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Activated Carbon from Waste Biomass

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1. Introduction

As a result of environmental requirements in many countries and new areas of application the demand on activated carbon is still growing. Due to the unavailability of the main basic materials like hard coal, wood or coconut shells in many countries other biomass matters were tested for their appropriateness of activated carbon production.

The objective of this experimental work is the conversion of waste biomass into activated carbon. Waste biomass like straw matters, olive stones, nut shells, coffee grounds and spent grain is converted thermally in two steps. First the biomass undergoes a pyrolysis process at 500°C–600°C in nitrogen atmosphere. The gaseous and liquid pyrolysis products can be used energetically either for heating the facilities or for electricity production.

Second, the solid residue, the char, is treated in an activation process at 800°C–1000°C in steam atmosphere in order to enhance the char surface area which was analyzed by standard BET method. The increase of surface area depends on the type of biomass and on the activation parameters. The production methods were investigated in lab-scale facilities whereas a pilot scale reactor was designed for the transformation of the discontinuous activation process to a continuous production process.

The use of agricultural by-products for activated carbon production as well as the influence of ash content, pyrolysis and activation conditions on the activated carbon quality is investigated by many authors. The high ash content of rice straw makes it difficult to achieve a sufficiently high surface area (Ahmedna et al., 2000). The influence of a one step and a two step thermal treatment of rice straw in CO₂ atmosphere is discussed in (Yun et al., 2001). The two step treatment leads to higher surface areas than the one step treatment which correspond to the own results. Higher temperatures of physical activation in CO₂ atmosphere leads to pore widening which causes an increase of mesopores. Physical activation by the use of an oxidizing gas like steam or CO₂ results in carbons with low surface area whereas chemical activation enhances the carbon surface area (Ahmedna et al., 2000). Chemical activation of rice husks and rice straw is investigated in (Guo et al., 2002; Oh & Park, 2002). The impregnation of rice precursors with KOH or NaOH enhances the surface area. In addition the activation temperature can be lowered. Washing rice straw with alkaline solutions like NaOH allows to reduce the ash content as shown in Table 1 and (Huang et al., 2001). Carbonisation and activation of pretreated rice straw leads to higher surface areas than of non-treated straw

matters but only in a certain range of washing time and temperature due to the effect that lignin and hemicelluloses are dissolved as well which leads to the reduction of straw carbon content (Finch & Redlick 1969; Sun et al. 2001). Ash extraction of straw matters is also discussed in (Di Blasi et al., 2000; Jensen et al., 2001a, 2001b). Activated carbons from olive stones and other waste biomass matters are given in (Daifullah & Girgis, 2003). High porosity can be attained by the use of phosphoric acid prior to heat treatment. Olive stones as precursor are also investigated in (El-Sheikh et al., 2004). They point out the microporous structure of their carbons which were activated in both steam and CO₂ atmosphere. Pretreatment of olive stones with hydrogen peroxide has a negative effect on porosity and surface area. The influence of gas atmosphere on the formation of mesopores in olive stone chars is investigated in (Gonzalez, 1994; Molina-Sabio, 1996). CO₂ activation leads to larger micropore volume than steam activation. Here, pore widening is the predominant effect. Compared to CO₂ activation chemical activation of olive stones with ZnCl leads to higher surface areas with a high amount of micropores (Lopez-Gonzalez, 1980). Highly microporous carbons with high surface areas are produced by chemical activation of hazelnut, walnut and almond shells and of apricot stones (Aygün, et al., 2003). Pistachio shells and fir wood were investigated in (Wu et al., 2005) by both physical and chemical activation. Chemical activation and the influence of KOH and NaOH on the formation of micropores of loquat stones is reported in (Sütcü & Demiral, 2009). High surface areas are attained with KOH and an increase of chemical agent leads to an increase of surface area. The influence of pyrolysis conditions on pore generation is investigated by pyrolysis of oil palm shells under both, nitrogen and vacuum (Qipeng & Aik, 2008). It is shown that vacuum pyrolysis avoids pore blocking which results in higher surface areas. The effect of binders and pressing conditions on the production of granulated activated carbons are worked out in (Ahmedna et al., 2000; Pendyal et al., 1999). Straw matters and binders from agricultural byproducts like molasses from sugarcane and sugar beet, corn syrup and coal tar were mixed and pressed prior to pyrolysis and CO₂ activation. Molasses as binder leads to lower hardness and higher ash content of the activated carbons than corn syrup or coal tar.

Also chemical activation leads to highly microporous activated carbons with high surface areas this work considers steam activation which is regarded be a low cost method for technical use.

2. Experimental method of biomass pyrolysis and char activation

The experiments on pyrolysis and activation of waste biomass matters were run in lab-scale facilities. The advantage of these small-scale equipments is that the experiments could be run very quickly without long heat-up times and with one operating person. Only small amounts of biomass were needed and the operation conditions could be changed quite easily. Not many efforts had to be made in gas cleaning procedure due to the low exhaust gas flow. The screening test to figure out the optimal char residence time in the activation facility was a one or two day work with an output of 6 - 10 data points. The description of the lab-scale experiments is given in detail for both, pyrolysis and activation activities.

2.1 Biomass properties

For the generation of activated carbon from waste biomass more than 12 different waste biomass matters were investigated. The properties of some of the investigated types of biomass are given in Table 1.

	C	H	O	N	S	Cl	Ash*	H ₂ O
Rice straw untreated	39.6	4.6	36.4	0.7	0.1	0.2	18.3	8
Rice straw pretreated	42.4	5.9	n.m	0.76	n.m	n.m	3.6	None
Olive stones	48	5.6	n.m	<1	n.m	n.m	5	4
Wheat straw	44.1	6	44.9	0.5	0.2	0.7	7.9	9.8
Wheat straw pellets	43.1	5.9	45.5	1	n.m	n.m	~8	6.5
Walnut shells	50.7	6	n.m	n.m	n.m	n.m	0.9	10.7
Pistachio shells	43.7	5.9	n.m	n.m	n.m	n.m	0.8	Dry

Table 1. Elemental analysis of different types of biomass based on dry matters (wt%).

*Appendix C.7 Alkali Deposit Investigation Samples Alkali Deposits Found in Biomass Power Plants: A Preliminary Investigation of Their Extent and Nature National Renewable Energy Laboratory Subcontract TZ-2-11226-1; n.m.: not measured

2.2 Lab-scale pyrolysis

The pyrolysis experiments were run in a “pocket”-reactor which was originally designed for fast pyrolysis experiments and which was reconverted to slow pyrolysis. Heating of biomass at low heating rates of 5-10 K/min was considered to be better than fast heating rates with respect to activated carbon production. A scheme of the reactor is shown in Fig. 1.

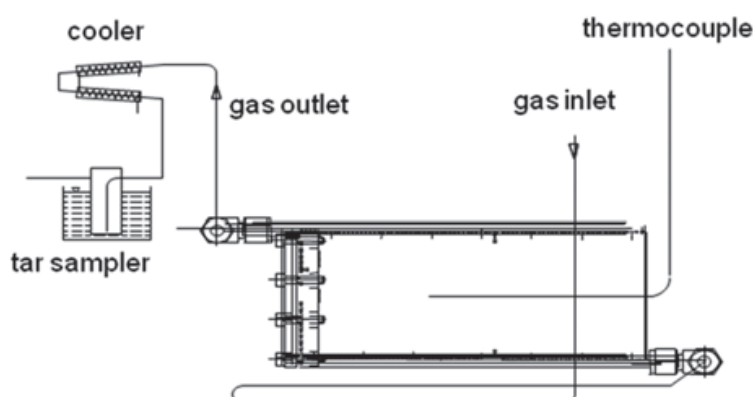


Fig. 1. Scheme of the pyrolysis reactor. Four pockets are connected in parallel and wrapped round with an electric heater. The width of the pockets was 5 mm.

The pockets altogether were filled with about 100 g of biomass. The feed was heated by a flow of hot nitrogen and additionally by electric heaters which were fixed to the walls of each pocket. The pyrolysis temperature was varied but it had only a marginal influence on the quality of the activated carbon because the biomass was not completely devolatilized after pyrolysis. The reason is that activation took place at higher temperature than pyrolysis therefore the entire devolatilization had been realized in the activation step. The disadvantage of incomplete pyrolysis is that some oils which are produced in the activation step require an additional cooling and filter system. The primary pyrolysis gases were cooled in a gas cooler to 5 °C and the oils were collected in order to use them as binder material for the production of granulated activated carbon. After the run of the experiments the char was taken out of the pockets and the mass balance was established.

The total amounts of the pyrolysis products char, tar and gas of the investigated biomass matters are given in Table 2:

Biomass	Char [wt% dm]	Tar [wt% dm]	Gas [wt% dm]
Rice straw	27	40	33
Rice straw washed*	19	30-40	50-40
Wheat straw	28	22	50
Wheat straw pellets	32	33	35
Olive stones crashed	30	49	21
Pistachio shells	29	36	35
Walnut shells	31	29	40
Coconut shells	33	40	27
Coffee grounds	23	53	24
Spent grain	29	20	51
Beech wood (525 °C)+	24	46	30
Coconut press residue	27	51	22
Rape seed	17	63	20

Table 2. Yields of pyrolysis products based on dry biomass matter. The pyrolysis temperature was 600 °C, the heating rate amounted to 10 K/min. * Based on washed and dried straw. + Pyrolysis temperature was 525°C.

The influence of heating rate on the pyrolysis product yields is shown in Table 3. The pyrolysis temperature was set to 600 °C for some biomass matters whereas the heating rate amounted to 30 K/min.

Biomass	Char [wt% dm]	Tar [wt% dm]	Gas [wt% dm]
Rice straw washed	24	36	40
Wheat straw pellets	31	25	44
Pistachio shells	24	54	22

Table 3. Yields of pyrolysis products. The pyrolysis was run at 600 °C, the heating rate amounted to 30 K/min.

As shown from Tables 2 and 3 the tar yield increases if the heating rate is enhanced whereas the char yield slightly decreases. From the aspect of using the tars/oils for energy production in a combined heat and power plant the higher heating rate is more reasonable. The influence of pyrolysis heating rate on the surface area of activated carbon is marginal in this range. A negative effect on the activated carbon quality can be detected at heating rates of more than 250 K/min. For optimization reasons, the amount and quality of the liquid pyrolysis products may be a decision criterion for higher heating rates.

2.3 Lab-scale activation

The activation experiments were run in a reaction tube which was installed in an oven. The scheme of the activation lab-scale facility is shown in Fig. 2.

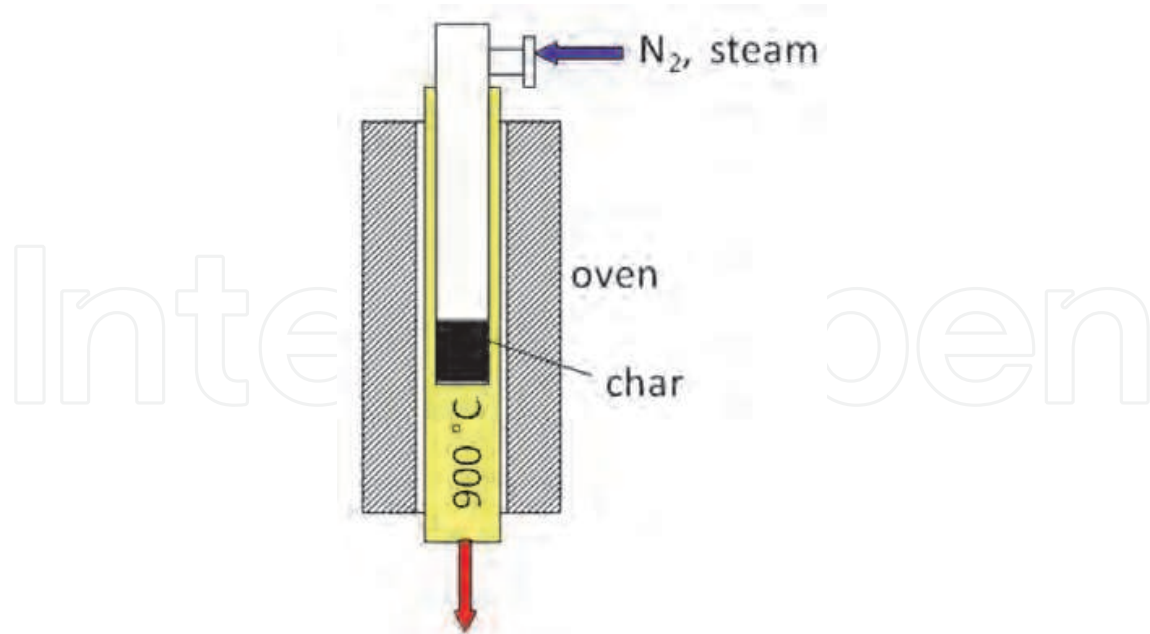


Fig. 2. Scheme of the activation reactor. The reaction tube can be passed through by steam flow. The case where the char is inserted has a porous bottom and can be removed from the tube.

The activation reactor consists of a tube furnace which can be heated to 1100°C. Inside of the furnace a tube with a small case at the bottom is inserted. The case contains the char and has a porous bottom to ensure, that the incoming gas (nitrogen or steam) flows through the char bed. The tube can be taken out of the oven. In the beginning of the experiment 5–10 g of char were inserted into the case with the porous bottom. Afterwards the case was fixed to the tube. The tube was then inserted into the hot furnace and the char was kept under nitrogen atmosphere. When the desired char temperature was reached the nitrogen flow was substituted by steam flow. After some minutes of reacting time, the steam flow was switched off, the tube was taken out of the reactor and cooled to ambient temperature under nitrogen atmosphere. The char mass was recorded and a sample of char was taken out of the case for surface analysis. The remaining char was again inserted into the oven for the next time interval. In this way the surface area of the char could be recorded as function of the conversion rate, i.e. actual char mass/initial char mass.

In the hot steam atmosphere the char got partially oxidized which lead to the loss of char mass and the production of gaseous products like H_2 , CO and CO_2 . Higher amounts of gaseous long-chain hydrocarbons were produced during the heat-up interval of the char as a result of incomplete pyrolysis at 600 °C. These gases may be of interest in terms of energetic utilization in order to rise the economy of the activated carbon production chain. One way of enhancing the calorific value of the exhaust gases may be a catalytic reforming process as reported in (Hornung et al., 2009a; Hornung et al., 2009b).

As a result of partial oxidation under steam atmosphere, the surface area of the char increases which is shown in Fig. 3-14. The surface area created by the chemical reactions in the steam atmosphere reaches a maximum. Higher char conversion leads to diminishing surface areas due to the lack of carbon. In the final stage, only ash remains.

Some of the char yields which remained at maximum surface area are given in Table 4 for rice straw and olive stones.

Time [min]	Rice straw [wt%] Act. Temp.: 800 °C	Olive stones [wt%] Act. Temp.: 750 °C
30	55	70
45	50	60
60	45	50
90	40	30

Table 4. Char yield as function of activation time for different biomass matters based on the dry initial char mass.

2.4 Surface measurement – BET method

The surface area 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. The char is exposed in nitrogen atmosphere at the boiling temperature of liquid nitrogen. The amount of nitrogen molecules which are adsorbed in a monolayer on the particles' surface specify the surface area. In addition pore size analysis and pore volume measurements are made with this technology (Klank, 2006).

2.5 Activation results

The following diagrams show the BET surface area as function of conversion rate, i.e. loss of char mass resulting from steam activation. The values are based on dry initial char mass. The initial char was produced in the lab-scale pyrolysis reactor by the use of various biomass matters. As shown from the diagrams the surface area increases with increasing conversion rate. At conversion rates of more than 80 wt% the surface area diminishes due to the lack of carbon.

Fig. 3 and 4 show the influence of conversion rate on the formation of surface area and the influence of activation temperature on activation time. The higher the activation temperature the lower the resulting activation time for the accessibility of a high surface areas. This example is given for crashed olive stones, but can be observed at all the other investigated biomass matters. Fig. 5-14 give a summary of the biomass type investigation for the applicability of activated carbon production.

From Fig. 3 to 14 it is shown that any kind of nut shell is appropriate for activated carbon production. Straw materials end up with surface areas around 800 m²/g which is the minimum value that commercially available activated carbons provide.

Activated carbon from rice straw with sufficient quality can only be attained if the straw matter is washed in alkaline solution like NaOH prior to the thermal treatment in order to extract the inorganic compounds (Finch, 1969). Intermediate surface areas can be attained with olive stones, spent grain, coffee grounds and sunflower shells. Due to the low feedstock price activated carbon which is made from these materials seems to have the most economic perspective.

The residence time of the biomass in the pyrolysis reactor averaged 1 hour at a heating rate of 10 K/min. A rotary kiln reactor which is described in (Hornung et al., 2005; Hornung & Seifert, 2006) was tested for pyrolysis of wheat straw pellets and rape seeds. Here the pyrolysis was run at heating rates of 30 K/min.

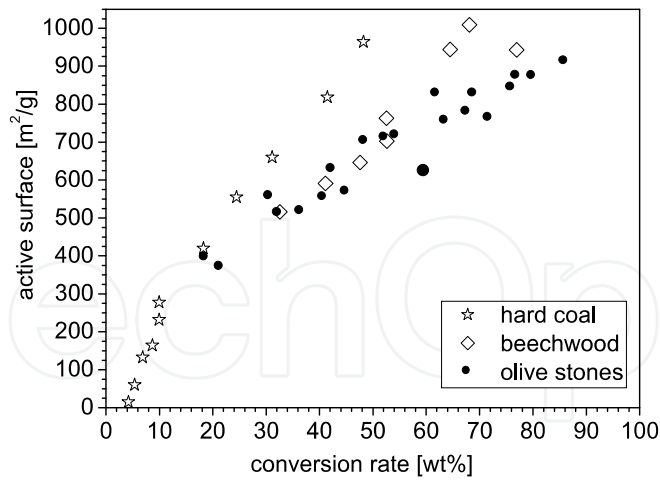


Fig. 3. Active surface of crashed olive stones compared with prevalent raw materials.

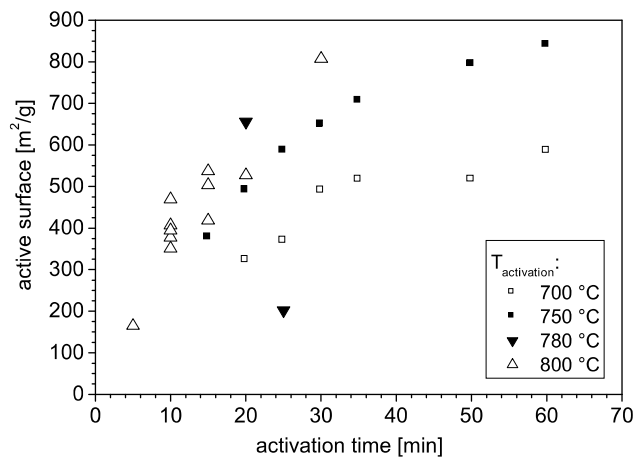


Fig. 4. Influence of activation temperature on activation time in the case of crashed olive stones.

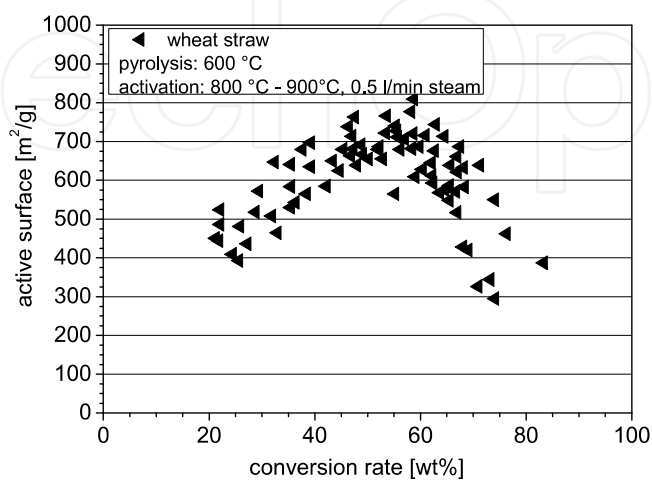


Fig. 5. Wheat straw

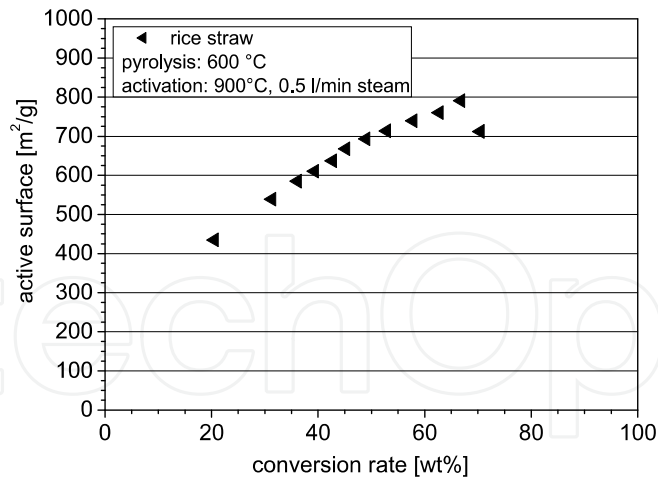


Fig. 6. Washed rice straw

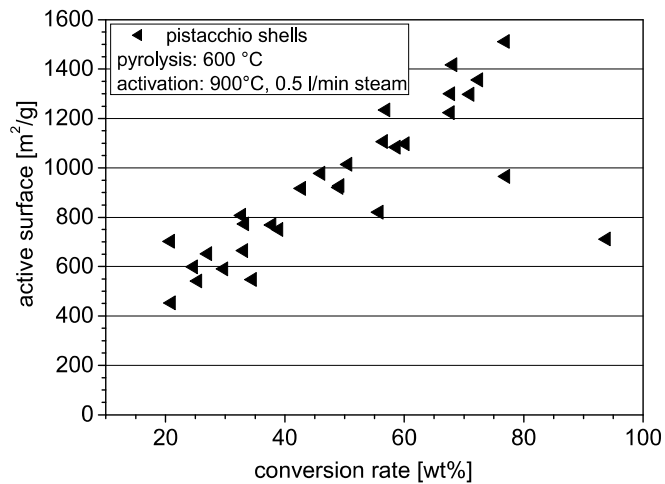


Fig. 7. Pistachio shells

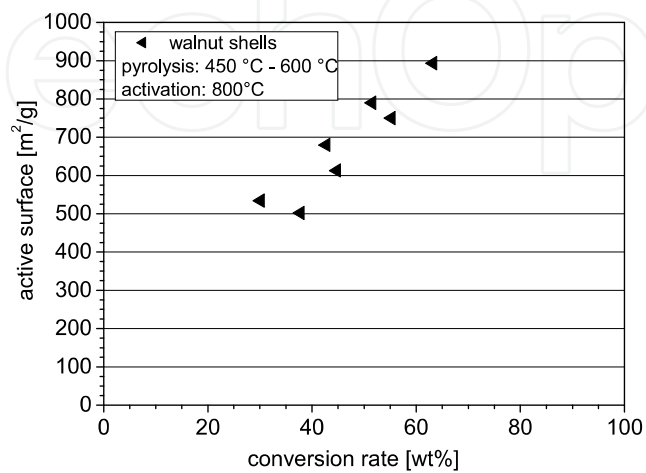


Fig. 8. Walnut shells. The steam flow was 0,5 l/min.

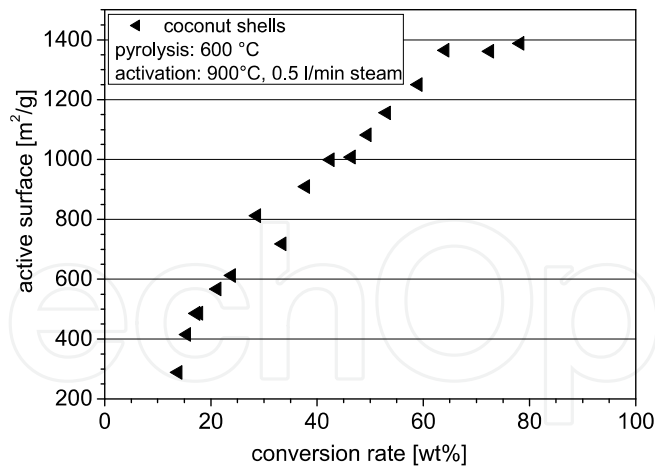


Fig. 9. Coconut shells

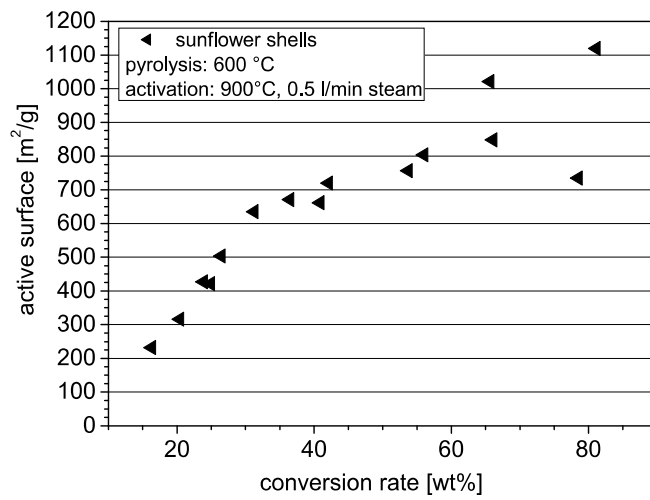


Fig. 10. Sunflower shells

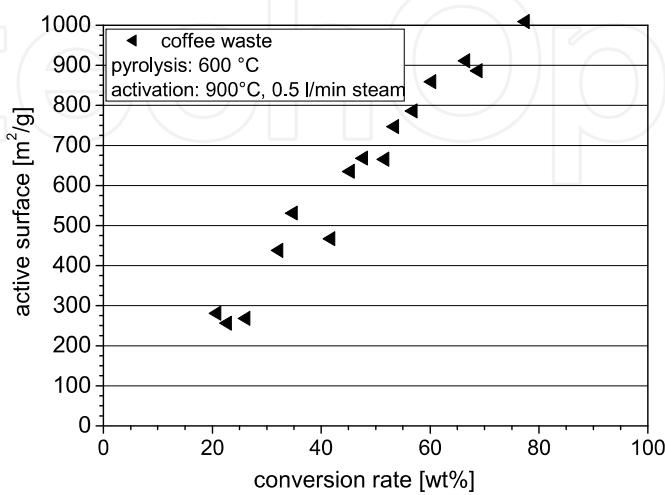


Fig. 11. Coffee waste

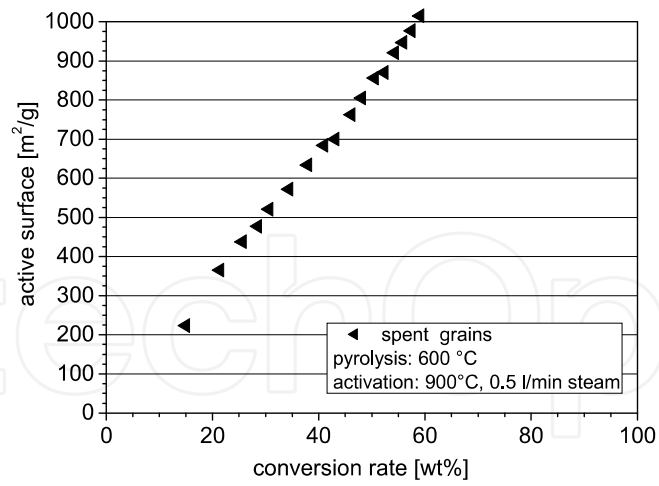


Fig. 12. Spent grain

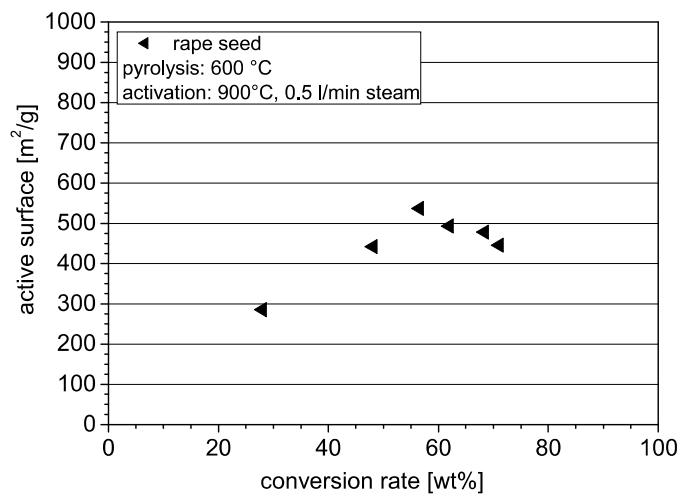


Fig. 13. Rape seed

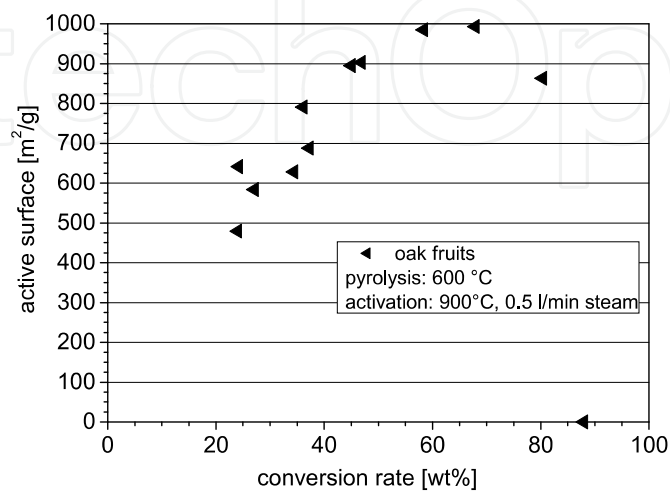


Fig. 14. Oak fruit

Within this heating range the influence of heating rate on the activated carbon quality is negligible. Lower residence times i.e. 10 - 20 min should be chosen for economic reasons. For this the use of the rotary kiln reactor (Hornung et al., 2005, 2006) is suitable. The residence time of char in the activation step is given as function of conversion rate in following diagrams, Fig. 15 and 16.

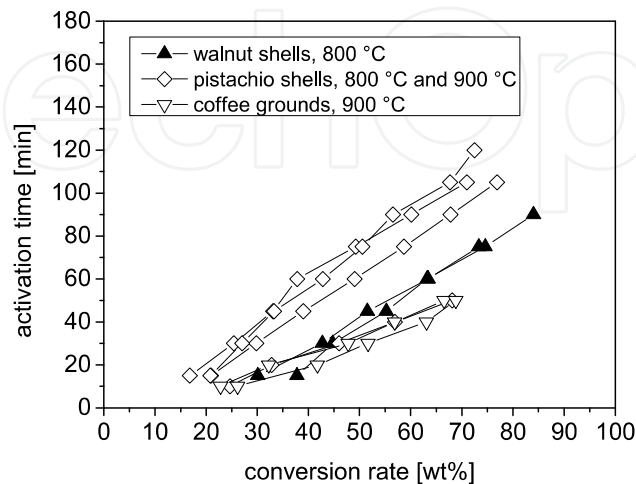


Fig. 15. Activation time as function of conversion rate.

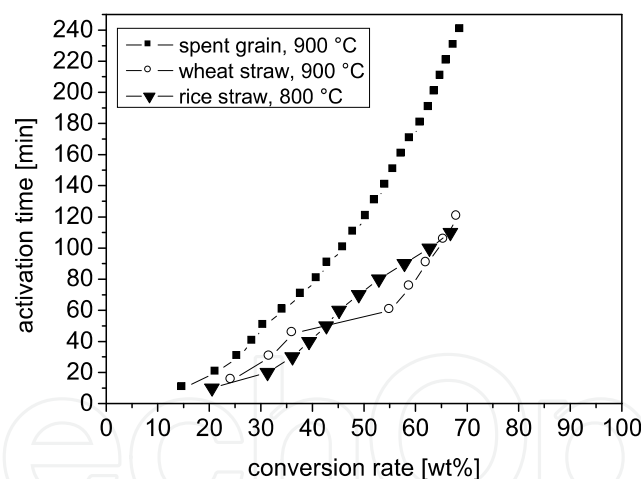


Fig. 16. Activation time as function of conversion rate.

In Fig. 15 the values of walnut shells and pistachio shells belong to 800°C activation temperature except the lower pistachio values which correspond to the activation temperature of 900°C. The activation time was varying from experiment to experiment. The reason for this might have been local effects due to inhomogeneous flow through of the small fixed bed. But nevertheless, experiments with wheat straw pellets exhibits that the char residence time needs to be in the range of 60 - 75 min. These results in combination with the lab-scale pyrolysis experiments are helpful to determine the production parameters of activated carbon from a special type of biomass in a continuous production process.

2.6 Pore size distribution

The pore size distribution of the investigated activated carbons were calculated by DFT method (Density Functional Theory) from the corresponding adsorption isotherms in Figure 17. DFT method (Evans et al., 1986) allows for the determination of the micro- and mesopore volume. The investigated carbons which were used for the isotherm measurements, Fig. 17, were high surface area carbons. As shown from Fig. 17 activated carbons from coconut shells, wheat straw, olive stones and walnut shells follow the same type of isotherm which was detected to be of IUPAC classification type I, indicating the presence of micropores (Sing et al., 1985; Klank, 2006). The hysteresis loops follow type H4 which refers to the presence of mesopores with a predominance of narrow slit-like pores.

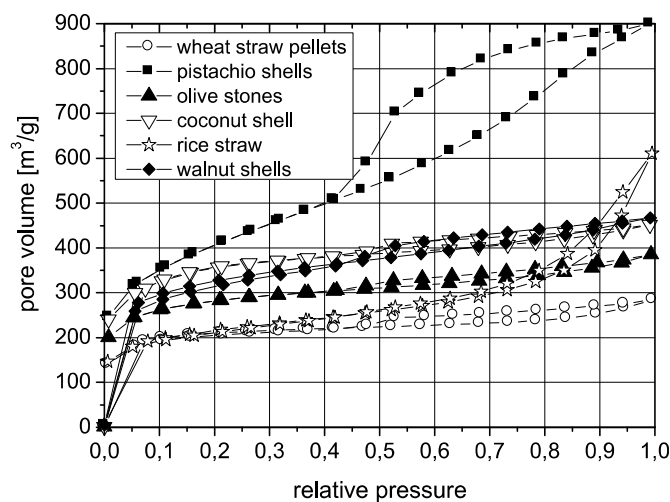


Fig. 17. Adsorption isotherms of nitrogen on various activated carbons.

Activated carbons from rice straw offer as well a high microporosity but at high pressure ratio, there is a steep increase in pore volume which gives rise to the presence of meso- and macropores. The adsorption isotherm of pistachio shells is different from the other curves and tends to type IV. There is a big hysteresis loop visible which can be regarded as hysteresis type H2 and gives rise to complex pore structure and network effects. Due to its resemblance to H1-hysteresis the pore size calculations were based on spherical pores.

The pore size diagrams of Fig. 18 a-d are similar and exhibit a predominant pore diameter of 40 Å, a high amount of micropores but nearly no macropores except the curves of pistachio shells and rice straw. The first one has a sharp peak in the range between 50 and 60 Å indicating a high amount of meso-/macropores. The micropore volume of pistachio shell char is lower compared to the other activated carbon types. The light slope of the curve at higher pore diameters gives rise to a high amount of macropores. For this activated carbons from pistachio shells are predominated by meso- and macropores. Activated carbons from rice straw are predominated by micropores but meso- and macropores are present as well. The shape of the isotherms indicates that all investigated biomass based activated carbons are characterized by a high amount of micro- and mesopores. Macropores are only present in activated carbons from pistachio shells and rice straw.

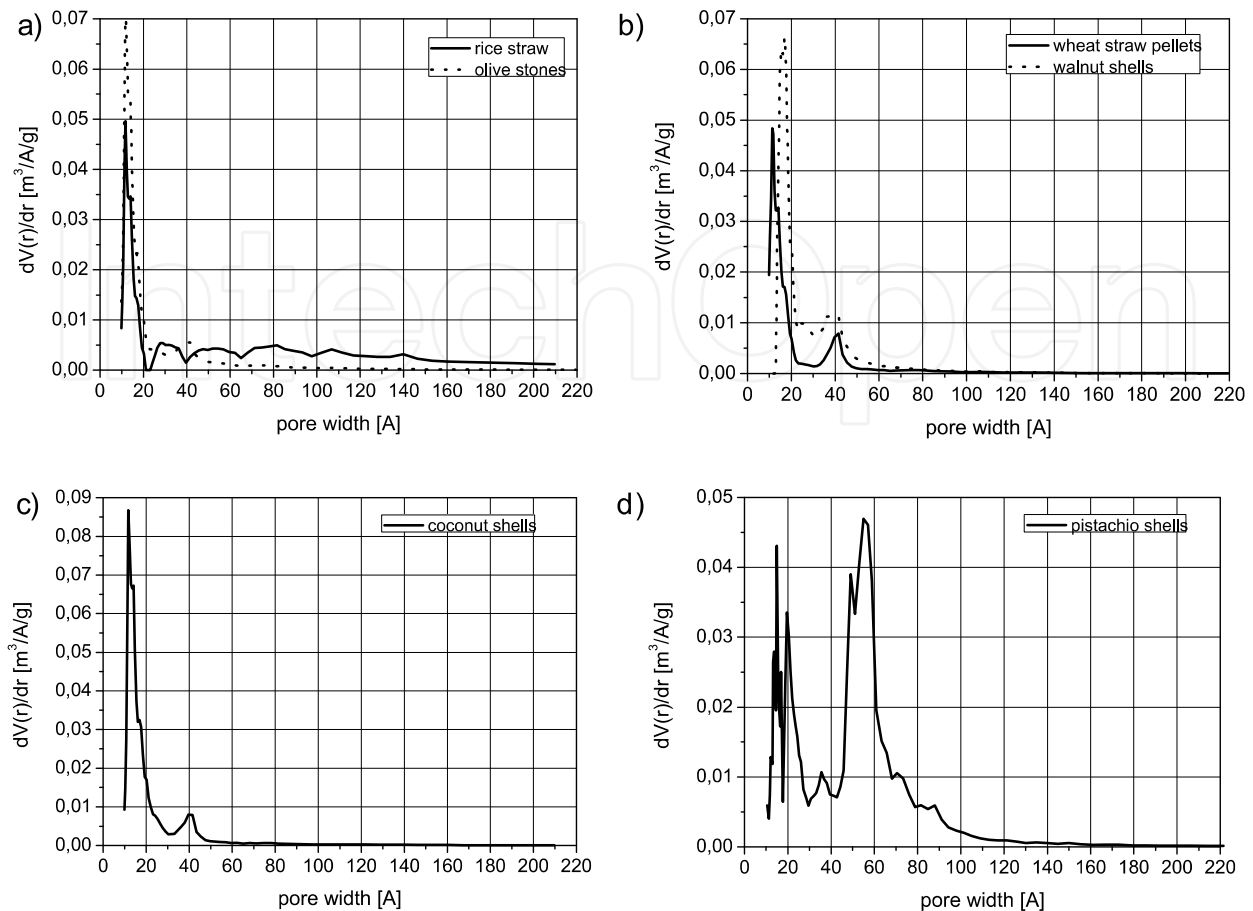


Fig. 18. a-d: Pore size distribution of various activated carbons by use of DFT-method. Activated carbons from pistachio shells are based on a cylindrical pore model whereas the others are calculated on a slit-like model.

3. Generation of granular activated carbon

Dependent on the application of activated carbon, the material has to be granulated for better handling purposes. For this pelletizing tests of char powder were made in order find out the pelletizing conditions. The chars which came out of the pyrolysis reactor were in nearly the same shape than the biomass was before. For this the chars had to be milled to particle sizes of 40 – 280 μm . To form stable pellets the use of a binder is necessary. State of the art is the use of molasses as binder material prior to pyrolysis (Pendyal et al., 1999). For economic reasons and from the aspect of using the high viscous pyrolysis tars for energetic applications the biomass pyrolysis tars were tested as binder material. The scheme of the pellet production is shown in Fig. 19.

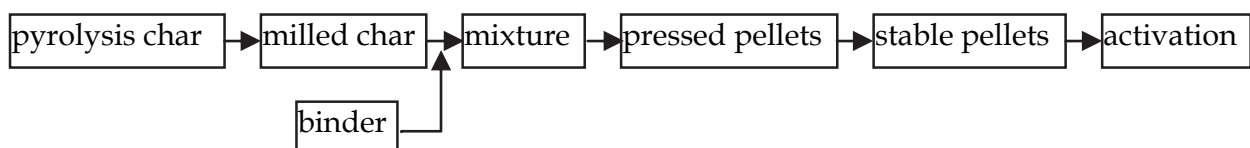


Fig. 19. Scheme of the pelletizing method.

The pelletizing procedure is implemented in between the pyrolysis and the activation step. During activation the binder was decomposed. For this many tar components passed into the gas phase during activation combined with the gaseous products from the char-steam reactions. This lead to an energy rich exhaust gas. Measurements of the exhaust gas composition were made in the pilot-scale rotary kiln reactor and are given in Section 4. For further applications and for economic reasons the possibility of using the exhaust gas energetically p.e. in a gas engine should be taken into account. This procedure allows for further use of pyrolysis tars which are too viscous in order to use them directly as a fuel in an engine. Especially for the energy rich tars from the pyrolysis of straw matters which are difficult to handle this procedure may be an option for further use.

The mixtures of chars and binder had to be put into a shape which was stable enough, to overcome the activation process. Test by extruding the mixtures were not successful. The extruder was either blocked or the pellets were unstable and melt after extruding. For this the concept of using a static press arose. A small lab-scale pressing unit was designed and build in order to test the pressing conditions. With the lab-scale pressing unit the pelletizing conditions were worked out. Several binders were tested and the char/binder ratios were varied. Furthermore the pressing conditions and the pressing temperatures were investigated.

The following Table 5 gives an overview of the pelletizing combinations.

Char	Binder Pyrolysis oils from	Pressing conditions	Temperature
wheat straw rice straw pistachio shells olive stones coffee grounds mixtures of wheat straw and pistachio shells mixtures of rice straw and pistachio shells	coconut press cake coffee ground wheat straw	150 bar - 350 bar	200 °C after pressing 200 °C while pressing

Table 5. List of pelletizing conditions. Combinations of these conditions were investigated.

The results of the pelletizing investigations can be summarized as follows. After activation the binder had passed into the gas phase. Therefore the loss of pellet mass was higher than the loss of unpelletized char mass at the same activation time. The surface area of the pellets corresponds to the surface area of the unpelletized char. With respect to surface area the influence of the binder is marginal.

Further, mixtures with different chars, i.e. chars with good and bad quality like rice straw and pistachio shells, lead to activated carbons with intermediate surface areas. This allows for the enhancement of surface areas from chars which are not of sufficient quality for activated carbon production.

The following pictures show the influence of the binder on the formation of surface area, Fig. 20, and the influence of char mixing, Fig. 21, for wheat straw carbons. Fig. 22 and 23 present the same effects of pelletizing and char mixing by the use of rice straw.

In Fig. 20 it is shown that the surface area of the pelletized char is similar to the unpelletized char but the values are shifted to higher conversion rates due to the fact that the binder evaporates and/or reacts with the steam atmosphere. Fig. 21 and 23 demonstrate that the

surface area is shifted to higher numbers when the wheat/rice straw char is mixed with char from pistachio shells.

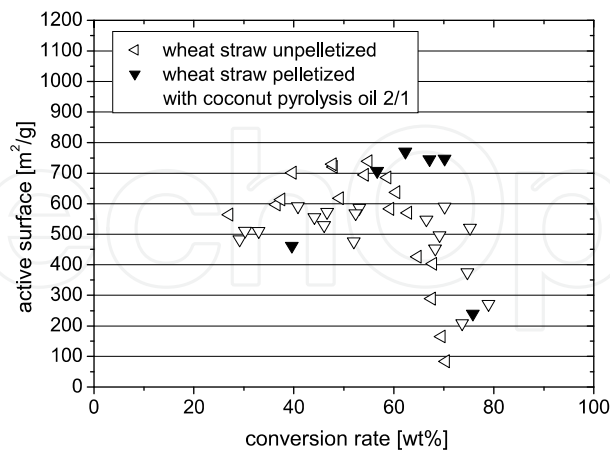


Fig. 20. Influence of binder on the formation of active surface during activation of wheat straw.

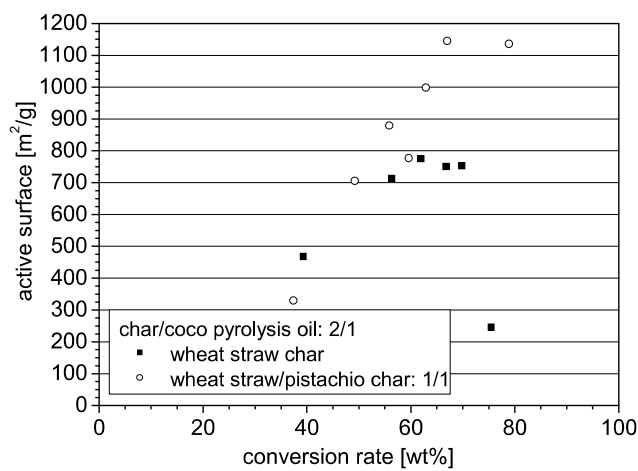


Fig. 21. Influence of char mixing on surface formation during activation in the case of wheat straw.

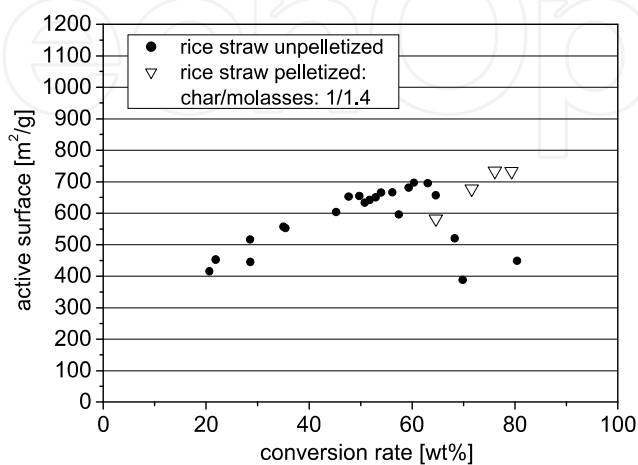


Fig. 22. Influence of binder on the formation of active surface during activation of rice straw.

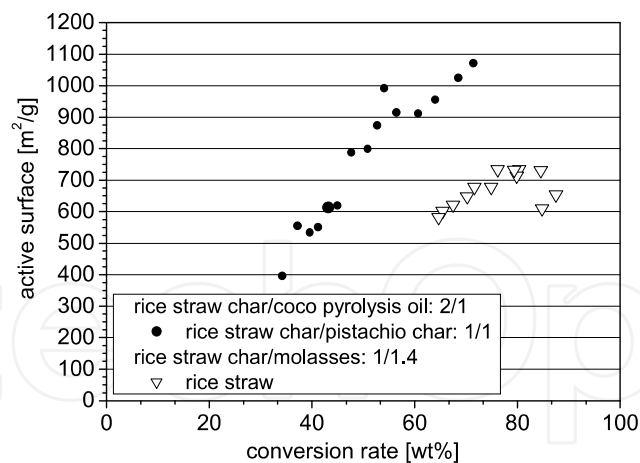


Fig. 23. Influence of char mixing on surface formation during activation in the case of rice straw.

The stability of the pellets, 4 mm in diameter and 20 mm long, was tested by the use of different char/binder ratios and pressing conditions. For this some of the pellets were disposed between the dies of a pressing unit. The break force of the pellets was recorded. These values are given in Tables 6 and 7. Best hardness was attained at a char/binder ratio of 2/1 and 1.5/1. To form the pellets, the char/binder mixtures were pressed at 20 bar and afterwards the matrix was heated in an oven for 2 hours at 200°C. Subsequently the hot matrix was put under the press again to form the pellets at 200 bar. After cooling to ambient temperature the pellets were taken out of the matrix. Another possibility of pellet formation was cold pressing at 200 bar and subsequent heating at 200 °C. As shown from Tables 6 and 7 heating and subsequent pressing leads to higher hardness of the pellets. A higher pressure did not enhance the hardness significantly.

The binders which lead to stable pellets were pyrolysis oil from coconut press residues, tars from wheat straw pellets and tars from coffee ground pyrolysis. Especially wheat straw and coffee ground tars are low in water content and of sticky consistency. Therefore they were regarded to offer good bonding conditions as reported in (Fütterer, 2008).

Binder: Pyrolysis oil	Char/Binder ratio	Pressing temperature	Pressure [bar]	Force [N]
Coffee waste	2/1	cold	250	136
Spent grain	2/1	200 °C	200	50.9
Coconut press residue	1/2	cold	250	103
	2/1	cold	100	50,6
			330	48.5
			200	34.2
250	88.6			
Wheat straw	2/1	cold	200	48
	1.5/1	200 °C	200	155
	2/1	200 °C	200	65.9
				44.5
				49.5

Table 6. Break strength of pellets made from wheat straw char. Bold: best combinations.

Binder: Pyrolysis oil	Char/Binder ratio	Pressing temperature	Pressure [bar]	Force [N]
Coconut press residue	1.5 / 1	cold	250	33.7
			350	73.6
		200 °C	200	38.7
Wheat straw	1.5 / 1	200 °C	200	205

Table 7. Break strength of pellets made from olive stone char. Bold: best combinations.

The stability of the pellets was not only influenced by the type of binder but as well by the type of biomass. Pellets from olive stone chars were very hard to form, due to the melting effects after pressing. Stable pellets could only be attained by the use of wheat straw tar as binder.

4. Rotary kiln reactor for char activation

The advantage of the lab-scale pyrolysis and activation facilities is the easy way of handling and the short heat-up times. Many experiments can be made in a short time interval. Unfortunately the possibility of treating larger amounts of biomass is not given. Likewise these facilities do not serve for an up-scale to an industrial production process neither for biomass pyrolysis nor for char activation. For this a new concept of an activated carbon production process had to be worked out.

For the pyrolysis step an already existing screw driven rotary kiln reactor (Hornung et al. 2005; Hornung & Seifert, 2006) was used to transfer the lab-scale experiments into a continuous production process. Unfortunately the pyrolysis temperature was limited to 500°C within this reactor. Tests were run with wheat straw pellets, olive stones, coconut press residues, rape seeds and spent grain. The chars were activated in the lab-scale facility. No influence of the chars from lab-scale experiments and rotary kiln pyrolysis was found after the activation step. The surface area of the chars from rotary kiln pyrolysis was similar to the area of the chars from lab-scale pyrolysis. The mass loss during activation was higher when the rotary kiln chars were used due to the lower pyrolysis temperature of 450°C–500°C. The lab-scale pyrolysis was run at 600°C. For this a lot of volatiles were left in the rotary kiln chars. Nevertheless, this type of reactor serves for the pyrolysis of biomass matters with respect of activated carbon production due to the latter heating of the chars to higher temperatures during activation.

The charcoal activation still needed a new upscale concept but some requirements had to be confirmed. First the production process had to be a continuous process with automatically operating feed and discharge systems. Second the char pellets had to be mixed with the steam quite well to ensure that partial char oxidation takes place over the entire particle's surface. Third the stirring of the particles had to be made softly because the char pellets were not stable enough to withstand high mechanical forces. Forth the residence time of the char inside of the reactor should be well controlled as well as the steam flux. Fifth the reactor should operate at 1000 °C and the possibility of changing the heat system from electrical heating to the use of gas burners should be taken into account.

As a result of these requirements the use of a further rotary kiln reactor seemed to be the most appropriate method for the scale-up of the activation process. To control the residence time of the char in the rotary kiln, it should be equipped with a rotating screw. The temperature control of the char is realized by the installation of five thermocouples along the screw axis. Although the principles of the rotary kiln pyrolysis reactor (Hornung et al. 2005; Hornung & Seifert, 2006) was used for the activation step, a total redesign of this reactor type was necessary in order to run the experiments at higher temperatures.

A sketch of the new, high temperature rotary kiln is shown in Fig. 24. It consists of a tube which is 2 meters long and the outer diameter amounts to 110 mm. The wall thickness is 6 mm. Inside of this tube a screw is located. Both parts consist of heat resistant steel. The tube and the screw can be turned independently from each other. The rotation of the tube insures the particle mixing whereas the rotation of the screw controls the char residence time. The tube is heated electrically by an oven over a length of one meter but it can be changed to gas burner heating if necessary. The axis of the screw is equipped with an electric heater and in the small gap between heater and wall of the screw axis the steam is flowing. Holes in the screw axis assure that the steam enters the reactor room. The steam itself is generated separately by a steam generator. In addition five thermocouples are fixed to the screw to allow for the char temperature control. The rotation speed of the screw is measured and controlled as well as the rotation speed of the tube. Both, the screw and the tube are driven by electric motors. Two valves, one at the feed system and one at the outlet prevent the air from entering the reactor. At the outlet steam, condensed water and the activated char is separated. The activated carbon is cooled to room temperature after leaving the reactor. The heat-up of the rotary kiln to 950°C needs about 3 hours and has to be run carefully due to the thermal expansion of the metal components. The reactor was designed for a char throughput of ~ 1 kg/hour. The valve on the right hand side of the reactor enables the char input. The steam flows through the screw axis and enters the reactor from the right. The steam and the exhaust gases leave the reactor via a small valve which is located close to the activated carbon outlet on the left hand side.



Fig. 24. Sketch of the high temperature rotary kiln reactor for char activation. The operation temperature is 950°C with steam flow and the char throughput amounts to max. 1 kg/h.

Fig. 25 gives an impression of the build-up of the activation rotary kiln reactor.



Fig. 25. Photograph of the high temperature rotary kiln reactor for char activation.

To proof whether this reactor is useful for char coal activation batch wise tests were run with char from wheat straw pellets and beech wood cubes. For this 80-100 g of char were inserted into the 950°C hot reactor. The residence time was varied between 40 min and 90 min and the steam flow was adapted to the lab-scale experiments and amounted to 1,7 – 2 m³/h. After collecting the activated carbon at the reactor outlet, the mass balance was established and the surface area measured. These results were compared with the lab-scale activation results and are given in Fig. 26 and 27. As shown from Fig. 26 and 27 the same or even higher surface areas could be attained with the rotary kiln activation. Only little mass got lost in the reactor as a result of particle destruction. Most of the particles left the reactor in the same shape as they got in but shrinkage due to the chemical reactions could be detected. As expected the particles were not pulverized due to the smooth transport and rotation.

The results are promising and this concept seems to have a good perspective for the activation of the biomass char. This principle allows for the scale-up of the activation step into a continuous production process. For the up-scale of the rotary kiln to a technical plant much attention has to be paid on the heat impact. Inner and outer heating ensures that the steam flux and the char reach the operating temperature.

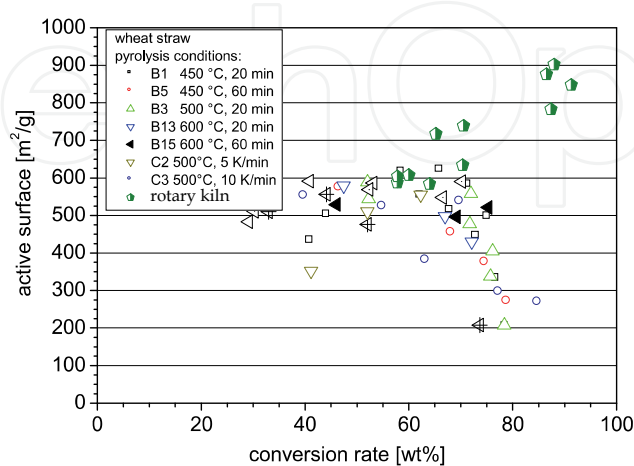


Fig. 26. Comparison of lab-scale and pilot-scale activation in the case of wheat straw pellets. The half-filled pentagons are the pilot scale results of the rotary kiln.

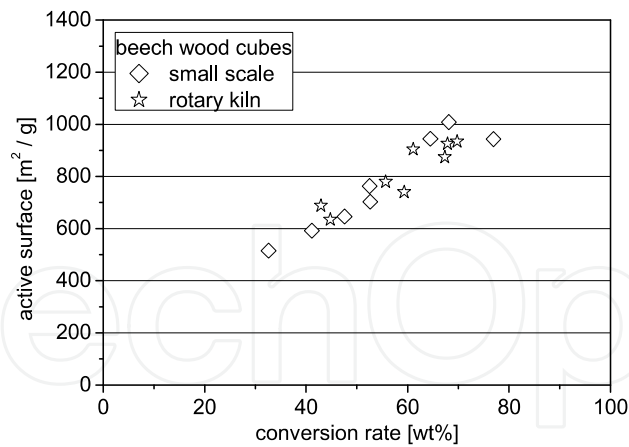


Fig. 27. Comparison of lab-scale and pilot-scale activation in the case of beech wood cubes.

gas component	Experiment 1: 600 g char input				Experiment 2: 600 g char input			
	[vol%] (1)	[wt%] (1)	[vol%] (2)	[wt%] (2)	[vol%] (3)	[wt%] (3)	[vol%] (4)	[wt%] (4)
H ₂	52,78	6,87	56,14	7,49	55,56	7,36	58,62	8,07
O ₂	0,31	0,65	0,20	0,43	0,01	0,03	0,26	0,58
N ₂	1,45	2,62	0,97	1,80	0,05	0,10	1,12	2,13
CO	19,52	35,29	23,27	43,12	23,12	42,52	22,46	42,94
CH ₄	10,33	10,70	4,95	5,25	5,97	6,29	3,31	3,63
CO ₂	15,18	43,12	14,26	41,52	14,82	42,84	14,18	42,57
C ₂ H ₂	0,01	0,01	0,00	0,00	0,01	0,02	0,00	0,00
C ₂ H ₄	0,41	0,75	0,21	0,38	0,46	0,84	0,05	0,09
H _u [MJ/kg]	17,5		16,15		16,67		15,87	
H _o [MJ/kg]	19,6		18,08		18,85		17,83	
BET [m ² /g]	516		482		474		519	

Table 8. Composition of water free gas atmosphere during steam activation of 600 g wheat straw pellet pyrolysis char. The values are based on the volume resp. mass of water free gas samples. The numbers indicate sampling after 25 min (1), 30 min (2), 37 min (3), 46 min (4).

To proof whether the exhaust gases which were produced during activation of the char in the rotary kiln reactor have the potential of being used energetically, the composition of the gas and steam atmosphere was analyzed by gas chromatography, (Agilent 6890A Plus, packed column Carboxen™ 1000 from Supelco with helium flow of 20 mL/min).

This method required a water free gas sample. For this, the exhaust gas flow was cooled to (-50) °C in several cooling units. An additional filter unit allowed for a water free gasflow.

At the outlet of the cooling section, gas samples were collected at different instants of time. The experiments were run with 600 g of wheat straw pellets and a steam flow of 1,7 – 2 m³/h. Prior to activation the wheat straw pellets were pyrolysed at 600 °C in the pyrolysis rotary kiln reactor for 20 min. The composition of the water free exhaust gas is documented in (Barth, 2009) and given in Table 8. The experiments were run batch-wise. The reason for it was the better control of the process due to the fact, that the in- and outlet valves did not operate automatically at this instant of time. As shown in Table 8 the calorific value is mainly determined by the gas contents of H₂, CO and by small amounts of CH₄. This gas composition corresponds to a typical synthesis gas which is produced during gasification of hydrocarbons and carbon matters. Behind the cooling unit, the gas flow was measured and amounted to 0.8 m³/h. Compared to the steam flow of around 2 m³/h the dilution of the exhaust gas was quite high. Therefore the steam flow should be reduced and its influence on activated carbon quality should be investigated.

5. Conclusion

The generation of activated carbon in a two step process of pyrolysis and steam activation from different waste biomass matters was investigated in both, lab-scale and pilot-scale facilities. The lab-scale experiments provided a database for the production parameters of best quality carbons with high surface areas. The surface measurements were determined by BET method. Activated carbons with high BET surface area can be generated with any kind of nut shells, like pistachio, walnut or coconut. The BET surface amounts to more than 1000 m²/g. Intermediate values of 800 – 1000 m²/g can be accomplished with beech wood, olive stones, spent grain, sunflower shells, coffee waste and oak fruits. Straw matters and rape seeds do not serve well for activated carbon production due to their low BET surface of 400–800 m²/g. Especially rice straw leads to low surface values unless it is not treated with alkaline solvents prior to pyrolysis. The activated carbons are mainly dominated by micro- and mesopores of 40–60 Å. Macropores are as well present in rice straw and pistachio shell carbons.

The composition of the exhaust gases which occur during char activation is determined mainly by H₂, CO, Methane and CO₂. This corresponds to a typical synthesis gas, which occurs during gasification of carbon matters. Due to the high amount of combustible components (50-80 vol%) the dry exhaust gas may serve for energy recovery of the activated carbon production process.

Investigations were made to prove whether pyrolysis tars can be used as binder material for granulated activated carbon production. The pelletizing conditions were worked out and the influence of the binder on the quality and stability of the pellets was tested as well as the influence of char mixing. Heating and pressing of the char/binder mixtures led to stable pellets by the use of pyrolysis oils of coconut press residues, wheat straw and coffee grounds. Mixing of different kinds of chars resulted in intermediate BET surface areas.

Finally a concept for a continuous production process was given. For this a new high temperature rotary kiln reactor was designed which can be heated to 1000 °C. An inner screw allows for a smooth transport of the pelletized material. The char residence time was controlled by the rotation speed of the screw. The experiments showed, that the activated carbons which were produced in the rotary kiln were of same quality than the carbons from the lab-scale facility with respect to surface area. It demonstrates that this type of reactor is suitable for a continuous activated carbon production process.

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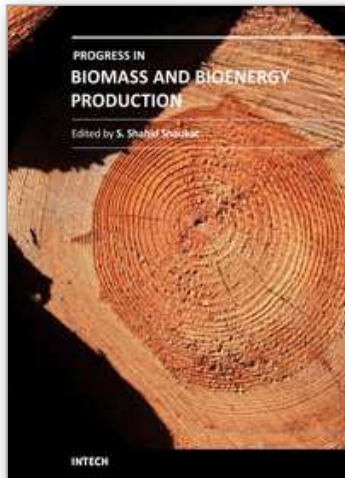
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Alternative energy sources have become a hot topic in recent years. The supply of fossil fuel, which provides about 95 percent of total energy demand today, will eventually run out in a few decades. By contrast, biomass and biofuel have the potential to become one of the major global primary energy source along with other alternate energy sources in the years to come. A wide variety of biomass conversion options with different performance characteristics exists. The goal of this book is to provide the readers with current state of art about biomass and bioenergy production and some other environmental technologies such as Wastewater treatment, Biosorption and Bio-economics. Organized around providing recent methodology, current state of modelling and techniques of parameter estimation in gasification process are presented at length. As such, this volume can be used by undergraduate and graduate students as a reference book and by the researchers and environmental engineers for reviewing the current state of knowledge on biomass and bioenergy production, biosorption and wastewater treatment.

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