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USE OF AGRICULTURAL RESIDUES BASED BIOCHAR AS SELF-CURING AND CARBON SEQUESTERING ADMIXTURE IN CEMENTITIOUS COMPOSITES: A REVIEW

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ABSTRACT

This article focusses on the possible applications of biochar in the concrete mixture from strength, durability, sustainable cementitious material, waste disposal and carbon sequestration points of view. The yield of the biochar has been reviewed only from the agricultural residues which are plentifully available and are mostly unutilized in agricultural based countries causing severe environmental problems. The findings of the studies undertaken by the various researchers reveal that there is a potential of improving strength, durability, enhancing internal curing activity, reduced permeability, decreased autogenous shrinkage etc. in concrete and sequestering carbon in civil infrastructures, if biochar is used as admixture in cementitiousmaterials. Based on the studies, it is inferred that the biochar would be the future potential cementitious material in construction industry to solve many problems related to self-curing activity, high performance concrete, environment and waste management.

KEY WORDS : Concrete, Biochar, Agricultural residues, Pyrolysis, Carbon sequestration, Wastemanagement

INTRODUCTION

Proper curing of concrete is an essential activity to obtain high performance of civil infrastructure in terms of increasing strength, reducing autogenous shrinkage and cracking, decreasing permeability and enhancing durability. Hence, high performance concrete is a growing area of research in construction industry to achieve longer life span and corrosion, abrasion as well as impact protection of the civil structures compared to conventional concrete mix. One of the approaches in high performance concrete is to include self-curing agents in the cementitious composites. Self-curing or internal curing agents provide required moisture internally to the concrete mixture thus facilitating hydration even after discontinuance of the conventional methods of curing. Generally, two ways such as use of light weight aggregates and addition of chemical curing admixtures are being followed in the construction industry to fulfil the purpose of high performance concrete. Among the light weight aggregates, use of biomass-derived biochar is nowadays gaining increasing importance among the researchers due to its high porosity and surface area in improving the performance of concrete mix along with the sustainable and cost effective way of producing from the abundantly and locally available underutilized agricultural residues through thermo-chemical conversion path. India being an agricultural based country produces enormous quantities of agricultural residues throughout the year. There are several ways to convert agricultural residues/organic wastes to bio-char and biofuel (i.e. gasification, fermentation, combustion, extraction, liquefaction, digestion, enzymatic conversion and chemical conversion), however, 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.

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 (Fig. 1). This paper discusses the studies undertaken by the researchers in recent past on the feasibility of using biochar obtained from the agricultural residues as a sustainable alternative material to sand/cement in concrete admixture.

Production of biochar from agricultural residues through Pyrolysis

Biochar is a carbon (C) rich material produced by thermal decomposition of biomass in the absence of oxygen or air through the process called pyrolysis, occurred at the elevated temperatures usually ranging from 450 to 550 °C (Khalid *et al*., 2018). Biochar consists of interconnected fibers, forming a microporous cellular structure that can absorband sustain a substantial amount of water to be used for internal curing. Heat needed for endothermic pyrolysis reaction is usually provided by direct heating or indirect heating through electrical energy, flue gas from burning of wood and agro-residues or under partial combustion. Microwave assisted pyrolysis (MAP) has been demonstrated as a promisingalternative to conventional pyrolysis in the past decades, mainly because of its fast heating rate, selective heating, volumetric and uniform heating, thereby accelerating reaction rates andincreasing energy efficiency. Microwave heating providesease of operation by instant on/off control and improves the yieldand quality of the products (Oliveira *et al*., 2017). Furthermore, it reduces hazardousproducts formation and minimizes emission of pollutants, thus making thetechnique environment-friendly (Li et al., 2016). The physical and chemical composition of biochar depends largely on the heating rate, combustion temperature, residence time and the particlesize of the feedstock. Table 1 describes the different operating conditions in the yield of solid (biochar), liquid and gaseous pyrolytic products.

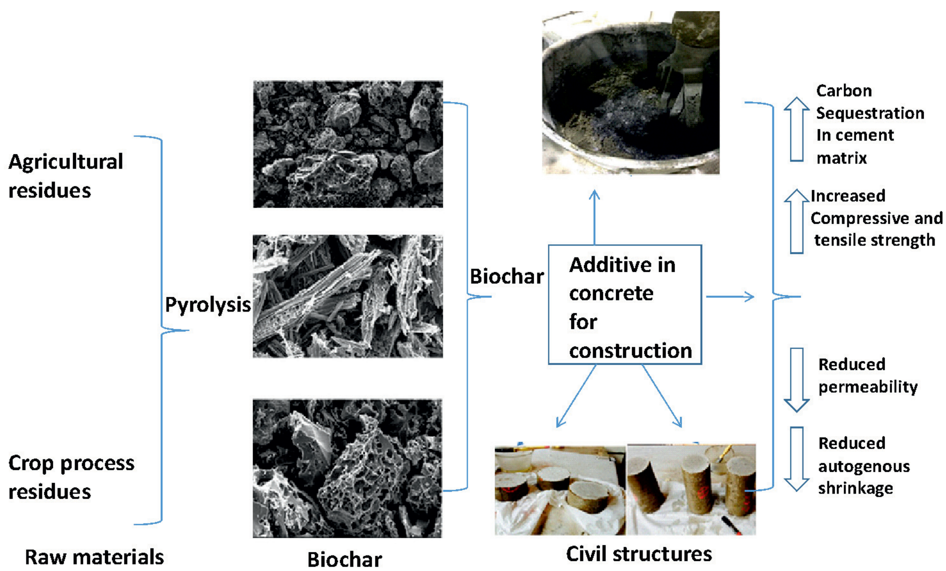

Fig. 1. Applications of biochar as green admixture for concrete

Table 1. Operating conditions for different types of pyrolysis

Pyrolysis type	Temperature (°C)	Heating rate (°C/s)	Residence time (s)	Particle size (mm)	Major pyrolytic products	Reference
Slow	300-700	0.1-1.0	450-550	5-50	Biochar, bio-oil and syngas, but biochar is dominant	(Luque *et al*., 2012).
Fast	550-1000	10-200	0.5-10	<1	Bio-oil, syngas and biochar, but bio-oil is dominant	
Flash	800-1100	<1000	< 0.5	< 0.5	Bio-oil, syngas, and biochar, but bio-oil and syngas are dominant	

The escape of volatiles and organic matters from the feedstock during pyrolysisinduces pores of different sizes which spread in the biochar forming a honeycomb-like pore structure thus making it a highly porous material that can absorb and sustain an appreciable amount of water inits pores for facilitating internal curing in concrete/mortar, as in the case with lightweight aggregate (LWA) applications. It has also been reported that the addition of catalysts in the feedstock for performing the pyrolysis process improve the yield and quality of the pyrolytic products. Table 2 summarizes the effects of various variables that affect the yield of biochar under microwave assisted pyrolysis.

Hence, it is revealed that agricultural residues can be processed successfully to obtain biochar by following MAP. Different pyrolysis conditions such as heating rate, microwave power, residence time and the additives/catalysts and their ratios with feedstock affect the yield of biochar. However, the yield of biochar can be increased by keeping thereaction temperatures low at corresponding low microwave powers, short reaction time, low heating rates as well as proper additives/catalysts with their appropriate blending ratios.

Use of Biochar from agricultural residues as cementitious materials

The use of biochar to replace cement in minor fraction for enhancing mechanical properties and improving durability has been studied by various researchers and is summarized in the Table 3 below.

From the above table, it is revealed that biochar obtained from different agricultural residues has the potential for partial replacement of cement, even at a small fraction, in improving mechanical strength, durability, enhancing internal curing activity, reduced permeability, decreased autogenous shrinkage etc. in the concrete mixture. Hence biochar from the agro-residues can be considered as a green admixture in the concrete technology due to sequestering carbon in civil infrastructures.

Biochar in cementitious materials for carbon sequestration

Cement in the construction industry is an essential component and its production is highly energy consuming causing severe environmental impacts due to emission of large amount of CO_2 because of mining, processing and transportation involved in the extraction of raw materials. In the production of cement, clinker, as carbonates (largely limestone, $CaCO_3$) are decomposed into oxides (mainly lime, CaO) and CO_2 by the addition of heat.Global cement production is the third largest source of anthropogenic carbon dioxide emissions. Anthropogenic emissions of carbon dioxide to the atmosphereare generally originated from three main sources: (i) oxidation of fossil fuels, (ii) deforestation and other land-use changes, and (iii) carbonate decomposition in cement production (Andrew, 2018). There is a massive increase of civil infrastructure around the world due to the population growth, urbanization and increasing living standards of the people. India, the world's second-largest cement producer with about 7% of global production in recent years next to China (Fig. 2).

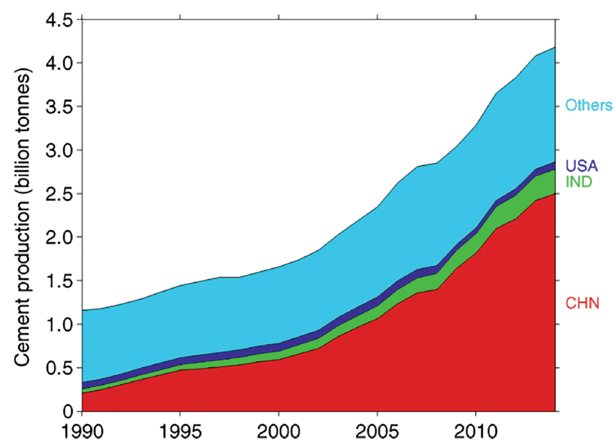

Fig. 2. Production of cement in some top countries in world

It has also been estimated that for the production of 1 ton of cement, around 0.5 ton of CO_2 is emitted (Klee, 2009). From the Fig. (3), it is revealed that the growth rate of production of fossil energy and cement in the world is almost similar and in the increasing trends. The current production of cement in the globe during 2020 is about 4.1 billion tons. Considering the present human population in the world (about 8.00 billion), the current levels of global cement production is equivalent to more than half a tonne per person per year (Fig. 3). With the replacement of 1 % biochar for cement in the concrete mix, there would be reduction in the production of 41 million tons of cement per year in the world. Considering carbon content in biochar to range from 80-95 % depending on the conditions of the pyrolysis followed, the amount carbon sequestration would range from 33 Mt-39 Mt, which is equivalent to 120 – 140 Mt $CO_{2(equivalent)}$ (3.66 times,

Table 2. Improvement in production of biochar through MAP of agricultural residues (Fodah and Ghosal, 2021)

Agro-residues	MAP conditions	Findings	Biochar yield (%)
Rice straw	10 g feedstock, 800 W (microwave power), catalyst HZSM-5/biomass ratio (1:4, 1:2, and 1:1), different temperatures (450, 500, 550, 600 and 650 °C)	Biochar yield was decreased by about 68% when the temperature increased from 450 °C to 650 °C. The catalyst has a slight effect on biochar yield	25-42
Rice husk	50 g feedstock blended with 15 g catalyst, 700 W for 20 min(reaction time), different catalysts (pure Rice Husk Char RHC, Ni/RHC, Fe/RHC, and Cu/RHC)	The biochar yields were decreased by about 9.3-18.6% by adding all types of catalysts compared to the non-catalyst conditions. Fe/RHC had a significant effect on the decrease of the biochar yield compared to other catalysts	35-43
Sugarcane bagasse	3-5 g feedstock, 500 W, 30 min, metal-oxide catalysts (NiO, CuO, CaO, MgO), catalyst ratios of 3%, 5%, and 10%	Biochar yields were slightly decreased with adding all the catalysts at different ratios. CuO with 3% ratio has a significant effect on decreasing the yield, decreased the yield by 27% compared to a non-catalytic case	14-19
Sugarcane bagasse	20 g feedstock, 550 °C, different absorber (charcoal) ratios of 0.1 and 0.3	Biochar yield was increased by 37.7% with increasing the absorber blending ratio from 0.1 to 0.3	61-84
Wheat straw	10 g feedstock, 800 W, different additives (biochar, K_2CO_3, Na_2CO_3, CuO, Fe_3O_4) at different ratios (10 % and 20%)	The pyrolysis condition with CuO and Fe_3O_4 produced the highest biochar yield compared to other additives	22-70
Wheat straw	10 g feedstock, different microwave power (400, 500, and 600 W), different additives (K_2CO_3, Na_2CO_3, CaO at 500 °C and 1:10 adding ratio)	Increasing the MAP from 400 W to 600 W decreased the biochar yield by 19%. At 500 °C and 1:10 adding ratio, all additives increased the yield as compared to the pure sample. CaO additive was the better option to produce the highest biochar yield of 59%	48-59
Corn stover	3-5 g feedstock, 500 W, 30 min reaction time, metal oxidase additive (CaO, MgO, CuO, and NiO), N_2 and CO_2 atmosphere	The biochar yield was higher by 10.5-47% under the CO_2 atmosphere than N_2. The catalytic effect on solid products was not significant	14-25
Corn stover	100 g feedstock, 875 W, 20 min, with observed pyrolysis temperatures of 450-550 °C, different catalysts (KAc, Al_2O_3, $MgCl_2$, H_3BO_3, Na_2HPO_4 $CuSO_4$, $ZnCl_2$, etc.)	AL_2O_3 increased the biochar yield by 6%, while KAc, $MgCl_2$, H_3BO_3, and Na_2HPO_4 decreased the biochar yield by 7%, 2%, 9%, and 16% respectively as compared to non-catalytic conditions	24-30
Bamboo	10 g feedstock, 850 g of SiC, 1000 W, 500 °C, HZSM-5 bed, different catalytic temperatures (200, 250, 300, and 350 °C), different feedstock to catalyst ratio (1:0, 4:1, 2:1, and 1:1)	Biochar yield approximately remained constant under different catalyst temperatures. The yield was decreased by about 54.5% when the feedstock to catalyst ratio increased from 1:0 to 1:1.	4-11
Wood sawdust	Feedstock loading of 0.5-5.5 g/min, 500 g of SiC as the microwave absorbent bed layer, 750 W, feedstock loading (1, 3, 5 g/min), temperature (450, 500, and 550 °C)	Increase of the temperatures from 450 to 550 °C decreased the biochar yield by 48% at 1 g/min loading. Increase of feedstock loading increased the biochar yield by 47% at 450 °C. The maximum biochar yield was at 450 °C and 5 g/min	14.5-50

Table 3. Use of agricultural residues based biochar as cementitious materials

Biochar from agro-residues	Biochar percentage replacement with respect to weight of cement	Effects on concrete mix	Reference
Rice husk	0.1	Compressive strength close to the control specimen. Improvement in splitting tensile strength. 20 % increase of flexural strength compared to control mix.	Akhtar and Sarmah, 2018
Coconut coir	0.08	Improvement in compressive strength and fracture toughness. Cracks in the sample follow their contours instead of straight trajectory thus increasing the energy required to fail the sample	G. Ferro *et al*., 2015.
Bamboo stem	0.08	Improvement in toughness, compressive and flexural strength compared to controlled sample. Increase in fracture surface area by diverting the crack path	Ahmad *et al*., 2015
Wood chips	2.0	Increase in flexural strength and fracture energy by about 15% and 150% respectively compared to the reference samples	Riera *et al*., 2020
Rice husk and bagasse mix biochar	5.0	Compressive and tensile strength improvement by about 50% and 78% respectively, compared to ordinary mix. However with 10 % biochar, compressive strength improvement by about 22 %	Zeidabadi *et al.* (2018)
Hazelnut shell	0.8	Increase in fracture energy by about 45 % compared to control mix after 28 curing days	Restuccia *et al*. (2017)
Wood saw dust	5.0	Increase of degree of hydration from 42% (in control mix) to 59% (biochar sample). Compressive strength (144 MPa in control mix) to (150 MPa in biochar sample) at 28-days curing period	Dixit *et al.* 2019.
Mixed wood saw dust	2.0	About 40–50% higher compressive strength at 28-day compared to plain mortar, especially under air curing condition. Similar trend is observed for flexural and split-tensile strength. Also improvement in permeability properties when pre-soaked biochar is used	Gupta and Kua 2018
Mixed kitchen food waste	1.0	Mechanical strength is at par with control mix (without biochar). About 40% and 35% reduction in water penetration and sorptivity respectively, indicating higher impermeability of mortar	Gupta *et al.* 2018
Mixed wood saw dust	2.0	Self-healing of cracks in concrete by biochar, derived from wood waste, as a carrier for carbonate precipitating bacteria spores in cement mortar to seal cracks, and recover strength and permeability of healed samples.	Gupta, *et al*., 2018

the ratio of atomic weight of CO_2 to C).

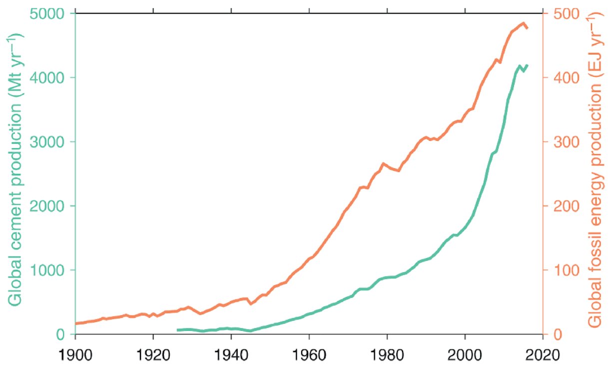

Fig. 3. Global fossil energy and cement production from 1990 to 2018

For this reason, there is a growing interest to explore the sustainable construction materials as a replacement of cementitious components mainly, the cement in concrete technology and to reduce the carbon foot prints in the infrastructure sector. It has been reported that there is the potential of sequestering carbon in civil infrastructures, if biochar is used as admixture in cementitious materials. The use of biochar as cementitious admixture would also promote waste recycling particularly organic waste in the form of agricultural residues. Huge amount of surplus agricultural residues is being produced per year in the agricultural based countries around the world. In the absence of sustainable management practices, on farm burning of agricultural residues is at present a global concern due to major environmental problem causing health issues and adverse effects on the soil (Fig. 4).

Therefore, utilization of agricultural residuesin the form of biochar in construction material would constitutean attractive alternative to the disposal and an eco-friendly solution to the above problem and to meet the challenges concerning the shortage and exploitation of non-renewable natural resources in the world for the raw materials used in the production of cement. Hence, use of biochar in the concrete mix would not only improve the strength and durability but also to reduce the carbon foot prints in the construction industry. Also there are several studies that have explored biochar as a potential material to store and fix carbon in stable form in the soil (Fig. 5).

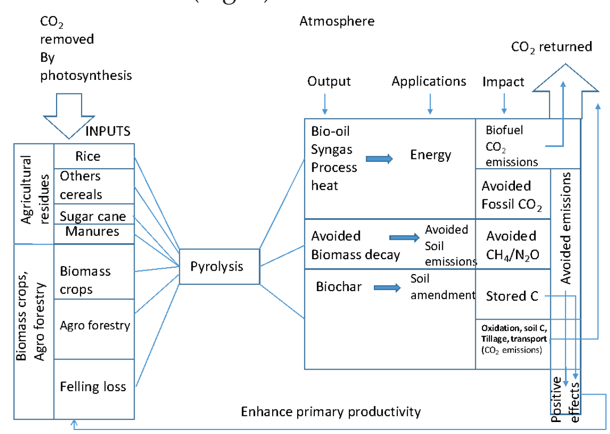

Fig. 5. Positive effects of biochar for environment and soil

The biochar stores carbon in a recalcitrant form that can increase soil waterand nutrient-holding capacities, which typically result in increased plant growth (Woolf *et al.*, 2010). This enhanced productivity is a positive feedback that further enhances the amount of CO_2 removed from the atmosphere. Slow decay of biochar in soils, together with tillage and transport activities in the farm, also returns a small amount of CO_2 to the atmosphere. Therefore, production of biochar from the biomass

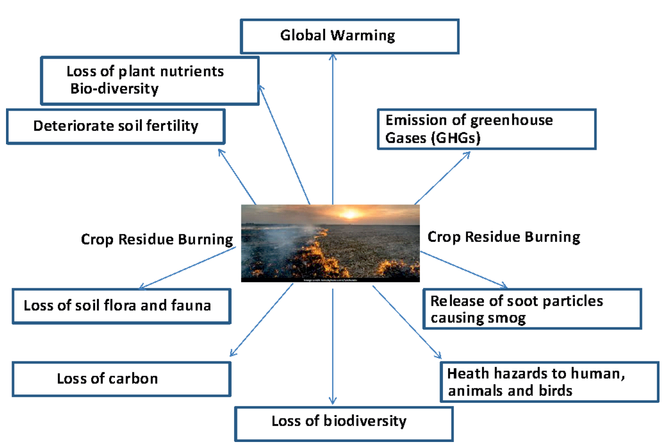

Fig. 4. Consequences of crop residue burning

and its use as cementitious material in combination with storage in soils would become a possible, viable and sustainable means of reducing the atmospheric CO_2 concentration, thus contributing reduced effects on global warming.

CONCLUSION

Based on the findings of the literatures reviewedon the feasibility of using biochar, produced through a novel approach of microwave assisted pyrolysis of agricultural residues, for its applications in the concrete technology, the following conclusions are drawn.

(i) Biochar has the potential to act as micro-reinforcement component in the concrete mix not only for increasing the strength but also improving durability and reducing permeability to become a promising candidate for high performance concrete

(ii) The feedstock for producing biochar can be sustainably obtained from the crop and crop process residues which are available cheaply and plentifully in agricultural based countries

(iii) The partial replacement of biochar for cement, even in a˙small percentage (1-5 %) would not only reduce the emission of CO_2 in the cement production industry but also promotes the safe disposal and effective utilization of agro-residues, waste recycling and environment sustainability

(iv) Pyrolysis is a promising approach to convert biomass wastes into energy in the form of biochar, pryo-oil and syngas. The yield and quality of biochar, a solid carbonaceous material, can be improved through the lower temperatures and heating rates but at higher residence time, resulting into the formation of carbon rich and microporous cellular structure based solid material for enhancing internal curing of the concrete mix because of the increased rate of hydration.Microwave assisted pyrolysis is however one of the efficient, cost effective and environment-friendly thermo-chemical conversion processes to control the operating conditions for obtaining desired yields and qualities of the pyrolytic products.

(v) It has been estimated that even 1 % replacement of biochar for cement in the concrete mix, would reduce the production of about 41 million tons of cement per year in the world and mitigate the emission of around 120–140 Mt $CO_{2(equivalent)}$ to the environment.

(vi) Biochar has the potential to be successfully deployed as carbon sequestering admixture in concrete technology and also improving the conditions of soil forstoring and fixing carbon in stable form if used in it.

Hence, the use of biochar needs to be emphasized in the civil infrastructurefor improved performance of concrete, as a potential candidate of cementitious material, effective disposal of biomass wastes and environmental sustainability.

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