Alternative material use of fast pyrolysis char and its impact on the bioliq process chain

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Abstract

Biochar is a significant by-product of bioliq® fast pyrolysis plant concept, developed by Karlsruhe Institute of Technology (KIT), Germany, amounting up to 28 % of reaction products. Given its quantity, it would be a good prospect to find an alternative use of biochar on industrial scale. After exploring a number of prospective solutions and applications, activated carbon (AC) has been chosen as the focus of this study. In this work, biomass based precursor (biochar) was demineralized and further used for production of activated carbon by using two different methods of activation: physical and chemical activation in which steam and potassium hydroxide were used, respectively. Activated carbon was analysed to check its physical and chemical characteristics by using experimental methods such as N_2 adsorption, iodine adsorption and scanning electron microscopy. The results indicated that biochar from wheat straw is promising for this purpose. The effective BET Surface and iodine number were determined to be 2900 m^2/g and 2567 mg/g, respectively, in case of chemical activated carbon. The bulk densities of powdered chemical activated carbon and pelleted physical activated carbons are 0.128 t/m^3 and 0.239 t/m^3 respectively. In this work, the proposed solution is for integration of activation into fast pyrolysis process on industrial scale. The waste thermal energy of flue gas was used to dry biomass and the the usage of waste thermal energy from hot char to produce steam for physical activation process. Physical activation process will be used for production of pelleted activated carbon.

Keywords: Biochar, demineralization, activated carbon, chemical activation, physical activation, and adsorption

Introduction

Biochar is a solid carbon rich product that results from thermal decomposition of natural organic feedstock (crop waste, municipal waste and manure etc.) in an absence of oxygen. Biochar is produced by from fast pyrolysis in a twin screw reactor along with organic condensate, aqueous condensate and pyrolysis char at a process demonstration unit. Pyrolysis gas is burnt in a gas burner to supply thermal energy for heat carrier loop and organic condensate directly fed to gasifier for gasification but biochar and aqueous condensate are left behind. Now-a-days only 10% of produced biochar is mixed with aqueous condensate to make pump-able bio-syncrude slurry for gasification and 90% of biochar is useless, which is not an economical way to use this biochar on industrial scale. Biochar can be used as an alternative use on industrial scale which will be economical for bioliq fast pyrolysis plant. There are a lot of applications for biochar which are discussed in upcoming chapter but most promising ones are Biochar as a soil conditioner or as a fertilizer and activated carbon used as adsorbent material in aqueous and gas phase applications. In this work biochar used as precursor for production of activated carbon.

Literature

Biochar

The term biochar known as charcoal is a carbon rich product that results from the thermal treatment of natural organic feedstock (crop waste, wood chips, municipal waste or manure) in an oxygen-limited environment [1]. Due to its aromatic structure biochar is chemically and biologically more stable than carbon(C) source from which it is produced. This makes bio-char difficult to breakdown and scientists have shown that the mean residence time of stable fraction is estimated to range from several hundreds to few thousands of years [2].

Applications of biochar

There are a lot of biochar applications depending on characteristics of biochar. Biochar can be used in animal farming, composting, building sector, textile, cosmetics, paints and energy production without any further up gradation of physical or chemical properties. But few applications need specific improvements in physical and chemical properties of biochar for their respective applications such as soil conditioner, decontamination, biogas production and treatment of water.

Animal farming

Biochar can be used as a feed additive up to 1%, which will increase the energy efficiency of digestion. 5-10% biochar can be used as a litter additive to prevent from hoof infection in cows. 1-1.5 % biochar can be mixed with liquid manure for removal of bad odour and reduction in ammonia and carbon dioxide emissions. [3] .The red colobus monkeys, *procolobus kirkii* eat charcoal from burnt trees to detoxify the poison (mainly phenolic) obtained from their leafy diet and convert them in to proteins [4].

Soil conditioner

Biochar can be used as a carbon fertilizer, compost, plant protection and compensatory fertilizer for trace elements. The strongest evidence for using high concentrations of charcoal in soil may be useful under some results comes from the Amazonian Dark Earths. Charcoal from the region’s rich soils contained about three times more soil organic matter, nitrogen and phosphorous than other soils with twice productivity [5]. The best method of loading nutrients is to co-compost the biochar. This involves adding of 20-30% biochar to the biomass for composting.

Use in building sector

In a ratio 50 % biochar can be added to clay, lime and cement mortar to create indoor plasters with excellent insulation and comfortable breathing environment, to maintain humidity levels in a room at 45-70 % in both summer and winter. Biochar can also be sprayed, mixing with lime through jet spray technique at outside of building up to 20 cm thickness as a thermal insulation, it's also a substitute of extruded polystyrene foam. By this method, houses become carbon sinks and healthy indoor climate. Biochar mud plaster can also be recycled as a valuable compost additive.

Activated carbon

Activated carbon is a fine black, odourless and tasteless powder made from coal, char and other materials that have been processed to make it extremely porous and thus to have a very large surface area available for adsorption. Because of blockage of the pores by tar [6],[7] the internal surface area of char is too low and it does not have developed porous structure. Porosity development is due to penetration of oxidizing agents in to internal structure of char and removal of carbon atoms by reaction, which results in opening, and widening of inaccessible pores [8].

Activated carbon can be produced by biochar and have a well-developed porous structure. Due to their microporous structure and chemical nature of their surface with acidic functional groups they have been considered as a potential adsorbent for removal of pollutants and nutrients from industrial and sewage waste water [9].

After reviewing all biochar significant applications, activated carbon seems to be a promising application for future in both gas phase and liquid phase adsorption processes.

Production methods

Physical activation

Physical activation involves high temperature activation using gasifying agents like carbon dioxide and steam in an inert atmosphere to increase the porosity of char.

Chemical activation

Chemical activation involves high temperature activation using chemical agents like potassium hydroxide, sulphuric acid and zinc chloride under nitrogen atmosphere to increase the porous structure of char.

Porous structure of Activated Carbon

The porous structure of activated carbon is formed by three types of pores, which are categorized as follows [10]:

Table 1: Types of pores

Pore	Width
Micropores	< 2 nm
Mesopores	Between 2 to 50 nm
Macropores	> 50 nm

Applications of activated carbon

Activated carbon can be used in both gas phase and liquid phase applications. In gas phase applications, Marsh *et al*. have outlined a few applications which have been widely explored [10]. Activated carbon can be used for cigarette filters, industrial gas masks, chemical warfare agent protection (including clothing and gas masks), effluent gas purification and industrial off-gas purification like (removal of SO_2, H_2S etc.). In liquid phase applications, activated carbon is used for removal of pollutant organic compounds like NOM (natural organic compounds), synthetic organic compounds and by-products of chemical water treatment produce bad odour, taste from water that becomes the source of infection. Activated carbon is also used to treat with effluent wastes from chemical factories, rubber factories, fabric dyeing, fertilizer plants, pulp and paper mills etc. Activated carbon is used for the removal of oil from effluent water in petrochemicals, petroleum refinery and metal extraction.

In this work, activated carbon will be used in liquid phase applications especially focussed on drinking water treatment. Clean water availability is a crucial issue in developing countries. In many parts of world, heavy metal concentrations in drinking water are higher than international guideline values. The main threats to human health from heavy metals are associated with exposure to cadmium, lead, mercury and arsenic. Utilization of activated carbon for removal of heavy metals from water will minimize water related health problems.

Experimental

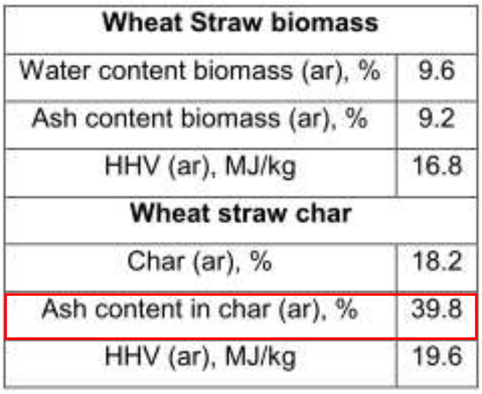
Materials

Biochar was derived from pyrolysis of wheat straw. Iodine solution (0.1 N) and sodium thiosulphate (0.1 N) were obtained from VWR, Germany. Potassium hydroxide used for chemical activation was purchased by Merck, Germany.

Methods

Biochar is received from Process demonstration unit. From **Table 2**, we can see that approximately 40% of ash content is present in biochar which blocks the pores of biochar and decreases its porosity.

Table 2: Mass yields of product as received from PDU



Wheat Straw biomass	
Water content biomass (ar), %	9.6
Ash content biomass (ar), %	9.2
HHV (ar), MJ/kg	16.8
Wheat straw char	
Char (ar), %	18.2
Ash content in char (ar), %	39.8
HHV (ar), MJ/kg	19.6

Demineralization of biochar

Dried biochar was soaked in a 1 N solution of $HCl:H_2SO_4$ (1:1) for 2 days in order to reduce ash content of biochar and then washed with distilled water (Millipore ultrapure water system) and dried at 110 °C for about 14 h. Ash reduced biochar was used for production of activated carbon.

Chemical activation

Ash reduced biochar was sieved. The particles having mesh number 60 (250 µm) size were collected for activation. The equipment Retech (AS 200) was used for sieving. In pre-treatment, biochar was impregnated with KOH having impregnation ratio of 2.34:1 (KOH/Biochar) in a 500 ml volumetric flask containing 250 ml demineralized water with different amount of biochar (2, 5, 10 and 15 g). Impregnated mixture was stirred on a magnetic stirrer for 2 h at 60 °C in a water bath. The resulting mixture was washed with demineralized water to remove KOH. The resulting slurry was dried at 110 °C overnight in an oven. The activation was carried out in a vertical electric muffle furnace. In this work, activation was conducted at different temperatures (450, 675 and 700 °C) with impregnation ratios such as 1.63:1 and 4:1 (KOH/Biochar) (‘’to clarify for chemical heat treatment ground KOH is used with biochar to prepare a homogenous mixture in a reactor (X6CrNiMoTi17-12-2,1.4571) but for pre-treatment prior to chemical heat treatment KOH pellets are used with biochar in distilled water''), under high purity nitrogen (99.995 %) with different flow rates 150, 258 and 800 ml/min was used for 1 h and 2 h. Time duration was noted, once the final temperature was reached. The reactor was cooled down in an ice tub and activated carbon was first washed with demineralized water to remove chemicals. For better removal of potassium compounds, activated carbon was washed with 250 ml (0.1 M HCl) solution. After washing with HCL, activated carbon was repeatedly washed with demineralized water until the pH of washing solution reached 6.5-7. Washed solution was cross checked with two drops of $AgNO_3$ (Merck 101512) to check the presence of chlorides with formation of clouds.

Physical activation

Pellets formation

Demineralized char had to be milled before pelletizing to make homogenous mixture of char and binder. Pyrolysis oil was used as a binder to form stable pellets. High viscous pyrolysis oil mixed with char and pressed through matrix to get pellets. Pressing conditions for stable pellets required pressure between 150 bar - 350 bar. The binding ratio for stable pellets was 1:0.65 (Pyrolysis char/Pyrolysis oil).

Steam activation

5-10 g pellets were activated at 750°C in a vertical tube reactor. The nitrogen gas was passed at the rate of 500 ml/min through pellets bed at the start and end of activation to create an inert atmosphere and to cool down the activated pellets respectively. After achieving desired temperature, steam was passed through pellets bed at the rate of 75 mg/min as an oxidizing agent to increase porosity of pellets.

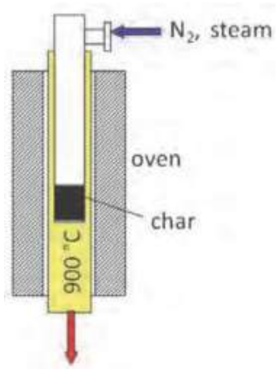


Figure 1: Scheme of activation reactor

Product characterization

Surface measurement – BET method

The surface of pyrolysis char and activated carbon is measured by standard BET method (Bunauer, Emmett, Teller) with the automatically operating measurement technique NOVA 4000e from Quantachrome Partikelmesstechnik GmbH.

Iodine adsorption

Activated carbon was analyzed by using the standard test method for the determination of iodine number of activated carbon (ASTM, D4607-94). Iodine number gives information about the adsorption capacity of specific material. The iodine molecule gives information on the surface area contributed by pores larger than 1 nm [11].

Results and discussion

Demineralization of char

Demineralization results in significant decrease in % of ash content in char, which further increases the porosity of char. From **Table 3,** we can conclude that almost 50% reduction in ash content by doing demineralization and 6 times more surface area than as received biochar.

Table 3: Demineralization of biochar results

	Elemental analysis, wt. %			Surface area, m^2/g	Ash Content, wt. %
	C	O	Si		
Raw biochar	65.14	19.12	6.06	4.1	39.8 (db)
Demineralized biochar (1 N)	72.81	18.26	6.51	23.5	20 (db)
Demineralized biochar (2 N)	72.67	18.23	6.27	-	22.2 (db)

Activation of wheat straw demineralized biochar

In chemical activation processes many parameters exist, variation of these parameters will affect the porous texture of the activated carbon. From previous research studies, the most promising parameters were selected for chemical activation of char. The values of properties in **Table 4** are given for the samples, which have the higher iodine number and highest surface area. Higher iodine number and surface area were found with triplicate CA 3 (chemical activation) sample. Above these 1.63 impregnation ratio, the oxidation reaction is predominant, and therefore the yield decreases with increasing mass ratio as a result of increasing burn-off of carbon and release of volatiles. It can be seen from **Table 4**, like in (CA 2) we have approximately 60% yield but by increasing impregnation ratio it reduces percentage of yield down to 40%. **Table 4** contains the porous texture characterization results obtained by applying the BET equation to N_2 adsorption at 77 K automatically and by iodine adsorption test. It can be seen that surface area increases with increasing impregnation ratio significantly.

Table 4: Effect of parameters on yield wt. % and Iodine Number value (mg/g)

Sample	KOH/Biochar Ratio	Temperature (C)	Nitrogen flow rate (ml/min)	Time (h)	Yield (%)	Iodine No. (mg/g)	N2 BET Surface Area (m^2/g)
CA 1	1 – 4	650 – 700	250 – 800	2	59.72 (db)	1003 ± 56.2	-
CA 2	1 – 4	650 – 700	250 – 800	2	59.36 (db)	1230 ± 68.5	-
CA 3	1 – 4	650 – 700	250 – 800	1	40.16 (db)	2440 ± 129.6	2860 ± 43.5

In case of physical activated carbon, pellets are activated only using promising parameters and the results are triplicate. **Table 5** contains physical activated pellet characteristics. In both activated carbon, the contents of carbon (**Table 6**) were increased and other contents were decreased when compared to the precursor. This is due to the release of volatiles during pyrolysis that results in the elimination of the non-carbon species and enrichment of carbon. In this work, chemical activated (CAC) carbon has lowest yield but highest carbon content percentage as compared to physical activated carbon (PAC). The density of the adsorbent depends not only on the nature of starting material but also on the preparation process. The bulk density of CAC is lower than PAC, but surface area is very high as compared to PAC, which shows its high adsorption capacity. Due to pellets, we have almost double the amount of bulk density in case of PAC as compared to CAC but it is less in comparison with biochar due to the porous structure. In case of CAC, bulk density is low due to highly porous material after removal non-carbon contents. Iodine number is a measure of iodine adsorbed in the pores, which indicates pore volume capacity and extent of micropores distribution in the carbon. Iodine number can be correlated with ability of adsorbent to adsorb low molecular weight substances. Iodine number is higher in case of CAC due to higher effective BET surface and has higher capacity to adsorb more iodine as compared to PAC

Table 5: Physical activated carbon results

	n = 3
BET Surface Area (m^2/g)	510 ± 26.97
Iodine number (mg/g)	485 ± 27.72
Yield (wt. %) (db)	48 ± 0.362

Table 6: Physico-chemical characterictics of actiavted carbon

Sr. No	**Parameter**	**Biochar**	**CAC**	**PAC**
1	Bulk density (t/m^3)	0.275	0.128	0.239
2	Surface Area (m^2/g)	4	2900	545
3	Iodine Number (mg/g)	-	2567	512
4	Ash content (%)	39.8	0.7	38.2
5	Yield (%)	-	40	48
6	C (%)	65.14	91.6	71

N_2 gas adsorption isotherms

The adsorption isotherms of CAC and PAC are shown in **Figure 2**. Both isotherms displayed a very large difference in volume, indicating the presence of mesopores in case of PAC and micropores in case of CAC. This is the reason for the smaller BET surface area and iodine number for the PAC.

The physisorption of nitrogen at 77 K, on non-porous surfaces, resulted in multilayers being formed. The BET equation does not predict surface areas; it predicts monolayer coverage (units of $cm^3\ g^{-1}$, $mmol\ g^{-1}$ of adsorbate). In some activated carbons, adsorption may occur such that several layers of adsorbate molecules adsorb together. This is named as *volume* *filling* and occurs in the largest of the micropores. It is termed *capillary condensation* when it occurs in mesoporosity. Such capillary condensation must not be included in values of n_m^a (monolayer capacity in mmol g^{-1}). Any value beyond 1000 m^2 g^{-1} must be associated with micropore volume filling and capillary condensation and should be treated with caution. [[10]]

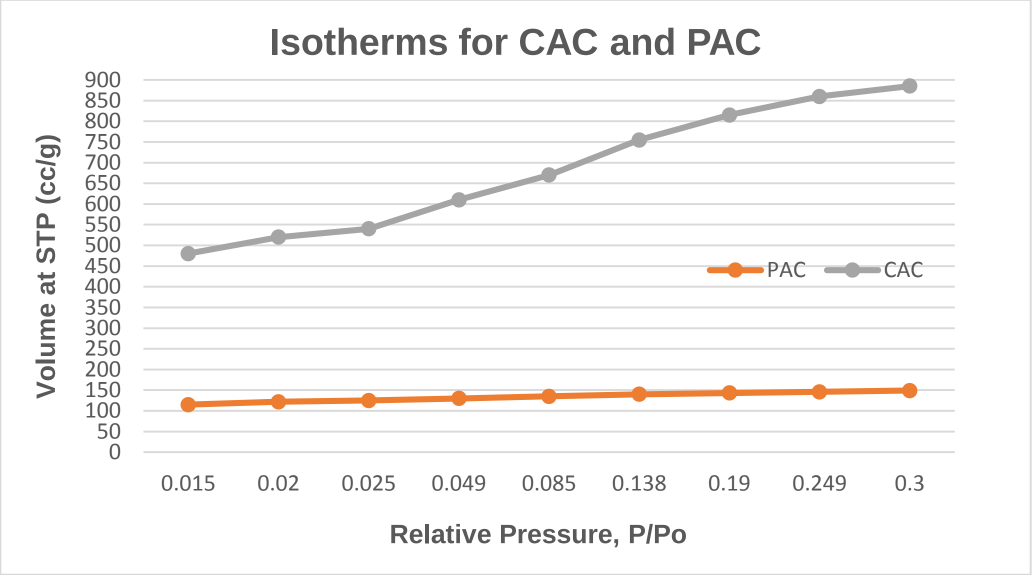


Figure 2: Nitrogen adsorption isotherms of activated carbons at 77 K

Optimization of plant

Waste flue gas can be utilized to dry the wet wheat straw biomass from 10% of water content down to 7.42% which will help in reduction of aqueous condensate and increase the relative percentage of biochar. Water content removal will also minimize the energy and time required during the start of fast pyrolysis. For drying, flash dryers will be preferred due to reduced environmental emissions and explosive fire risk. Steel balls will be preferred to use in fast pyrolysis bioliq plant in replacement of sand because sand increases the impurities in char and few fraction of char stuck with sand, during heating of sand Flue gas polluted by this char particles cannot be used directly for drying process and cannot be released in the environment before burning all char particles to control pollution and emissions before leaving to the atmosphere. Due to this reason, we have very low BET surface area with no developed porous structure. Waste heat from char recovery can utilized for production of steam for physical activated carbon. In case of physical activation, required thermal energy for steam production can be fulfilled by internal heat recovery up to 43.82% .

Conclusions

Employment of wheat straw biochar as a precursor or raw material for production of physical or chemical activated carbon is beneficial on industrial scale. The higher adsorption capacity of chemical activated carbon suggests the process is potentially suitable for industrial scale. In case of chemical activated carbon, impregnation ratio has a large effect on iodine adsorption capacity. Sample (CAC 3) activated at 4:1 impregnation ratio had the best iodine adsorptive properties. Increasing KOH amount used for chemical activation may help in the development of internal microporous cavities, which result in an increased surface area, considered to be most important factor for adsorption [12]. The surface area can be controlled by means of experimental parameters. Iodine adsorption tests show that adsorption capacities conform to the results based on nitrogen adsorption isotherms. According to American water works association, the requirement for water purification BET surface area should be greater than 500 m^2/g and density should not be less than 0.2 t/m^3. These both requirements are fulfilled by physical activated pellets and can used for water purification. Chemical activated carbon can be used in gas phase applications due to their higher effective BET surface area.

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