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Conversion of Rice Straw to Biochar Through Microwave Pyrolysis for its Use as Partial Replacement of Cement

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ABSTRACT

Background: An experimental study was conducted to explore the feasibility of partially substituting biochar in cement, for making concrete mixture in civil infrastructures. The biochar was derived from the pyrolysis process in thermo-chemical conversion of the most under-utilized agricultural residue *i.e.* rice straw. Demand of cement is increasing day by day due to fast growth of construction sector all around the world. The current scenario of rampant on-farm burning of rice straw is a great concern not only for maintaining the fertility aspects of the cultivating land but also for the degradation of surrounding environment. Production of cement is equally very energy intensive and contributes a lot in emitting greenhouse gases, mostly carbon dioxide to the environment. An attempt was therefore made in the present study to partially replace the rice straw biochar with cement to reduce the production of the later and to evaluate the key performance parameters of biochar based concrete.

Methods: The study was carried out in the Department of Agricultural Structures, Civil and Environmental Engineering, Odisha University of Agriculture and Technology, Bhubaneswar, Odisha, India during 2021-22. Microwave assisted pyrolysis was followed for quick and efficient heating of the biomass feedstock. Efforts was also made to supply power to the microwave pyrolyser from a reliable source of power *i.e.* solar photovoltaic system for its popularization even in remote and off-grid rural areas.

Result: The yield of biochar was found to be higher (about 28%) at 600 W input power to the microwave reactor and 15 minutes' reaction time in the pyrolysis process of rice straw. The performance parameters of biochar based concrete such as initial setting times, final setting times and workability were found to be decreased by 8, 5 and 9% respectively and compressive, split tensile and flexural strengths were increased by 13, 18 and 5% respectively compared to the reference concrete. Biochar from rice straw can hence ultimately be utilized as partial replacement of cement for use in construction industry.

Key words: Biochar, Carbon sequestration, Concrete, Microwave pyrolysis, Rice straw, Thermo-chemical conversion of biomass.

INTRODUCTION

Valorisation of some of the surplus, unutilized as well as underutilized lignocellulosic biomasses in general and agro-residues (Rice straw, wheat straw, corn stover, corn cobs, green coconut shell, jute stick, pulses stalk, groundnut shell, millet straw *etc.*) in particular, into biofuels (biochar, wood vinegar and syngas) through a simple, affordable, user-friendly and environment-friendly practice by their microwave assisted pyrolysis in a small scale production system, is the need of the hour for suitability of the resource poor crop growers (Fodah *et al*., 2021). Pyrolysis of biomass is usually followed in thermo-chemical conversion process and was carried out for the heating of the feedstock in the absence of oxygen for its thermal decomposition to various chemical compounds (Ates *et al*., 2008). Microwave assisted pyrolysis (MAP) is a new approach and an emerging area of research for undertaking pyrolysis process with a view to save time, energy, achieving higher heating performance, precise control over the process and higher yield of desired pyrolytic products compared to the conventional pyrolysis (Menéndez *et al.,* 2010). This may be one of the sustainable approaches not only for the safe disposal of surplus agricultural residues and to prevent the growing concern of on-farm burning of crop residues (Jain *et al.,* 2014) and improper dumping of other agro residues here and there, leading to adverse effects on the environment (Bhuvaneshwari *et al.,* 2019), but also to enhance the livelihood avenues of the users by earning income from the value added and useful pyrolytic products, having high commercial values in agricultural, industrial and domestic sectors. Very limited works have been carried out till date by the researchers at national level on microwave assisted pyrolysis of agro-residues and also the potential supplementary use of biochar with the cement (Gupta *et al.,* 2018). Hence, MAP of the most under-utilized biomass *i.e.* rice straw has been tried to derive biochar for its feasibility as a supplementary material for cement. Higher yield of the biochar has been focussed in the present study by conducting experiments with the suitable microwave

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power, reaction time and heating rate in the microwave pyrolysis process. Higher yield of biochar from the rice straw is desired for its use as a supplementary material with cement in making concrete mixtures. Studies on the yield of the other biofuels such as bio-oil and syngas from the same experimental set up have been overlooked for their analysis in the present research work, though these two fuels have been collected. Biochar, a solid biofuel, having higher carbon content, can be obtained from the slow pyrolysis process (Halim and Swithenbank, 2016).

In India, rice is a major food grain crop with the cultivated area of about 43.95 million hectares and annual total production of about 106.54 million tonnes (Anonymous, 2016). Approximately the annual production of rice straw in our country is 160 million tonnes in a ratio of grain to straw as 1:1.5 (Nokala *et al.,* 2019). Pyrolysis has been proved to be the promising conversion route for both soft and hard organic materials to derive useful products such as biochar, pyro-oil and syngas (Czernik and Bridgwater, 2004). Moreover, use of biochar in concrete mixture also ensures higher waste recycling, effective disposal of agro-residues and carbon sequestration in civil infrastructure besides improving strength and durability of the structures (Riera *et al.,* 2020).

The use of biochar for carbon sequestration and soil amendment (Fig 1) is an established fact (Aleksandra *et al.,* 2022). Efforts are being continued among the researchers for other effective applications of biochar, particularly in civil infrastructures such as carbon sequestration due to the decreased use of cement, additive in concrete for construction work, increased mechanical strength, reduced permeability of water and autogenous shrinkages *etc*. (Riera *et al.,* 2020).

In conventional pyrolysis, either electrical energy or heat energy is used for burning of the biomass. The heat energy in this process, is transferred from outside to the feedstock inside the reactor through convection, conduction and then by radiation causing its losses in the way of transference. On the contrary, in Microwave Assisted Pyrolysis (MAP), microwave penetrates directly into the feedstock through the transparent reactor (usually a quart reactor) without any loss of energy and the entering radiation after striking and absorption is then transformed into thermal energy in the feedstock particle (Mutsengerere *et al.,* 2019). The microwaves are the electromagnetic radiations whose frequencies range from 300 MHZ (wavelength 1m) to 300 GHZ (wavelength 1 mm) (Haque, 1999). The heating mechanism in MAP is therefore a type of energy conversion rather than transfer of heat.

One difficulty however, commonly encountered during MAP is the low capacity in absorption of microwave by the biomass feedstock as it has poor dielectric properties Ferrera-Lorenzo *et al.* (2014) causing the necessity of addition of microwave receptor for maximizing heating efficiency and better yield of the products. One such easily and conveniently available receptor is the biochar which may be obtained from the same pyrolyser without any additional cost involvement.

Hence, the objectives of the present study are to follow the MAP for carrying out pyrolysis process in order to derive higher yield of biochar from rice straw and to explore its feasibility for use as a supplementary cementitious material in concrete making. This would ultimately accomplish the effective disposal of rice straw to prevent on-farm burning and to save the environment.

MATERIALS AND METHODS

Feedstock preparation

Rice straw (*Oryza sativa*) was considered as the biomass feedstock for its pyrolysis in the present study. The locally available variety *i.e.* Lalata, a semi-dwarf and medium duration rice crop, cultivated widely in Odisha was collected. The collected rice straw was initially washed with tap water for removing dust, soil or any other unwanted material stick to it during harvesting and transportation work. The straw was then naturally dried in the open air in order to reduce

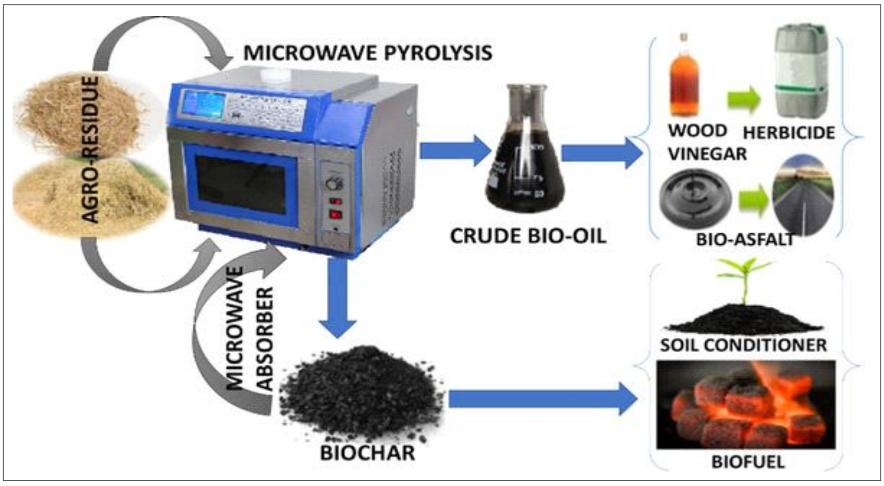


Fig 1: Biochar applications in agricultural sector.

the moisture content to about 10%. The dried straw was finally shredded into small pieces and sieved in 3/8 mesh screen to make the size of the feedstock particle to about 10 mm. No pre-treatment was done with the straw.

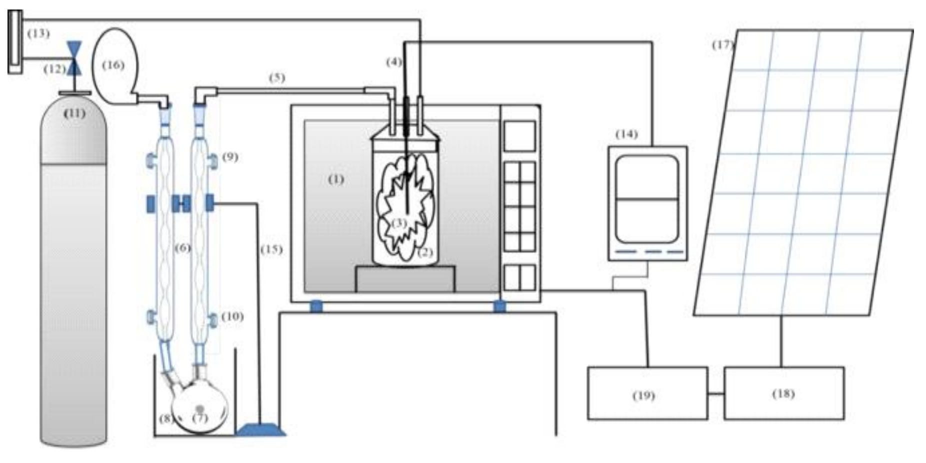
Experimental set up

A domestic microwave oven (model LG, 28 L convection type), available commercially was modified to suit for the incorporation of thermocouple, condensing system, entry of nitrogen gas into the reactor by nitrogen cylinder and pyrolytic gas exit unit. The power supply to the microwave reactor varied from 300-1200 W according to the attainment of suitable temperature ranges for slow pyrolysis to occur with a view to the higher yield of biochar and microwave radiation frequency was of 2.45 GHz. Quartz reactor which is transparent to the microwave radiation was used inside the oven where feedstock was kept for its thermo-chemical conversion. The dimensions of the used quartz reactor were of 19 cm in height and 14 cm in diameter. The nitrogen gas with a purity of 99.9% was allowed to enter into the reactor for about 4-5 minutes before starting the experiment in order to create an inert atmosphere inside the reactor and to avoid the burning of the biomass feedstock when exposed to high temperature during pyrolysis process. A temperature controller with digital display unit was connected with the thermocouple in order to show and record the changes of temperatures occurring inside the reactor during experimentations. The condensing system was consisted of two-stage condensers, quenched with the supply of normal water of about 20-25°C for its circulation in converting the condensing vapour to bio-oil. The non-condensable vapour was collected in a tedlar bag to know its yield but not for analysis purpose. Similar was also in case of bio-oil. The power required for operating the microwave reactor was supplied from solar photovoltaic system. The schematic diagram of solar powered microwave assisted pyrolysis system for the present study is shown in Fig 2.

Biochar, as a microwave absorption enhancer, was mixed with the feedstock before placing in the reactor and its percentage was taken to be 5 % with respect to the weight of the input feedstock as per findings of previous researchers. For each batch of experiment, 450 g of shredded and sieved rice straw was kept in the quartz reactor. The reaction times during the pyrolysis process were varied from 15-20 minutes and power supply was at 700 W microwave power. The power supply was cut off to the reactor after attaining the above time duration. Self-cooling was allowed for the product remaining in the reactor after pyrolysis process was over. After about 3 hours, the cooled product *i.e.* biochar was collected from the reactor, grinded into finer particles and stored in the air tight polythene bag for future use as a cementitious material. The percentage of biochar obtained after pyrolysis was about 30% of the input feedstock.

Preliminary studies undertaken

The quality and quantity of pyrolysis products depend significantly on the various operating parameters such as size of biomass feedstock, effects of nitrogen gas flow rate into microwave reactor, types and amount of microwave absorbers, input power, heating rate and residence time. The sizes of the feedstock and nitrogen gas flow rate were decided as per the previous studies of the researchers and were kept fixed for the present study. The size of rice straw at about 10 mm (Ravikumar *et al*., 2017, Mutsengerere



1- Microwave chamber	6- Condensers	11- Nitrogen cylinder	16- Gas bag
2- Quartz reactor	7- Bio-oil collection	12- Regulator	17- Solar PV module
3- Biomass sample	8- Water bath	13- Nitrogen flow meter	18- Battery
4 Thermocouple	9- Water inlet	14- Temperature controller	19- Inverter
5- Glass connection	10- Water outlet	15- Holder	

Fig 2: Schematic diagram of the experimental set-up with PV system.

et al., 2019) and nitrogen gas flow rate at 50 ml/min (Huang *et al*., 2013; Huang *et al*., 2015) were kept constant all through the experiments. Biochar (5% of the weight of the feedstock) was considered as an additive due to its low cost and easy availability among the users. Heating rate generally varies linearly with the level of input power. Hence the levels of input power to the microwave oven and the residence time for the pyrolysis process were considered to be the two important factors for the yield of the pyrolytic products during microwave pyrolysis. Preliminary studies were therefore carried out to decide the input power levels and reaction times for better yield of biochar before undertaking the final set of experiments for the study. In the present study, the five different microwave power levels (600 W, 700 W, 800 W, 900 W and 1000 W) and five different reaction times (5 min, 10 min, 15 min, 20 min and 25 min) were considered for their optimization with a view to obtain the higher yield of biochar. All the experiments were carried out in triplicate to ensure the good reproducibility of the experimental results. From the experimental investigations, the input power level and reaction time were respectively found to be 600 W and 15 minutes for higher yield of biochar i.e. about 28 per cent. The biochar obtained with 600 W input power level and 15 minutes' reaction time was used for partial replacement of cement for further experimental investigations.

Composition analysis of cement and rice straw biochar using XRF analyser (IS: 12803: 1989)

XRF (X-ray fluorescence) analyser was used to study the composition of cement and biochar based cement. The facility of XRF analyser was availed in the Institute of Minerals and Materials Technology, (IMMT), Bhubaneswar, Odisha. XRF (X-ray fluorescence) is a non-destructive analytical technique used to determine the elemental composition of materials. XRF analyzer determines the chemistry of a sample by measuring the fluorescent (or secondary) X-ray emitted from a sample when it is excited by a primary X-ray source. Several techniques have been used for chemical analysis of cement, however, X-ray fluorescence (XRF) is the most popular technique used today. Because of its accuracy and simplicity of procedures, XRF is used by several researchers (Elbagermia *et al.,* 2014) and (Bediako and Amankwah, 2015). In this method, about 10 g of each cement sample was mixed with boric acid in 10: 1 ratio and then the mixture was milled in a milling machine for two minutes with 800 rpm to produce a homogeneous mixture. The sample was placed in dice and pressed by a briquetting press machine for one minute and then transferred to the X-ray fluorescence analyzer for analysis, following IS 12803: 1989.

Concrete preparation

The reference concrete for the present investigation was prepared from cement, sand, coarse aggregates and water without any admixture. The aim of the study was to partially replace the cement with a supplementary cementing material i.e. biochar from rice straw. The proportion of the ingredients was estimated for preparing M 30 concrete with OPC 53 grade cement. This was considered as a reference material following IS 10262-2009. The cement: sand: aggregates ratios in the study were 1:1.4:2.2 and water cement ratio (W/C) = 0.4, following the IS code. To investigate the properties of the concrete that were used for casting the specimens, various laboratory tests were performed following the related IS codes. Literatures reveal that the performance of biochar based concrete is improved compared to the reference one with the same water cement ratio by replacing less than 10% of the biochar with the cement and beyond that, the quality of concrete is decreased due to dilution effect *i.e*. production of less carbon silicate hydrate (C-S-H) gel, a hardening material in the concrete (Akinyemi *et al.,* 2020). Hence, in this study, the percentage of biochar, added with the cement was taken to be 5% with respect to the weight of the cement. The parameters studied were setting times and workability for fresh concrete and mechanical strengths (Compressive, split tensile and flexural strength) for the hardened concrete.

Performance assessment of concrete

(i) Setting time

Setting is defined as the onset of rigidity in fresh concrete. Setting precedes hardening. Initial setting time is the time elapsed between the moments that the water is added to the cement, to the time that the paste starts losing its plasticity. The final setting time is the time elapsed between the moment the water is added to the cement and the time when the paste has completely lost its plasticity and has attained sufficient firmness to resist certain definite pressure.

(ii) Workability

Workability refers to the property of fresh concrete and it indicates how easily the concrete can be handled and placed in the constructing structures with the ability for concrete to remain a stable, coherent, homogeneous mass during handling and vibration without the constituents segregating.

(iii) Strength

Compressive strength is the ability of material or structure to carry the loads under compression on its surface without any crack or deflection. A material under compression tends to reduce the size, while in tension, size elongates. The maximum compression that concrete bears without failure is noted. Split tensile strength is used in the design of structural light weight concrete members to evaluate the shear resistance provided by concrete. Flexural strength is one measure of the tensile strength of concrete. It is a measure of an unreinforced concrete beam to resist failure in bending.

RESULTS AND DISCUSSION

The focus of the present research work was to identify the influence of biochar on the fresh and hardened concrete by directly mixing it with the cement when additional water demand of the biochar particles was not taken into account

Table 1: Chemical composition of used cement and rice straw biochar.

Chemical composition	Cement (OPC)	Rice straw biochar
SiO_2	21.5	49.2
Al_2O_3	5.2	-
Fe_2O_3	3.5	0.79
CaO	65.4	6.58
MgO	1.2	4.91
SO_3	2.7	5.31
Na_2O	0.2	1.37
K_2O	0.2	20.2

Table 2: Comparative findings of biochar (5%) based concrete with reference concrete.

Properties	Reference concrete (Mean value)	Concrete with 5% biochar (Mean value)	% age change with reference
Initial setting time (min)	59	54	(-) 8.47
Final setting time (min)	207	195	(-) 5.79
Slump (mm)	98.71	89.45	(-) 9.38
Compressive strength (N/mm^2) 28 days	43.08	48.78	(+) 13.23
Split tensile strength (N/mm^2) 28 days	3.96	4.69	(+) 18.43
Flexural strength (N/mm^2) 28 days	8.51	8.96	(+) 5.28

and biochar was added with partial replacement of cement. Biochar tends to absorb and hold a significant part of mixing water, thus resulting into a stiffer mix. The physically absorbed water in biochar is later released during the hardening of concrete and can contribute to internal curing of the mixtures. Biochar has no cementitious property of its own but when finely ground and in the presence of moisture, it chemically reacts at ordinary temperatures with Ca $(OH)_2$, a hydration product of cement, to form compounds having cementitious characteristics. Chemical composition of used cement and rice straw biochar was analysed in Odisha University of Agriculture and Technology, Bhubaneswar, Odisha and is presented in Table 1. The performance of the biochar based concrete was also studied compared to the reference one and is presented in Table 2.

From the above Table 1, it is evident that the rice straw biochar contains more percentage of SiO_2 (49.2%) compared to 21.5% in case of OPC, causing it to facilitate and enhance the secondary hydration reaction for production of C-S-H, the hardening product.

From the above Table 2, it is revealed that the setting times and workability of concrete were decreased and the mechanical strengths were increased. The incorporation of biochar resulted into decrease of setting (Initial and final) times. This may be attributed to the improvement in the cohesiveness of concrete mixture because of the filler effect of the biochar and reduction in the availability of free water. Due to this, the hydration reaction is accelerated and setting times are decreased.

Biochar is porous in nature and due to this; it absorbs and retains water in its pores causing less availability of water for easy flowability and thus low workability of the concrete mixture. Similarly, due to absorption water in the pores of the biochar, it acts as internal curing agent resulting into the acceleration of hydration reaction and thus improvement in the mechanical strengths of the concrete compared to the reference one. Hence, biochar may be used as a supplementary cementitious material without much difference in the performance of biochar based concrete compared to the reference one.

CONCLUSION

The following conclusions are inferred from the present research work.

(i) Waste to useful products can be derived by valorising underutilized rice straw into biofuels (biochar, bio-oil and syngas) through microwave pyrolysis.

(ii) The higher yield of biochar was obtained to be about 28 per cent in 600 W input power to the microwave reactor and 15 minutes' reaction time during pyrolysis process of rice straw compared to the other operating conditions of power level and reaction time.

(iii) The performance parameters of biochar based concrete such as initial setting times, final setting times and workability were found to be decreased by 8, 5 and 9% respectively and compressive, split tensile and flexural strengths were increased by 13, 18 and 5% respectively compared to the reference concrete.

(iv) Biochar can therefore be used as a cementitious material by replacing partially with the cement for making concrete mixture in the construction sector.

(v) The practice of microwave assisted pyrolysis of surplus agricultural residues would accomplish their safe disposal and produce biofuels of high commercial and industrial values with a scope of income generating approaches even in a small scale.

(vi) The promotion of the practice would reduce on-farm burning of rice straw among the growers if encouraged, thus prevent air pollution.

It is thus required to have wide and extensive research in future on rice straw (one of the most abundantly available biomasses) biochar for its higher yield through Microwave Assisted Pyrolysis (MAP) technique and possibility of taking up the practice in a very large scale for its feasibility as cementitious material with cement replacement in concrete.

Conflict of interest

The authors declare that there is no conflict of interest in this study.

REFERENCES

Akinyemi, Banjo A. and Adesina, A. (2020). Recent advancement in the use of biochar for cementitious applications: A review. Journal of Building Engineering. 32(2020): 101705. https://doi.org/10.1016/j.jobe.2020.101705.

Aleksandra, R., Krasucka, P., Oleszczuk, P. (2022). Sustainable biochar-based soil fertilizers and amendments as a new trend in biochar research. Science of The Total Environment. 816(2022): 151588. https://doi.org/10.1016/j.scitotenv.2021.151588.

Anonymous, (2016). Agricultural Statistics, Govt. of India, New Delhi.

Ates, F. and Isıkdag, M.A. (2008). Evaluation of the role of the pyrolysis temperature in straw biomass samples and characterization of the oils by GC/MS. Energy and Fuels. 21: 22(3): 1936-43.

Bediako, M. and Amankwah, E.O. (2015). Analysis of chemical composition of portland cement in Ghana: A key to understand the behaviour of cement. Advances in Materials Science and Engineering. 21: 32-41.

Bhuvaneshwari, S., Hettiarachchi, H., Jay, N.M. (2019). Crop residue burning in India: Policy challenges and potential solutions. Int. J. Environ. Res. Public Health. 16(832): doi: 10.3390/ijerph16050832.

Czernik, S. and Bridgwater, A.V. (2004). Overview of applications of biomass fast pyrolysis oil. Energy and Fuels. 18: 590-598.

Elbagermia, M.A., Alajtala, A.I., Alkerzab, M. (2014). Chemical analysis of available portland cement in libyan market using X-Ray fluorescence. International Journal of Chemical and Molecular Engineering. 8(1): 212-225.

Ferrera-Lorenzo, N., Fuente, E., Bermúdez, J.M., Suárez-Ruiz, I., Ruiz, B. (2014). Conventional and microwave pyrolysis of a macroalgae waste from the agar-agar industry. Prospects for Bio-fuel Production Bioresource Technology. 151: 199-206.

Fodah, A.E.M., Ghosal, M.K., Behera, D. (2021). Microwave assisted pyrolysis of agricultural residues: Current scenario, challenges and future direction. Int. J. Environ. Sci. Technol. 19(3): 2195-2220. https://doi.org/10.1007/s13762-020-03099-9.

Gupta, S., HarnWei, K., Koh, H.J. (2018). Application of biochar from food and wood waste as green admixture for cement mortar. Science of the Total Environment. 619-620: 419-435.

Halim, SA. And Swithenbank, J. (2016). Characterisation of Malaysian wood pellets and rubber wood using slow pyrolysis and microwave technology. J. Anal Appl Pyrol. 122: 64-75.

Haque, KE. (1999). Microwave energy for mineral treatment processes-A brief review. Int J. Min Process. 57: 1-24.

Huang, Y.F., Kuan, W.H., Chang, C.C., Tzou, Y.M. (2013). Catalytic and atmospheric effects on microwave pyrolysis of corn stover. Bioresource Technology. 131: 274-280.

Huang, Y.F., Chiueh, P.T., Kuan, W.H., Lo, S.L. (2015). Effects of lignocellulosic composition and microwave power level on the gaseous product of microwave pyrolysis. Energy. 89: 974-981.

Jain, N., Bhatia, A., Pathak, H. (2014). Emission of air pollutants from crop residue burning in India. Aerosol and Air Quality Research. 14: 422-430.

Menéndez, J.A., Arenillas, A., Fidalgo, B., Fernández, Y., Zubizarreta, L., Calvo, E.G., Bermúdez, J.M. (2010). Microwave heating processes involving carbon materials. Fuel Processing Technology. 91: 1-8.

Mutsengerere, S., Chihobo, C.H., Musademba, D. and Nhapi, I. (2019). A review of operating parameters affecting bio-oil yield in microwave pyrolysis of lignocellulosic biomass. Renewable and Sustainable Energy Reviews. 104: 328-336.

Nokala, M., Kumar, M.T., Sagar, M., Rahul, A. (2019). Performance of traditional rice (*Oryza sativa* L.) varieties under system of rice intensification during *kharif* season in South Odisha conditions. International Journal of Agriculture, Environment and Biotechnology Citation: IJAEB. 12(3): 287-292.

Ravikumar, C., Kumar, P.S., Subhashni, S.K., Tejaswini, P.V., Varshini, V. (2017). Microwave assisted fast pyrolysis of corn cob, corn stover, saw dust and rice straw: Experimental investigation on bio-oil yield and high heating values. Sustainable Materials and Technologies. 11: 19-27.

Riera, D., Restuccia, L.S., Ferro, G.A. (2020). The use of biochar to reduce the carbon footprint of cement-based materials. Procedia Structural Integrity. 26: 199-210.