000 years and appropriateness for soil application as well as carbon sequestration.

1. Introduction

Debarking is an important unit operation practised in wood based pulp and paper mills for removing bark from the wood logs before processing them for cooking. It is estimated that during this process around 124,000 tons of bark is generated in a pulp and paper mill having 500,000 tons of production capacity per year (Mota et al., 2012). Bark is generally considered as waste and is used for land filling, incineration, wooden panel making, production of bio-oil and low calorific value fuel (Mourant et al., 2013). Recently, Feng et al. (2013) made a state-of-art review on valorisation of bark for various chemicals and materials. These associates found that bark incineration or land filling is detrimental to environment and bark cannot also be considered ultimate for direct energy combustion, for secondary fuel production as well as for bio-ethanol or bio-oil production. These researchers, however, found bark more promising for preparing foams, adhesives and wooden panels though several improvements in process and properties of these materials remain to be made. Another product that can be effectively prepared from bark is biochar for application as a soil amendment in agriculture (Yamato et al., 2006). Production of biochar from wood wastes like bark piling up at pulp and paper mills can open a new market for them to generate additional revenue streams (Hamaguchi et al., 2013).

Biochar is defined as a pyrogenic black recalcitrant organic carbon rich porous material with fine grains and high stability developed from the thermal transformation of lignocellulosic feedstocks within an inert environment (Tang et al., 2013; Sun et al., 2014). Its application as a soil amendment in agriculture provides several ecological and environmental advantages such as enhanced adsorption of water, nutrients, and contaminants; increase in crop yield; and suppression of soil greenhouse gases i.e. CO_2, N_2O and CH_4 emissions (Case, 2013). The physical and chemical properties of a biochar greatly depend on two factors viz. the type of feedstock and production conditions such as pyrolysis temperature and residence time (Pereira et al., 2011). Thus, there are two important aspects from the perspective of biochar production: first, selection of suitable parent material from a

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Table 1
Values of independent variables at different levels of CCD.

Independent variable	Symbol	Levels				
		−1.414	−1	0	+1	+1.414
Pyrolysis temperature (°C)	*T*	308.579	350	450	550	591.421
Residence time (min)	*t*	35.147	60	120	180	204.853

wide range of lignocellulosic feedstocks, comprising wood-based materials, agricultural residues and manures (Singh et al., 2010); and second, critical understanding of crucial production parameters influencing the physicochemical characteristics of biochar (Sun et al., 2014). Further, realizing the benefits of biochar in agriculture, it becomes necessary to devise the easily adoptable and economically feasible technique to produce biochar from common biomass wastes at simple and optimum pyrolysis conditions so that farmers can implement them to prepare biochar on their own (Masto et al., 2013).

Bark, as stated above, is a common biomass waste generated at a wood based pulp and paper mill but studies relating transformation of bark to biochar for soil applications are limited. There are only few researches that describe agricultural application of biochar obtained from bark of some wood based raw materials utilized for pulp and papermaking such as *Acacia mangium* and *Pseudotsuga menziesii* (Yamato et al., 2006; Granatstein et al., 2009). *Leucaena leucocephala* is another raw material for pulp and papermaking (Jiménez et al., 2008) whose bark can be hypothesized for biochar preparation from the point of view of application as soil amendment. Further, understanding of interactions between biochar manufacturing conditions, biochar yield and its characteristics are vital and for this reason, optimization of carbonization conditions for manufacture of biochar with chosen properties is indispensable (Mašek et al., 2013). However, literature review reveals that maximum of investigations have adopted single parameter at a time approach to study and optimize the effect of pyrolysis variables on biochar physicochemical properties. The greatest disadvantage of such time taking and cost intensive approaches are that they cannot quantify the interacting effect among pyrolysis parameters and authenticate the scaling up of the process. But these shortcomings can be addressed with the help of response surface methodology. Response surface methodology is basically an anthology of mathematical and statistical procedures that uses quantitative data to solve multivariate model equation and to determine optimum process conditions through combination of experimental designs with interpolation by polynomial equations in a sequential testing procedure with the advantage of reduced experimental trials, less time consumption, presence of interactions between different variables and efficiency to predict the true optimum (Myers and Montgomery, 2002; Fang et al., 2010; Zu et al., 2013).

Hence, the aim of this work is to suggest a new biomass waste from pulp and paper sector i.e. *L. leucocephala* bark for biochar preparation as soil amendment through easily adoptable and economically feasible technique, and to provide the best optimum conditions of pyrolysis through the application of response surface technique for this purpose. The main objective behind using this statistical modelling and optimization technique is to identify and understand interaction among parameters affecting biochar manufacturing which is rarely reported. To the best of our knowledge, there is no report available in the literature related to the preparation of biochar from *L. leucocephala* bark and the application of response surface methodology for modelling and optimization of biochar preparation for soil application. A detailed comparison of physico-chemical properties of *L. leucocephala* bark and biochar with those reported in the literature has also been presented in order to evaluate the quality of this feedstock and its biochar for soil application.

2. Materials and methods

2.1. Feedstock collection and biochar production

The bark portion of *L. leucocephala* wood was removed manually from the fresh cut trunks to be utilized for pulping at Physical Chemistry, Pulping and Bleaching Division of Central Pulp and Paper Research Institute, Himmat Nagar, Saharanpur 247001, Uttar Pradesh, India. The bark was smooth, light to brownish gray in color, and contained several lenticels on its outer surface. The bark was chipped into pieces of 2–3 cm size and then sun and air dried for couple of days. Some quantity of bark samples were converted into dust having mesh size 40 using the laboratory dust making machine for determining their proximate, elemental and

Table 2
Elemental analysis of *Leucaena leucocephala* bark – comparison with other raw materials used to prepare biochar in literature.

Feedstock	C	H	N	O	O/C[a]	H/C[a]	Reference
Leucaena leucocephala bark	45.78	10.67	1.77	32.08	0.53	2.80	Present work
Hickory wood	45.51	6.17	0.15	47.83	0.79	1.63	Sun et al. (2014)
Bagasse	45.82	6.25	0.36	47.18	0.77	1.64	Sun et al. (2014)
Bamboo	46.52	6.11	0.20	46.89	0.76	1.58	Sun et al. (2014)
Conocarpus wastes	44.96	5.41	0.62	45.82	0.76	1.44	Al-Wabel et al. (2013)
Cocopeat	61.57	4.37	1.02	33.04	0.40	0.85	Lee et al. (2013a)
Paddy straw	48.75	5.98	1.99	43.28	0.67	1.47	Lee et al. (2013a)
Palm kernel shell	55.82	5.62	0.84	37.73	0.51	1.21	Lee et al. (2013a)
Maesopsis eminii stem	50.52	5.81	0.23	43.44	0.64	1.38	Lee et al. (2013a)
Maesopsis eminii bark	53.42	6.12	1.40	39.06	0.55	1.37	Lee et al. (2013a)
Miscanthus	46.34	5.88	0.31	47.62	0.77	1.52	Mimmo et al. (2014)
Rape	44.70	5.80	0.80	48.10	0.81	1.56	Sánchez et al. (2009)
Sunflower	43.60	5.80	1.00	49.03	0.84	1.60	Sánchez et al. (2009)
Mallee bark	52.50	5.60	0.20	41.60	0.59	1.28	Mourant et al. (2013)
Pinus rigida	48.80	6.00	0.20	45.00	0.69	1.48	Kim et al. (2012)
Amur silver grass	47.60	5.50	0.80	46.10	0.73	1.39	Lee et al. (2013b)
Mangrove wood	44.09	5.06	0.28	50.00	0.85	1.38	Zailani et al. (2013)
Switch grass	43.20	6.20	0.47	44.00	0.76	1.72	Sadaka et al. (2014)
Pinus radiata bark	48.70	6.39	0.28	46.10	0.71	1.57	Hina (2013)
Eucalyptus cinerea bark	45.80	6.55	0.33	48.20	0.79	1.72	Hina (2013)

C, carbon (%); H, hydrogen (%); N, nitrogen (%); O, oxygen (%).
[a] O/C and H/C molar ratio calculated in this work.