

Physical Activation of Wooden Chips: Effect of Particle Size, Initial Humidity and Acetic Acid Extraction on the Properties of Activated Carbons

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Abstract

In this research, two different wooden biomasses (birch and pine) were thermally carbonized and steam activated into activated carbons in a one-stage process. The effects of particle size and humidity (as received and oven dried) on the properties like specific surface areas, pore volumes and pore size distributions of final activated carbon characteristics has been studied. Another set of biomasses (birch, spruce and pine) was pre-treated before the carbonization and activation steps in an extractive process using a weak acetic acid in Soxhlet extractors. According to the results, dried samples have slight lower surface area while no difference could be found regarding the yields. Regarding the extracted samples there is a significant difference especially in the pore size distributions compared to the non-extracted ones. There appears to be a shift from a meso-microporous distribution to a microporous distribution as a result of the extractive pre-treatment.

Keywords: Biomass, Carbonization, Activation, Activated carbon, Acetic acid, Pore distribution.

Introduction

Activated carbons are used for many purification applications in different industrial processes including wastewater treatment, gas cleaning processes and metal removal from waste streams [1-3]. Activated carbon has also been used as a support for heterogeneous catalyst [4-6] or as a catalyst itself [7,8]. The consumption and possible applications of AC are continuously increasing in the world scale prospective [9].

Most carbon containing substances, including industrial waste fractions, can be carbonized in thermochemical processes into substances with a high carbon content. These substances can be further converted into activated carbons (AC) through chemical or physical activation processes including thermal treatment steps [10].

Traditionally activated carbons have been prepared from a number of carbon rich biomasses like coconut shells, coal (lignite) and sawdust as raw materials [3,11]. The thermal conversion of biomass into activated carbon is a two-step process starting with a carbonization phase performed in an inert atmosphere. In this first step, the biomass is converted into solid carbon. This carbonization occurs under inert gas atmosphere (i.e. nitrogen) at temperatures ranging from 873 to 1073K [12]. The product from the initial carbonization step contains a high level of carbon (up to 60%), but metals and ashes are also present, concentrated from the initial biomass during this process.

In the second step the carbon is activated chemically or physically creating structures with well-defined pore size distributions depending on the final use of the AC. Most biomass-based materials with significant

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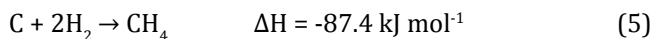
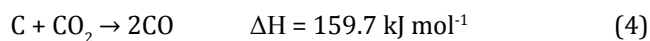
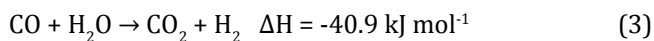
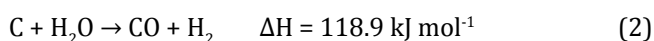
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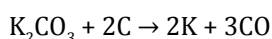
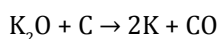
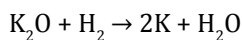
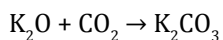
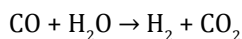
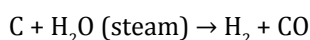
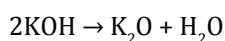
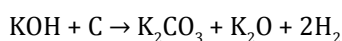
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carbon content can be steam activated in a two-stage process following the reactions below [13]. Reaction (1) describes a summary of the carbonization step and reactions (2-5) are reactions during the steam activation step.



In chemical activation process, the carbonized biomass is first impregnated with activating agents like phosphoric acid, sodium or potassium hydroxides, dried and then activated at temperatures between 670 and 870 K in an inert atmosphere. The activating agents in the carbons are removed by acid wash, the activated carbons are washed with distilled water, dried and characterized. One of the advantage of chemical activation is the production of more uniform pore distribution and higher carbon yields.

A typical chemical activation mechanism involves KOH because of the capability of K at high temperatures (700-1225 K) to form intercalating compounds with carbon and K_2O that reduced by carbon release CO_2 that creates the pores [14]:



There is an extensive research ongoing for new raw materials that can be converted into activated carbon. New sources that can be used include fractions regarded as industrial waste like lignin from pulping processes and even used car tires [15-17]. One problem with these materials is that they can contain rather high levels of metals and other inorganics, resulting in an ash content in the final products (particularly acid-water soluble ashes) higher than the level that can be accepted by end-users of activated carbons [18] but the quality demands are highly dependent on the final use. Most of the ashes are not soluble in water at pH close to neutral but they can easily dissolve if the carbons are used at low pH conditions contaminating the stream.

A number of methods have been used in order to decrease the amount of ashes accumulated during the carbonization and activation process. The demineralization process can be applied directly to the biomass used, to the intermediate formed during carbonization or to the final product. In order to minimize the ash content different chemicals have been tested. In a study rice straw was demineralized using

a number of chemicals like distilled water, acetic acid and low concentration (5%) of hydrochloric, sulfuric, nitric and orto-phosphoric acid [19]. Carbon black prepared from used car tires was demineralized using sulfuric acid in different concentrations [20].

In the present study, a series of wood-based biomasses were carbonized and steam-activated in a one-stage process. Four different sizes of wood-chips were used (2mm, 6mm, 2cm, sawdust), and the effects of particle size, wood species, moisture content and extraction pretreatment were studied regarding yields, carbon content and specific surface areas. The extraction was performed using Soxhlet extraction with weak organic acid (acetic acid). The results obtained give new knowledge about the factors affecting the properties of the activated carbons produced. The pre-extraction presents a novel method to produce highly microporous wood-based activated carbons.

Material and Methods

Biomasses used for carbonization and activation

Wooden chips from birch (*Betula pendula*), and spruce (*Picea abies*) were used for carbonization and activation studies. The chips were sieved to three different sizes 2mm, 6 mm and 2 cm. In the carbonization and activation studies, the chips were processed as received (Ar) and dried (D) for 24 hours at 378 K. In the extraction tests (Ex), saw dust (Sw) of birch (*Betula pendula*), spruce (*Picea abies*) and pine (*Pinus sylvestris*) were used.

Determination of moisture content

Known masses of the chips were weighted into tared beakers and dried at 378 K until constant weight. Moisture content, given as percent, was calculated as mass lost divided by the initial mass.

Carbonization and activation procedure

Carbonization and activation of the different particle size samples was performed in a single-stage process using a rotating quartz reactor inserted in a Nabertherm oven. About 400 g of each sample was inserted in the reactor, during the carbonization step the temperature ramped from room temperature to 1073 K (10 K/min). At 1073 K the temperature was kept for 2h, during this period the reactor was flushed with 120 g/h of overheated steam (413 K) produced by a Bronkhorst steam generator, fed with a constant, known, volume of water using nitrogen gas as carrier. During the whole process the reactor was flushed with nitrogen in order to prevent oxidation of the samples. The oven was cooled down over night, continuously flushed with nitrogen.

Due to the small amounts of extracted samples available, the carbonization and activation of the sawdust samples was performed as a one-stage process in a fixed-bed, stainless-steel reactor (Φ 12mm) inserted in a tubular oven (Nabertherm GmbH). The parameters used for carbonization and activation are the same with the exception that the mass of samples were 5 grams/sample and the steam feed of 30g/h. The setup of the equipment is presented in Figure 1.

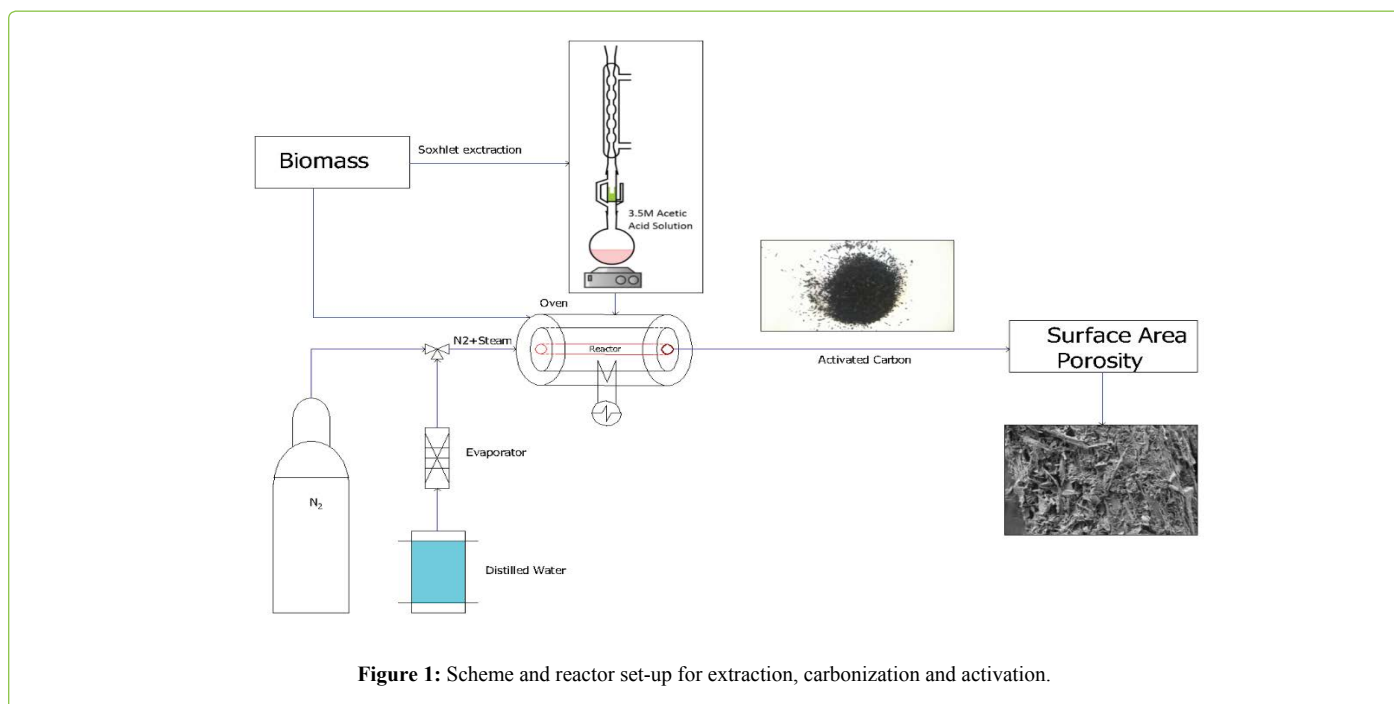


Figure 1: Scheme and reactor set-up for extraction, carbonization and activation.

Determination of yields and total carbon content

The mass yield from each sample was calculated as the mass of wood-based activated carbon divided by the mass of the initial sample used for carbonization and activation.

The content of carbon present in the initial chips (dried) used and in the activated carbons produced, given as total carbon (TC) percent, was measured using a solid phase carbon analyzer (Skalar Primacs MCS). Dried and crushed samples were weighted in quartz crucibles, combusted at 1373 K in an atmosphere of pure oxygen and the CO₂ formed was analyzed by an IR analyzer. Carbon content values were obtained by reading the signal of IR analyzer from a calibration curve derived from known masses of a standard substance, citric acid. The total mass of carbon in each sample was calculated as a percent of the mass initially weighted and was measured.

Specific surface area and pore size distribution

Prior to measurements portions of each sample (about 200 mg) were pretreated at low pressures and high temperatures to clean the surfaces. Adsorption isotherms were obtained by immersing sample tubes in liquid nitrogen (76 K) in order to obtain isothermal conditions. Nitrogen was added to the samples in small steps and the resulting isotherms were obtained. Specific surface areas were calculated from adsorption isotherms according to the BET (Brunauer-Emmett-Teller) method [21]. Pore size distributions were calculated using the DFT (Density functional theory) algorithm with slit geometry. The t-Plot model has been used considering Harkins and Jura thickness curve and Langmuir surface area considering correlation coefficient higher than 0.999. With the setup of the instrument used, a Micromeritics ASAP 2020, pores down to 1.5 nm in diameter can be measured.

Extraction process

A 4 hours long time demineralization was performed using 3.5 M acetic acid (Sigma Aldrich 100%) as extracting agent. Aliquots of each wood species were transferred into cellulose thimbles of the Soxhlet extraction unit. Sawdust size less than 2 mm was selected for the extraction. After demineralization the samples were suction filtered on glass filters and washed with distilled water until the pH of the filtrates was neutral. Finally, the samples were dried for 24 hours at 378 K in an oven equipped with mechanical convection. The samples were finally carbonized and steam activated according to the procedure described in section carbonization and activation procedure. The carbons produced were analyzed for specific surface areas and pore size distributions as described in section specific surface area and pore size distribution.

Results and Discussion

The biomass fractions from different wood species used in this study can be regarded as waste fractions. These biomasses are also known to have a rather high initial level of carbon and can rather easily be converted into activated carbon.

Effect of particle size on the activated carbon porosity

The biomass fractions from different wood species used in this study can be regarded as waste fractions. In table 1, the values of yield, humidity and total carbon divided for the different particle size and initial moisture content are reported. The results show a small difference between wood species and the particle sizes considered. In particular, the yield for the process parameters selected is about 5%. On a dry base this value increases to 10-15% coherently with the moisture content (around 50%).

In table 2 the porosity characteristics of the different

Table 1: Total carbon content, humidity and overall yield after activation.

Sample	Total carbon content (%)	Yield (%)	Humidity (%)
Spruce_2cm_ar	71.1	5	50
Spruce_6mm_ar	94.5	4.9	-
Spruce_2cm_dry	-	12	-
Spruce_2mm_ar	-	5	-
Birch_2cm_ar	87.6	4	52
Birch_6mm_ar	89.9	2.5	-
Birch_2cm_dry	-	14	-
Birch_2mm_ar	-	4.5	-

Table 2: Specific surface areas and pore size distributions of the different activated carbons.

Calculation method	Unit	Spruce 2cm_Ar	Spruce 2cm_D	Spruce 6mm_Ar	Spruce 2mm_Ar	Birch 2cm_Ar	Birch 2cm_D	Birch 6mm_Ar	Birch 2mm_Ar
BET									
SSA	m ² /g	1066	983	1048	990	906	833	1063	1029
Pore volume	cm ³ /g	0.848	0.710	0.800	0.700	0.625	0.590	0.765	0.740
C value		1438	2229	1646	2783	2702	2371	934	3123
Langmuir surface area (c.corr.>0.999)	m ² /g	1323	1217	1287	1227	1121	1040	1280	1262
t-plot									
Micropore volume	cm ³ /g	0.221	0.208	0.205	0.210	0.186	0.165	0.225	0.199
Micropore area	m ² /g	499	398	496	509	364	322	551	472
External surface area	m ² /g	555	505	576	498	472	473	538	575
DFT									
Pore volume	cm ³ /g	0.736	0.627	0.689	0.623	0.535	0.544	0.656	0.647
μpores	cm ³ /g	0.289	0.276	0.289	0.279	0.256	0.236	0.298	0.282
Mesopores	cm ³ /g	0.446	0.348	0.397	0.343	0.27	0.305	0.355	0.355
Macropores	cm ³ /g	0.001	0.003	0.003	0.001	0.009	0.003	0.003	0.010
μpores	%	39	44	42	45	48	43	45	44
Mesopores	%	61	56	58	55	50	56	54	55
Macropores	%	0	0	0	0	2	1	1	1

Ar= Carbonized and activated as received, D= Oven dried before carbonization and activation

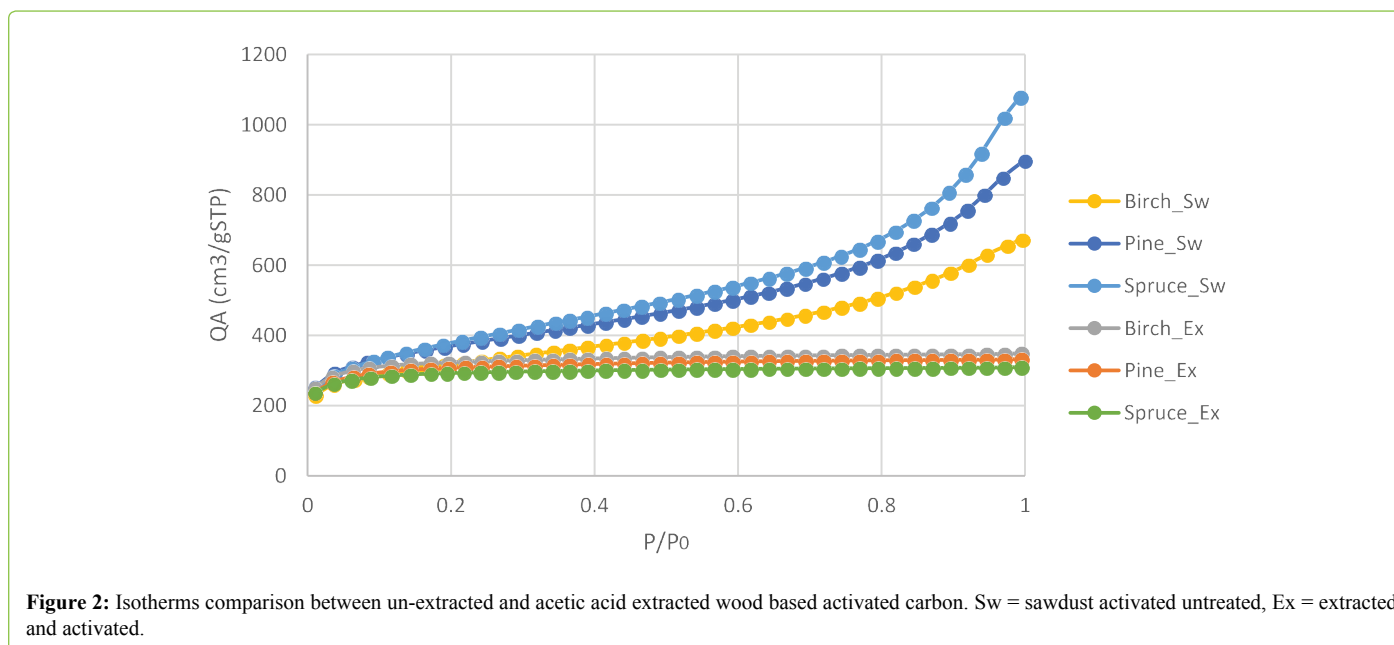


Figure 2: Isotherms comparison between un-extracted and acetic acid extracted wood based activated carbon. Sw = sawdust activated untreated, Ex = extracted and activated.

particle size are reported. In this case, it is more evident a small reduction in BET surface for the samples pre-dried. Concerning the pore distribution from both DFT model and t-Plot no evident changes has been detected with an almost equal distribution between micropores and mesopores. As possible to see, the wood type has also a small influence on

the porosity suggesting that the main factor is correlated with the activation process parameters. It is evident that steam activation, as known, favors the creation of mesoporosity. The different particle size in the range considered for this experiment, is not affecting the porosity characteristics indicating that the activation process is a surface reaction

suggesting that optimizing the surface-to-volume ratio more than just the size can be a probable option to improve the activated material. About pre-dried samples, no relevant difference can be evidenced on the porosity of the final activated carbon.

Effect of extraction process on the activated carbon porosity

During the thermal steam activation, some mass was removed from the precursors, in this case wood sawdust. The remaining mass obtained after drying of the activated samples was calculated as % of the initial mass and denoted yield. In general, the yield after the activation step was higher for the extracted samples compared to the direct activated ones, 14-17 % and 3-10 % respectively. The main reason for this difference might be the removing of moist content and that easily removable structures are extracted already in the pretreatment step. The same structures are most likely also removed during the thermal activation of the untreated precursors. Eventual mass losses during the extraction step was, however, not measured in this study.

Even if the specific surfaces are rather similar there is an evident difference regarding the pore size distributions. This is visible by a shift in the shape of the adsorption isotherms as presented in figure 2.

The isotherms obtained from the untreated samples are all of Type II indicating the presence of mesopores. The isotherms obtained from extracted samples before the carbonization and activation, are all of Type I indicating that most of the pores are in the micropore region.

The results from the analysis of specific surface areas (BET model) and pore-size distributions (DFT model) show that the steam activated samples have specific surface areas exceeding 1000 m²/g as presented in table 3. This concerns both untreated activated and extracted activated samples.

The change in pore volume distribution can also be noticed from the calculations of pore volumes according to DFT algorithm. Particularly, results show that the extraction process increases the micropores percentage in the activated samples while the untreated activated samples have a predominant presence of mesopores. For untreated and activated wood samples biomass, the portion of micropores it is around 30% while the portion of micropores in the extracted ones it is around 90% as calculated from the pore volumes.

A possible explanation of the shift in pore distribution to micropores in the extracted samples compared to the untreated ones can be a decrease in the content of the metals needed to create mesopores during the thermal activation process. These findings are also an indication that the reaction of steam with the biomass (physical activation) is the most important factor in the production of activated carbons but not the only one, therefore appears to occur some degree of chemical activation. In table 3, the comparison with untreated sample sawdust in order to confront samples run in the same reactor and in the same process conditions is reported.

There is a significant difference in the pore volumes as presented in tables 2 and 3 even if the same species of wood

Table 3: Porosity characteristics of the activated carbons produced from un-extracted and extracted sawdust.

Calculation method	Unit	Spruce_Sw	Birch_Sw	Pine_Sw	Spruce_Ex	Birch_Ex	Pine_Ex
BET							
SSA	m ² /g	1302	1190	1296	1125	1109	1141
Pore volume	cm ³ /g	1.669	1.053	1.260	0.538	0.476	0.511
C value		3611	1415	1657	1095	3812	4043
Langmuir surface area (c.corr.>0.999)	m ² /g	1407	1393	1464	1530	1335	1462
t-plot							
Micropore volume	cm ³ /g	0.090	0.160	0.138	0.397	0.321	0.396
Micropore area	m ² /g	155	346	275	993	824	990
External surface area	m ² /g	1147	843	1020	231	284	151
DFT							
Pore volume	cm ³ /g	1.370	0.973	1.280	0.455	0.395	0.427
μpores	cm ³ /g	0.290	0.310	0.330	0.408	0.376	0.392
Mesopores	cm ³ /g	1.050	0.640	0.900	0.046	0.016	0.033
Macropores	cm ³ /g	0.030	0.023	0.05	0.001	0.003	0.002
μpores	%	21	32	26	90	95	92
Mesopores	%	76	66	70	10	4	7
Macropores	%	2	2	4	0	1	1

Sw=Sawdust activated untreated, Ex=Extracted and activated

Table 4: Total carbon content and yield of extracted sawdust based activated carbon.

Sample	Total carbon content (%)	Yield (%)
Spruce_Ex	89.5	14
Birch_Ex	87.8	17
Pine_Ex	84.1	12

and the same carbonization and activation parameters were used. There are, however, two major differences between the series. One it is in the shape of the biomass used. In table 2, wood chips made in a cutting mill producing needle shaped chips in fiber direction were used, while in table 3 sawdust where the fibers are cut in a direction perpendicular to the wood-fibers was selected. The other major difference it is the oven used: for data in table 2, a rotating quartz oven while in table 3 a fixed-bed stainless steel reactor.

The total carbon content in the pretreated samples as evident in table 4 results to be slight lower compared to the untreated one probably due to the previous extraction of organic compounds in the starting material that “compensates” the ash reduction. A further investigation not part of this study would be to know how acetic acid affects the biomass structure during the extraction differently from the thermochemical decomposition process.

Conclusion

It is well known that a number of parameters affect the properties of activated carbons produced from biomass. The results achieved in this study indicates that different particle size of the starting biomass has a small but measurable influence on the activated carbon porosity. Previously dried biomass appears to produce activated carbons with a slightly lower BET surface area.

The pre-extraction of the biomass using acetic acid induces a significant increase in the microporosity during the steam activation. This change in pore-size distribution is most likely due to the lack of chemical activating agents in the form of metals and minerals present naturally in the wood. To some extent, the change could be a result of alterations in the biomass composition because of the extraction process. The use of a pre-extraction process with the resulting change in pore-size distribution represents a versatile method to produce activated carbons with specific pore-size distributions without affecting the specific surface-areas.

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