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# PYROLYSIS OF BIOMASS

- **Rapid Pyrolysis at High Temperature**
- **Slow Pyrolysis for Active Carbon Preparation**

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**Dissertation**

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## SAMMANFATTNING

Pyrolys av biomassa innebär uppvärmning av biomassa i inert atmosfär. Produktutbytet (char, tjära, gas) beror av processbetingelserna. I första delen av avhandlingen behandlas snabb pyrolys av ved (björk och vit quebracho) och några jordbruksavfall (olivavfall, sockerrör bagass samt obehandlad och pelletiserad halm) vid hög temperatur (800°C – 1000°C) i en falltubsreaktor. Betingelserna är av intresse för förgasning i fluidiserade bäddar. Char och gasproduktion, gassammansättning samt charreaktivitet har studerats.

När temperaturen ökar samt när partikelstorleken minskar, ökar uppvärmningshastigheten, som orsakar ett minskande charutbyte. Vid högre temperatur ökar krackningen av kolväten med ett ökande väteinnehåll i produktgasen som resultat. Ved ger mer flyktiga produkter och mindre char än halm och olivavfall. Det höga askinnehållet i jordbruksavfall gynnar charproduktionen. Char från olivavfall och halm har högre reaktivitet i förgasning än char från björk p.g.a. det höga askinnehållet. Björk och bagass ger mer flyktiga produkter och mindre char än vit quebracho, halm och olivavfall. En längre uppehållstid ökar tiden för kontakt mellan tjära och char och charen blir mindre reaktiv. Charen blir mer reaktiv när de flyktiga produkterna snabbt får lämna partikeln, dvs vid hög uppvärmningshastighet, hög temperatur och små partiklar.

Den andra del av avhandlingen behandlar långsam pyrolys i närvaro av vattenånga för framställning av aktivt kol. Påverkan av typen av biomassa, typen av reaktor och processbetingelserna, huvudsakligen temperatur och aktiveringstid, på egenskaper och utbyte av aktivt kol redogörs för. Som råmaterial används björk (ved) och olika jordbruksavfall som sockerrör bagass, olivavfall, pelletiserad miscanthus och halm, både obehandlad och pelletiserad.

Gasutbytet ökar och tjärutbytet minskar när en roterande reaktor används istället för en stationär fastbäddsreaktor.

Råmaterialet har stor inverkan på egenskaper och utbyte av produkter. När temperaturen höjs, vid samma behandlingstid, minskar utbytet av aktivt kol och adsorptionsförmågan hos kolet ökar tills ett maximum nås. En ytterligare höjning av temperaturen orsakar en minskning av kolutbytet utan förbättring av adsorptionsförmågan. Detta beror på intensifiering av förgasningsreaktionerna. Ångflödet påverkar produktutbytet. Tjärutbytet ökar och gasutbytet minskar när ångflödet ökar. Vid stora ångflöde består en stor del av tjäran av vattenlösliga polära föreningar.

**Nyckelord:** snabb pyrolys, pyrolys, ved, jordbruksavfall, biomassa, char, tjära, gas, charreaktivitet, förgasning, vattenånga, aktivt kol.

## ABSTRACT

Pyrolysis of biomass consists of heating solid biomass in the absence of air to produce solid, liquid and gaseous fuels. In the first part of this thesis rapid pyrolysis of wood (birch) and some agricultural residues (olive waste, sugarcane bagasse and wheat straw in untreated and in pelletized form) at high temperature (800°C – 1000°C) is studied in a free fall reactor at pilot scale. These conditions are of interest for gasification in fluidized beds. Of main interest are the gas and char yields and compositions as well as the reactivity of the produced char in gasification.

A higher temperature and smaller particles increase the heating rate resulting in a decreased char yield. The cracking of the hydrocarbons with an increase of the hydrogen content in the gaseous product is favoured by a higher temperature and by using smaller particles. Wood gives more volatiles and less char than straw and olive waste. The higher ash content in agricultural residues favours the charring reactions. Chars from olive waste and straw are more reactive in gasification than chars from birch because of the higher ash content. The composition of the biomass influences the product distribution. Birch and bagasse give more volatiles and less char than quebracho, straw and olive waste. Longer residence time in rapid pyrolysis increase the time for contact between tar and char which makes the char less reactive. The secondary char produced from tar not only covers the primary char but also probably encapsulates the ash and hinders the catalytic effect of the ash. High char reactivity is favoured by conditions where the volatiles are rapidly removed from the particle, i.e. high heating rate, high temperature and small particles.

The second part of this thesis deals with slow pyrolysis in presence of steam for preparation of active carbon. The influence of the type of biomass, the type of reactor and the treatment conditions, mainly temperature and activation time, on the properties and the yield of active carbons are studied. The precursors used in the experiments are birch (wood) and different types of agricultural residues such as sugarcane bagasse, olive waste, miscanthus pellets and straw in untreated and pelletized form.

The results from the pyrolysis of biomass in presence of steam are compared with those obtained in inert atmosphere of nitrogen. The steam contributes to the formation of solid residues with high surface area and good adsorption capacity. The yield of liquid products increases significantly at the expense of the gaseous and solid products. Large amount of steam result in liquid products consisting predominantly of water-soluble polar compounds.

In comparison to the stationary fixed bed reactor, the rotary reactor increases the production of energy-rich gases at the expense of liquid products.

The raw materials have strong effect on the yields and the properties of the pyrolysis products. At equal time of treatment an increase of the temperature results in a decrease of the yield of solid residue and improvement of the adsorption capacity until the highest surface area is reached. Further increase of the temperature decreases the yield of solid product without any improvement in the adsorption capacity. The rate of steam flow influences the product distribution. The yield of liquid products increases while the gas yield decreases when the steam flow is increased.

**Keywords:** rapid pyrolysis, pyrolysis, wood, agricultural residues, biomass, char, tar, gas, char reactivity, gasification, steam, active carbon

*In memory of  
Martin Vazquez,  
my fellow student at the Faculty of Engineering, Buenos Aires University  
Guillermo Moralli  
and my classmates at the Colegio Nacional de Buenos Aires<sup>1</sup>  
Augusto Conte Mac Donell, Hebe Garcia and Gustavo Marotta  
and other students  
who had disappeared or were murdered  
by State terrorism in Argentina  
in the black years of the dictatorship (1976-1983).*

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<sup>1</sup> Colegio Nacional de Buenos Aires: The oldest secondary school in Argentina, founded in 1772.

The work presented in this thesis is based on the following papers, referred to by their Roman numerals. The papers are appended at the end of the thesis.

- I Zanzi, R., Sjöström, K. and Björnbom, E. Rapid high-temperature pyrolysis of biomass in a free-fall reactor, *Fuel*, 1996, 75 (5), 545-550.
- II Zanzi, R., Sjöström, K. and Björnbom, E. Rapid pyrolysis of bagasse at high temperature, in *Proceedings of the third Asian-Pacific international symposium on combustion and energy utilization*, Published by The Hong Kong Polytechnic University, Hong Kong, 1995, vol. 1, pp. 211-215.
- III Zanzi, R., Sjöström, K. and Björnbom, E. Rapid pyrolysis of agricultural residues at high temperatures, submitted to *Biomass & Bioenergy*, 2001.
- IV Minkova, V., Marinov, S.P., Zanzi, R., Björnbom, E., Budinova, T., Stefanova, M. and Lakov, L. Thermochemical treatment of biomass in a flow of steam or in a mixture of steam and carbon dioxide, *Fuel Processing Technology*, 2000, 62, 45-52.
- V Minkova, V., Razvigorova, M., Björnbom, E., Zanzi, R., Budinova, T. and Petrov, N. Effect of water vapour and biomass nature on the yield and quality of the pyrolysis products from biomass, *Fuel Processing Technology*, 2001, 70, 53-61.
- VI Zanzi, R., Bai, X., Capdevila, P. and Björnbom, E. Pyrolysis of biomass in presence of steam for preparation of activated carbon, liquid and gaseous products, submitted to *6<sup>th</sup> World Congress on Chemical Engineering*, 2001.

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# 1. INTRODUCTION

## 1.1 Biomass as a source of energy.

Biomass includes a wide range of fuels such as wood, agricultural crops especially cultivated for energetic purpose, forest and agricultural residues and is closely related to other fuels such as waste from both industries and households, black liquor from pulp industries and peat. Peat consists in plants that have been in the ground for up to 10000 years and have been humidified (decomposed). Biomass contains stored chemical energy, originally derived from the energy in sunlight. Most biomass is living or dead plants, which use the process of photosynthesis to create stored chemical energy. Photosynthesis involves the use of energy in sunlight to convert carbon dioxide (from air) and water into carbohydrates, which are a source of chemical energy.

The supply of energy from biomass plays an increasing role in the debate on renewable energies. The relative large amount of biomass already used for energy generation reflects mainly the use of wood and traditional fuels in the developing countries. But the use of biomass in industrialised countries is also significant. Wood energy is a very common form of bioenergy in Sweden, especially in the north of the country. The black liquor from the pulp industry has in Sweden a large contribution to bioenergy. Today the production of heat from biofuels is competitive. Biomass uses often in thermal power station. The bio-energy sector is also able to produce electricity in an economically sound way. There are combined power and heating plants using biofuels in Växjö (56 MWel), Brista (41 MWel), Skellefteå (38 MWel), Nyköping (35 MWel), Borås (25 MWel), Enköping (24 MWel) and Karlstad (20 MWel)[1].

In Sweden the large-scale use of biomass fuels has increased from about 50 TWh in 1980 to 84 TWh in 1995. This represents a 7% shift of the national energy balance and is one of the best examples of a successful transition from fossil fuels to renewable energy in the industrialised world. Today about 18% of the Swedish energy balance comes from large-scale biomass [2]

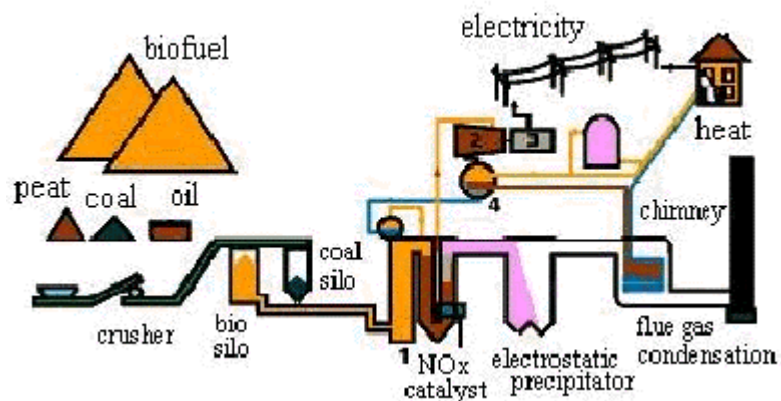


Figure 1. Combined power and heating plant Idbäcken in Nyköping (80 MWh heat and 35 MWh el.[3]

Figure 1 shows the today traditional way for producing heat and electricity from biomass. The biofuel is combusted in the boiler (1). The steam produced in this boiler is used to drive a steam turbine (2). The electrical generator (3) connected to the turbine produces electricity. After turbine the steam is cooled down and is condensed to water

that is sent back to the boiler. Cooling take place using water from the district heating system, that is heated up.

The energetic and industrial usage of biomass is becoming more and more technologically and economically attractive. The use of biomass offers the advantage of benefits, such as:

- Biomass is available in every country in various forms and thus assures a secure supply of raw material to the energy system. Maintaining biomass as a significant contributor to the national energy supply is, for many countries, the best way of ensuring greater autonomy and a cheap energy for the industry.
- Socio-economic benefits including the creation of new employment opportunities in rural districts.
- Environmental benefits. The utilization of biomass for energy is an alternative for decreasing current environmental problems such as CO<sub>2</sub> increase in the atmosphere caused by the use of fossil fuels. Furthermore, bio-fuels contain minimal sulphur, thus avoiding SO<sub>2</sub> emissions.

## **1.2 Environmental impact.**

The earth's temperature is regulated by atmospheric gases. Mainly carbon dioxide but also other gases such as nitrous oxide, ozone, CFCs and methane, allow the sun's energy to penetrate to the earth, but trap the heat radiated from the earth's surface. Scientists and others are concerned that those gases being added to the atmosphere by human activities will increase the warming at a rate unprecedented in human history. The CO<sub>2</sub> emissions from the use of fossil fuels that provide about 85% of the total world demand for primary energy, cause the observed increase of the CO<sub>2</sub> concentration in the atmosphere.

The use of biomass fuels in a closed carbon cycle, as a substitute for fossil fuels, is one of the most promising ways for halting the increase of the CO<sub>2</sub> concentration. Biomass fuels make no net contribution to atmospheric CO<sub>2</sub> if used sustainably to allow regrowth.

Biomass can play a significant role in reducing CO<sub>2</sub> by acting both as a reservoir of carbon, absorbing CO<sub>2</sub> from the atmosphere during growth and as direct substitute for fossil fuels. It is more efficient to use land to grow biomass (trees and energy crops) for energy, offsetting fossil fuel use, than to simply sequester CO<sub>2</sub> in forests [4]. Furthermore, reforestations and introduction of alternative crops are needed to stop and revert phenomena like erosion and desertification.

Acid rain is caused mainly by SO<sub>x</sub>, NO<sub>x</sub> and HCl emissions. SO<sub>x</sub> and NO<sub>x</sub> can be transformed in the atmosphere to H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>. SO<sub>x</sub> is produced in combustion of sulphur-bearing fuels such as petroleum and coal. SO<sub>x</sub> emissions from the utilization of biomass fuel are negligible because biomass contains minimal sulphur. Another acidic gaseous pollutant is HCl, produced from chlorine and mainly associated with combustion of municipal wastes [5, 6]. HCl plays also an important role for dioxin formation during combustion [7]. Other high-chlorine biofuels are straw and some peats.

Special attention is being paid to the NO<sub>x</sub> emissions from combustion of nitrogen-containing fuels such as biomass, coal, peat or municipal waste. The NO<sub>x</sub> emission from combustion of a nitrogen-containing fuel comes from two sources: thermal NO<sub>x</sub> and fuel NO<sub>x</sub>. The former is formed from the nitrogen in the combustion air and its formation is



more or less dependent on the temperature and pressure in the combustor [8]. The latter comes from the oxidation of nitrogen in the fuel and is not particularly temperature sensitive. All the nitrogen oxides also enhance the greenhouse effect. During gasification, the fuel-nitrogen mainly forms  $\text{NH}_3$ . Some HCN and NO may also be formed [9, 10]. During combustion of the gases, ammonia and cyanides undergo oxidation to  $\text{NO}_x$ . The pyrolysis is the initial step in both gasification and combustion. During pyrolysis part of the nitrogen in the fuel is converted to ammonia ( $\text{NH}_3$ ) (the main product), hydrogen cyanide (HCN) and nitric oxide (NO). The conversion of nitrogen may also form  $\text{N}_2$ . Other part of the nitrogen remains in the char [11].

### 1.3 Properties and composition of biomass.

On a dry basis, biomass is constituted from 88% to 99.9% of organic compounds. The average composition based on dry weight for wood is: cellulose 40-45% (about the same in softwoods and hardwoods); lignin 25-35% in softwoods and 17-25% in hardwoods; hemicellulose 20% in softwoods and 15-35% in hardwoods; and 25-35% lignin while extractives vary from 1 to more than 10% (table 1).

Table 1. Typical composition of different biomass species

Species	Cellulose	Hemi-cellulose	Lignin	Extractives	Ash
Scandinavian Birch <sup>1</sup>	40.0	39.0	21.0	n.a.	0.3
Softwood <sup>1</sup> (average)	45.8	24.4	28.0	n.a.	1.7
Hardwood <sup>1</sup> (average)	45.2	31.3	21.7	n.a.	2.7
Scandinavian pine <sup>2</sup>	40.0	28.5	27.7	3.5	n.a.
Wood bark <sup>1</sup>	24.8	29.8	43.8	n.a.	1.6
Bagasse <sup>2</sup>	41.3	22.6	18.3	13.7	2.9
Coconut shell <sup>2</sup>	36.3	25.1	28.7	8.3	0.7
Corn stalks <sup>2</sup>	42.7	23.6	17.5	9.8	6.8
Olive husk <sup>1</sup>	24.0	23.6	48.4	n.a.	4.0
Wheat straw <sup>2</sup>	30.5	28.9	16.4	2.4	11.2-6.6
Rice husk <sup>2</sup>	31.3	24.3	14.3	8.4	23.5
Rice straw <sup>2</sup>	37.0	22.7	2.6	2.1	19.8-16.1

<sup>1</sup> wt% dry and extractive free basis, <sup>2</sup> wt% dry basis, n.a.: not analysed

Cellulose (figure 2) is a homopolysaccharide composed of  $\beta$ -D-glucopyranose units linked together by (1 $\rightarrow$ 4)-glycosidic bonds. The cellulose molecules are linear; the  $\beta$ -D-glucopyranose chain units are in a chair conformation and the substituents HO-2, HO-3, and  $\text{CH}_2\text{OH}$  are oriented equatorially (figure 2). Cellulose shows strong tendency to form intra- and intermolecular bonds, which makes the molecules form microfibrils with partly highly ordered (crystalline) regions and partly less ordered regions (amorphous).

Microfibrils in turn build up fibrils and finally cellulose fibres. The fibrous structure and strong hydrogen bonds gives cellulose a high tensile strength and make the fibres insoluble in most solvents [12].

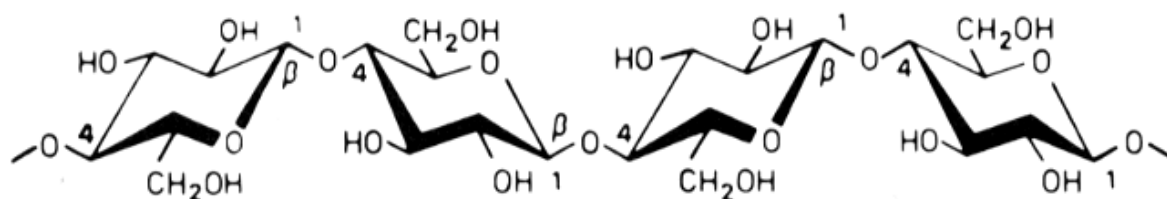


Figure 2. Structure of cellulose

In contrast to cellulose, which is a homopolysaccharide, hemicelluloses are heteropolysaccharides. The monomeric components of hemicellulose are primarily D-glucose, D-mannose, D-galactose, D-xylose, L-arabinose but to some extent it can be L-rhamnose in addition to D-glucuronic acid, D-galacturonic acid, and 4-O-methyl-D-glucuronic acid. In birch wood the most common hemicelluloses are glucuronoxylan approximately, about 25 % of the dry wood weight, and glucomannan about 2 %. Hemicelluloses can be hydrolysed with acids [12].

Lignin are polymers of phenylpropane units, they contains methoxyl groups, phenolic hydroxyl groups, and some terminal aldehyde groups in the side chains. Relatively few of the phenolic hydroxyls are free most of them are occupied through linkages to neighbouring phenylpropane. Links between the phenylpropane units can be formed with C-C or C-O-C bonds. The ether linkage is the dominant one, about two thirds or more are of this type. The macromolecule of lignin is very complex and the structure varies for different biofuels [12].

Extractives derive their name from the fact that they can largely be removed from the biomass by extraction with neutral solvents. The extractives are compounds of varying chemical composition such as gums, fats, resins, sugars, oils, starches, alkaloids and tannins. The composition varies according to species as well as from sapwood to heartwood in a given stem. The extractives are responsible for the characteristic colour and odour of various species, or, in some biomasses, for resistance to decay and insect attack.

The inorganic part is usually very small and is made up of alkali (Na, K), earth alkali (Mg, Ca) and other compounds: S, Cl, N, P, Si, Al, heavy metals (Cd, Zn, As, Pb, Cu, Hg). The remaining inorganic part after total combustion is called ash. Storage and transportation can bring impurities too: earth, sand, stones. The inorganic fraction varies from 0.1 to 12 %. Globally, forest biomass contains less inorganic matter than straw and cereals.

Among those impurities, some are more harmful than others are. Special attention must be paid to alkali, which play a major role in ash deposition, bed agglomeration, hot corrosion, and particle emissions. Si, K, Mg are important, too, for the properties of the formed ash. Cl, S may induce corrosion problems, poisoning of SCR catalysts. Heavy metals must be taken into account for an approach to the environmental issues raised by the process. Nitrogen is partially converted into  $\text{NH}_3$  and HCN, which lead afterward to  $\text{NO}_x$ .

Biomass is rich in oxygen and thus has a low heating value. Biomass has very great advantages as a gasification and combustion feedstock. The reactivity is extremely high. A large volatile fraction and a highly reactive char are obtained after devolatilization [13]. Ash content tends to vary considerably between different biomass fuels.

Dry wood has an elementary composition of about 50 weight% carbon, 6 weight% hydrogen and 44 weight% oxygen. Table 2 shows elemental composition, ash content and heating value of some biomass species, peat and coal [14].

Table 2. Elemental composition, ash content and calorific heating value (mf basis) of biomass, peat and coal.

Fuel	C % maf	H % maf	O % maf	N % maf	S % maf	Ash % mf	Heating value KJ/g
Birch wood	48.8	6.0	44.2	0.5	0.01	0.5	20.0
Poplar wood	49.8	5.9	44.4	0.6	0.04	1.9	18.3
Aspen wood	48.8	6.0	44.7	0.5	0.01	0.5	20.0
Pine wood	49.3	6.0	44.2	0.5	0.01	0.5	20.1
Bark	47.2	5.6	46.9	0.3	0.07	3.9	20.9
Wheat straw (Den)	49.6	6.2	43.6	0.6	n.a.	4.7	18.6
Miscanthus (Ger)	49.7	6.1	43.9	0.3	n.a.	2.3	18.4
Miscanthus (It)	49.5	6.2	43.7	0.6	n.a.	3.3	18.5
Sugar cane (It)	49.5	6.2	43.8	0.5	n.a.	3.7	18.5
Reed canary grass	49.4	6.3	42.7	1.6	n.a.	8.8	18.8
Hasselfors peat	53.1	5.5	38.1	1.3	0.20	5.6	20.5
Coal Daw Mill	80.4	5.0	6.7	1.3	0.53	7.0	30.4

mf: moisture free. maf: moisture and ash free n.a.: not analysed

Den: Denmark It: Italy Ger: Germany

In comparison with conventional fossil fuels, biomass has the following inferior characteristics:

- Lower thermal content compared with fossil fuels.
- Higher moisture content, rendering the material putrifiable, which in turn presents storage problems. The high moisture content also causes significant energy loss in combustion, mainly as latent heat of steam.
- Biomass has a low bulk density, which necessitates the use of relatively large equipment for handling, storage and burning.
- The physical form is not homogeneous and free flowing, which poses difficulties in their vehicular transportation, metering, storage and feeding to end-use equipment.

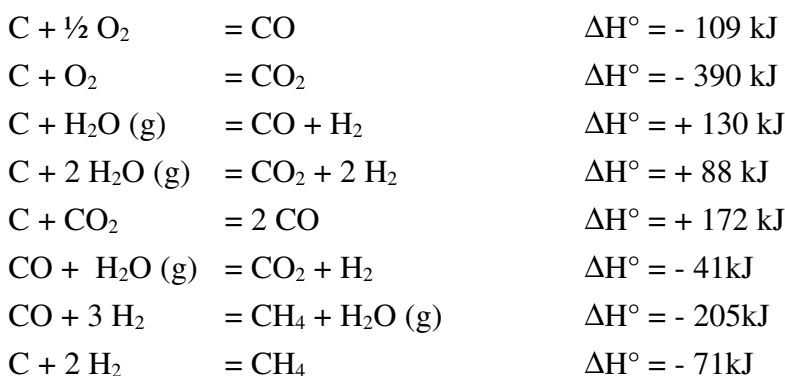
#### 1.4 Conversion of biomass.

The conversion processes of biomass usually involve a reduction of the water content of the material, resulting in the simultaneous increase in its thermal value and preservation potential, and in an improving the handling characteristics of the biomass, for example turning it into a fluid, which may be either gas or liquid. Oxygen removal from the

biomass in the form of carbon dioxide (and carbon monoxide) will result in products with high hydrogen to carbon (H/C) ratio.

Wood and other biomass can be treated in a number of different ways to provide such fuels. In general such methods are divided into biological and thermal. The biological conversion processes are hydrolysis, fermentation and anaerobic digestion. The main thermal conversion processes are combustion, gasification, pyrolysis and liquefaction. Direct combustion provides heat, for steam production and hence electricity generation. Gasification also provides a fuel gas that can be combusted, generating heat, or used in an engine or turbine for electricity generation. The produced gas can be also further processed towards methanol or towards liquid hydrocarbons by Fisher-Tropsch synthesis. Fast pyrolysis process provides a liquid fuel that can substitute for fuel oil in any static heating or electricity generation application. Although slow pyrolysis is well known and an established process, for instance in charcoal production, fast pyrolysis is still under development. Conversion of feedstock organic compounds into liquid products by liquefaction is a relatively low temperature (250°C-500°C), high-pressure (5-35 MPa) catalytic process, carried out in a reducing atmosphere (hydrogen or carbon monoxide) or using a hydrogen donor system [15,16].

Gasification and pyrolysis represent partial processes of combustion, where the product mix (gas, liquid and solid) can be controlled by altering temperature, particle size, residence time, pressure and composition of the atmosphere under which the biomass is treated. Gasification is a high temperature process in which a solid fuel is reacted with steam, carbon dioxide, air or hydrogen under oxygen-deficient conditions giving a mixture of gases including hydrogen and carbon monoxide. The most important reactions during gasification are:



Pyrolysis of biomass is the heating of solid biomass in an inert atmosphere to produce gaseous products (mainly  $CO_2$ ,  $H_2$ ,  $CO$ ,  $CH_4$ ,  $C_2H_2$ ,  $C_2H_4$ ,  $C_2H_6$ , benzene, etc.), liquid products (tars, high molecular hydrocarbons and water) and solid products (char). By changing the rate of heating and the final temperature it is possible to modify the proportions of the gas, liquid and solid product.

The method of wood conversion to charcoal by slow pyrolysis (slow heating rate) has been practised for many years. This requires relatively slow reactions at low temperatures to maximize solid char yield. A number of different approaches are being developed in order to optimize an efficient pollution-free system. Some studies aim at increasing the yields of charcoal by using elevated pressure [17]. High heating rate is used to maximize either gas or liquid products according to the temperature employed.

Liquid fuel production by fast pyrolysis is a promising technology. High yields of liquid products can be obtained under optimised conditions: very high heating and heat transfer rates that requires a finely ground biomass feed, carefully controlled temperature of around 500°C and rapid cooling of the pyrolysis vapours to give the bio-oil product [18]. Pyrolysis oil consists of water and a complex mixture of organic compounds that are condensed and collected after the pyrolysis step. The time and temperature profile between formation of pyrolysis vapours and their quenching influences the composition and quality of the liquid product. High temperatures will continue to crack the vapours and the longer the vapours are at higher temperatures, the greater the extent of cracking. Vapour residence times of a few hundred milliseconds are necessary for optimum yields of chemicals and food additives, while fuels can tolerate vapour residence times of up to around 2 s [18]. The oils produced by pyrolytic techniques have a relatively higher oxygen content and lower stability than those produced by hydrothermal liquefaction.

The amount of primary tar converted to gases increases markedly with increased temperature. At temperatures above 500°C the primary tar will crack into low molecular gases, such as methane, ethane and hydrogen. Thus a high gas production can be achieved at high temperatures (700-900°C). Rapid pyrolysis at high temperature plays an important role as the initial step in gasification and combustion.

The pyrolysis is a fast reaction at temperatures above 300°C. Pyrolysis of cellulose proceeds through two types of reactions: a gradual degradation, decomposition and charring on heating at lower temperatures, and a rapid volatilization accompanied by the formation of levoglucosan on pyrolysis at higher temperatures [15]. The initial degradation reactions include depolymerization, hydrolysis, oxidation, dehydration and decarboxylation [19]. The high char yield obtained at low heating rate and low temperature can be explained by a predominance of the dehydration reactions. At temperatures below 300°C the dominating reaction of cellulose is dehydration. The gaseous products are carbon dioxide, water and carbon monoxide, while the cellulose is converted to more stable anhydrocellulose. The anhydrocellulose is more stable than cellulose, which results in a high char production. At temperatures above 300°C cellulose depolymerizes producing mainly levoglucosan. High heating rates provide shorter time for the dehydration to take place, which results in a more unstable material left for depolymerization to primary volatiles and therefore lower final char yields [20].

Also the high char yield at low heating rate has been explained by the vapour-solid interactions (secondary reactions) [21].

A pyrolysis pathway which leads to the selective formation of glycolaldehyde from cellulose has been identified [22]. The glycolaldehyde-forming pathway is competitive with the formation of levoglucosan. Conditions which result in the selective formation of levoglucosan from cellulose realize very low yields of glycolaldehyde, and vice versa [23,24,25]. Temperature exercises only a weak influence on the productivity of two pathways; instead it is primarily the presence of trace amounts of salts and metal ions which determines the product slate. The addition of 0.05% NaCl to an ash-free cellulose reduce the yield of levoglucosan and increase the glycolaldehyde yield [24]. K, Li and Ca ions may promote the formation of char from wood at the expense of tar (and levoglucosan) formation. Other metal ions (particularly Fe and Cu) enhanced the yield of levoglucosan (and char) from wood and newsprint [25].

## 1.5 Gasification of biomass and production of electricity and heat.

The most common thermal conversion of biomass is combustion. In some circumstances it is advantageous to gasify biomass. When electricity is produced from biomass, the electrical energy efficiency is increased by gasification and use of a gas turbine and a steam turbine, in comparison with combustion followed by a steam turbine. Internal combustion engines for producing energy can be run on gasification gas. Synthesis gas for production of methanol, ammonia and H<sub>2</sub> can be produced by gasification of biomass. The gas volume after gasification is considerably smaller than after combustion, so, in some cases, there are possibilities for simpler and less expensive gas cleaning.

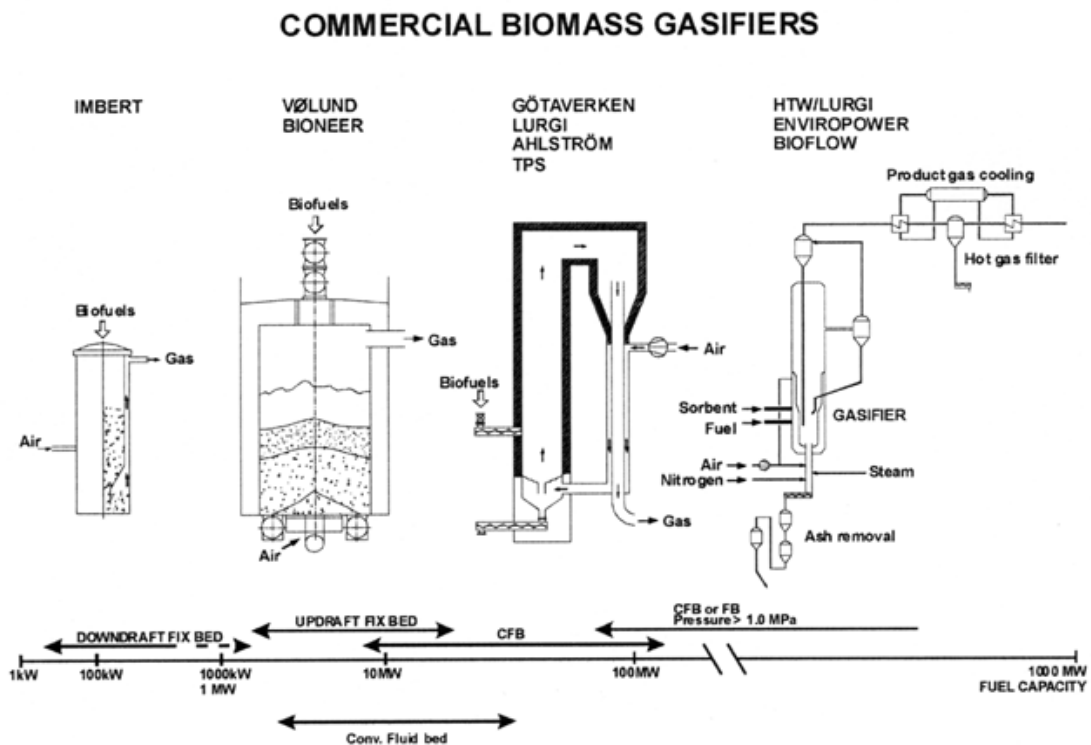


Figure 3. Types of gasifiers [26]

There are many types of gasifiers with varying schemes for both reactor design and reaction media. The most common types are counter- and co-current fixed bed, bubbling and fluidised beds. The mainly used reaction media are air and oxygen/steam. The processes can work either at atmospheric pressure, or be pressurised.

The fixed-bed gasifiers are also called "moving beds" since the solid material moves downward in the gasifier. These types of gasifiers require relatively large particles of uniform size for the pressure drop over the bed not to become too large.

In the downdraft (co-current) gasifier, the drying zone is situated at the top followed by a pyrolysis zone, a gasification zone and, finally, a combustion zone. Downdraft gasifiers were developed mainly before and during World War II, to generate gas for use in motors, both stationary and automotive [27]. The gas from this type of gasifier contains a little tar, beside the desired gaseous components. All gasification gases contain tar, but the co-current gasifier contains the least amount because gas passes combustion zone before being taken out [28,29]. Because of the physical limitation of the diameter and particle size relation, the usual size of this type of gasifier is up to 1

MW (Figure 3). For power production this technology is limited in both capacity and efficiency.

In the updraft (counter-current) gasifier the downward-moving biomass is first dried by the upflowing hot product gas. After drying, the solid fuel is pyrolysed, giving char which continues to move down to be gasified, and pyrolysis vapours which are carried upward by the upflowing hot product gas. The produced gases have a high tar content (100-200 g/Nm<sup>3</sup>) formed at low temperature. Usually the gases are directly used in a closely coupled furnace or boiler. Updraft gasifiers are suitable for sizes between 2 and 20 MWe [30](Figure 3).

Fluidized bed reactors constitute the most promising type of reactors for large-scale application of biomass thermochemical conversion because of their high heat and mass transfer rates, which result in a high rate of production, and their flexibility towards feedstock. They are more complicated than the fixed bed units and so need to be built in larger sizes to pay for the increased complexity. Fluidized bed gasifiers include bubbling fluidized bed at atmospheric pressure, circulating fluidized bed (CFB) at atmospheric pressure and pressurized fluidized beds. CFB technology is favourable for gasifiers with fuel capacities greater than 10 MWth (figure 3). Electricity is most likely to be generated using a gas turbine combined cycle. These larger plants will produce the most competitive power for grid connection [31]. In a Biomass Integrated Gasification Combined Cycle (BIG-CC), the wood is first converted to a gas in the fluidised bed gasifier. The gas is combusted in a combined cycle plant that contains a gas turbine and a steam turbine to maximise efficiency. The gas is compressed and injected into the gas turbine where it is combusted at high temperature. The gas turbine exhaust gases are at high temperature and pass to a boiler to recover further energy. Steam raised in this boiler is used to drive a steam turbine.

The gas produced must be cleaned of tars and impurities before it can be used in the generating plant. Tars are heavier hydrocarbons that could condense later in the process causing clogging of the pipework. The amount and composition of tars formed in gasification of biomass depend on the fuel, the pyrolysis condition, gasifier, secondary gas phase reactions.

In atmospheric gasification, the gases need to be compressed before feeding to the gas turbine (Figure 4). This is most efficiently done at low temperature (40 °C) and after condensation of the water vapour. Because of the high volumetric flows, the costs of high temperature filters are not justified. The filtering takes place at 200 °C in conventional filters [27]. The temperature in the gasifier is maintained as low as possible while maintaining high carbon conversion. The outgoing gas contains a relatively large amount of tar. The tar is cracked in a fast fluidised bed with calcined dolomite as bed material. The low temperature filtering puts high demands on tar cleaning prior the cooling in order to avoid the condensation occur in the filter or the scrubber. The gas is washed with water. Through high tar conversion the problem of cleaning condensed water is kept at an acceptable level. Besides tar, NH<sub>3</sub> as well as alkali is removed from the gas. Thus, the need for elimination of fuel nitrogen and alkali disappears. Finally the cleaned gases is compressed and burned in the turbine.

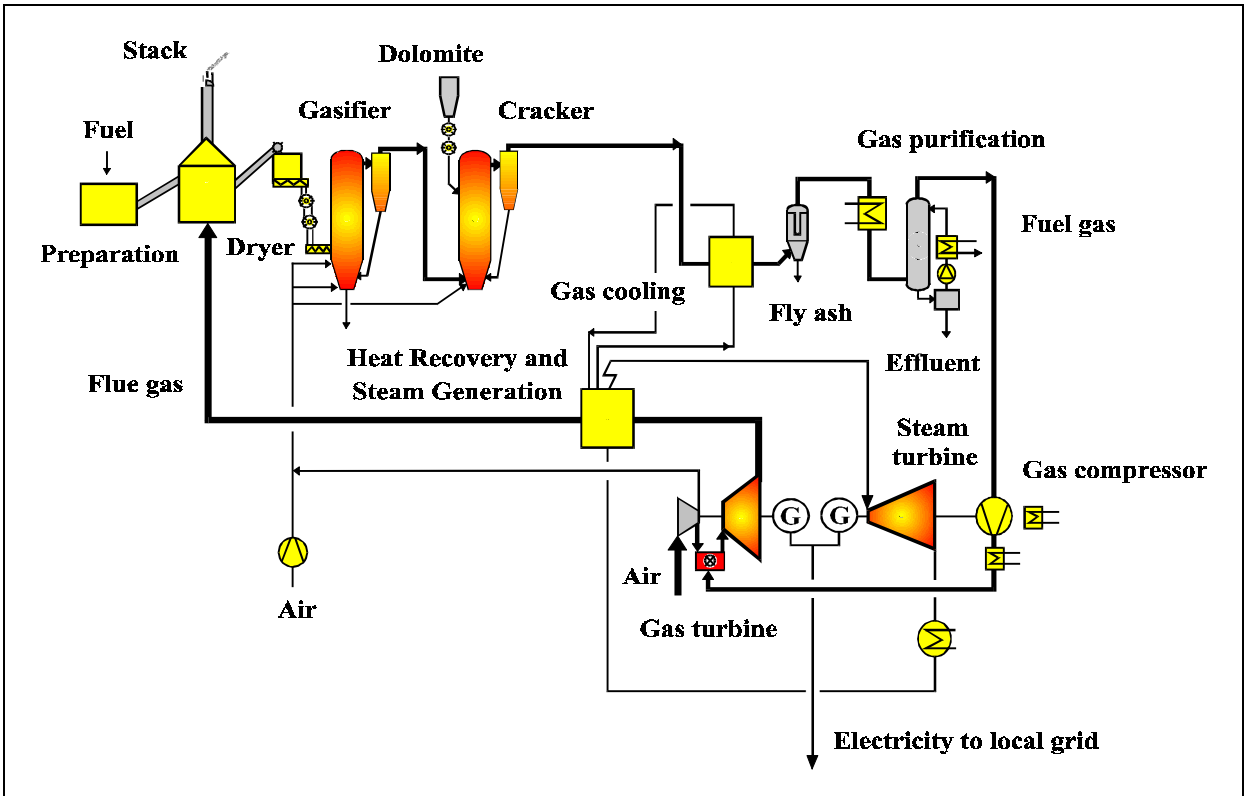


Figure 4. Biomass gasification according to the TPS BIG-CC-process [32]

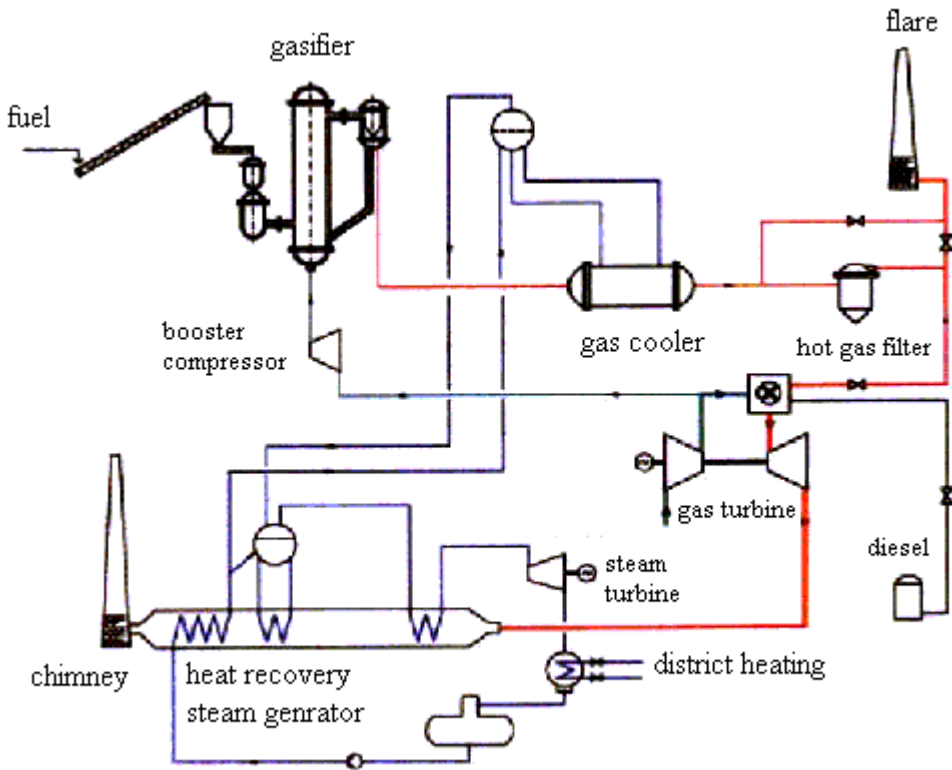


Figure 5. Sydskraft's pilot plant in Värnamo [33]



In pressurized gasification, the gases can be fed to the gas turbine directly after dust removal (Figure 5). Dust removal takes place at sufficient low temperature to remove the alkali and at sufficient high temperature to maintain tars in vapour phase. The temperature in the gasifier is above 900 °C and a MgO-based bed material is used to minimise tar. Temperature must be lowered to 400 °C for the alkali to condense, allowing it to be caught in the subsequent high-temperature filter.

### **1.6 Rapid pyrolysis at high temperature, the initial step in gasification in fluidised bed reactors.**

Rapid pyrolysis of biomass consists of rapid heating (in a range of hundreds of degrees per seconds, normally around 500 °C/s or higher) of solid biomass in an inert atmosphere to produce solid, liquid and gaseous fuels. In a fluidised bed gasifier the rapid pyrolysis is the initial reaction of the biomass. The heat transport into the particle takes place at high rate resulting in pyrolysis of the biofuel at the high operating temperature, normally between 750-950 °C depending on the biomass and the gasifier. During the pyrolysis gases are produced. While the pyrolysis gases are leaving the particles, the reactant gas in gasification, normally steam and/or air, is not allowed to come into the particles. When the pyrolysis ends, the steam and /or air are transported into the solid residue of the pyrolysis, the char, resulting in gasification of the solid material. The reaction rate of char with gasifying agents such as steam, air, carbon dioxide and so on, is much lower than that of the devolatilization reaction. Therefore gasification of char is the limiting step (controlled by either reaction kinetics or diffusion of reactive agents and products) of the whole process of pyrolysis/gasification of the solid fuel [34]. The rapid pyrolysis at high temperature plays an important role in gasification, because during the devolatilization the char is produced. The conditions under the pyrolysis determine the char yield and its reactivity. Char yield and char reactivity are important for the capacity of the gasifier. Reaching the lowest char yield and the highest char reactivity in pyrolysis is advantageous for gasification. Better quantitative understanding of the separate effects of temperature, heating rate, residence time, pressure and particle size on both primary pyrolysis and secondary reactions is needed in order to develop gasifier models that can predict yields, compositions and rates of formation of products.

This work presents a study concerning the rapid pyrolysis of biomass at high temperature (800°C-1000°C) performed in a free fall reactor at pilot scale. These conditions are of interest for gasification in fluidized beds. Of main interest are the gas and char production, the gas composition and the reactivity of the produced char in gasification.

The results are presented in tables in the annexed papers. In the summary of the papers the results are presented explicitly in figures. In the figures the lines connecting the points have only the function of coupling together the points to compare.

## 2. SUMMARY OF THE PAPERS ON RAPID PYROLYSIS OF BIOMASS AT HIGH TEMPERATURE

(Papers I, II and III)

### 2.1 Experimental

#### 2.1.1 Raw materials

Two types of wood (birch and white quebracho) and different types of agricultural residues are selected for the experiments. A mixed hardwood consisting of 10% aspen and 90% birch is also used. The used agricultural residues are olive waste from oil production (composed by a crushed mixture of kernel and pulp), wheat straw in untreated and in pelletised form and sugar cane bagasse and trash.

The used materials are characterized. The elemental analyses and chemical composition of these materials are shown in the papers.

Biomass samples are milled, sieved and pneumatically classified to obtain fractions of uniform particle size (figure 6)

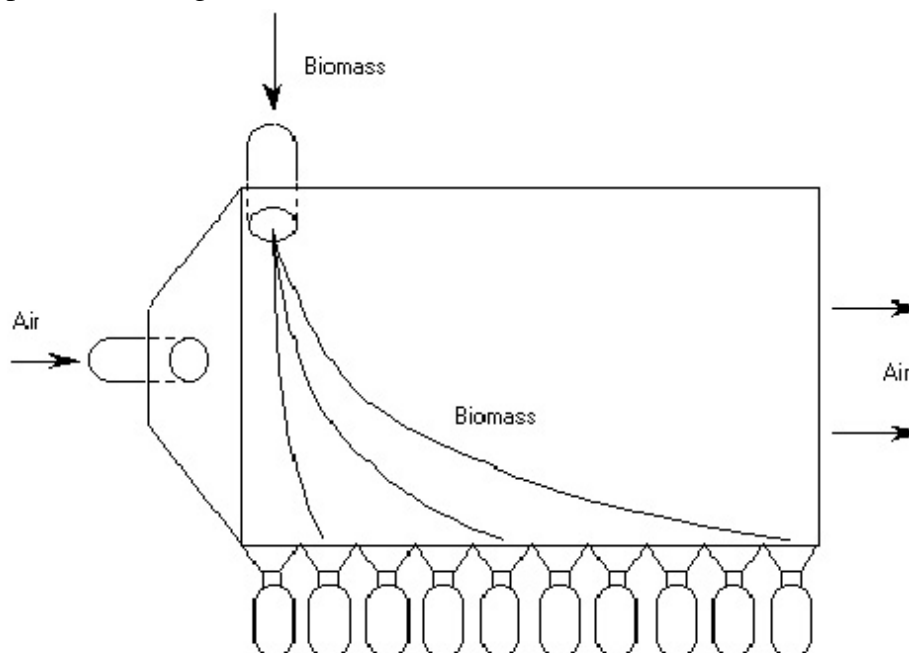


Figure 6. Pneumatic classifier

#### 2.1.2 The equipment

The free-fall tubular reactor (figure 7) has a heated length of 2.9 m and an inner diameter of 0.04 m. The carrier gas, nitrogen, is preheated before it enters the reactor. The nitrogen flow is 15 litres/min. The reactor tube is heated by eight independent electric heaters. The heated length of the reactor can be selected to fit the desired residence time for the solids. The heating rate in the equipment is about 500°C/s. The heating rates of the particles in a free fall reactor are of the same magnitude as those obtained in a fluidized bed gasifier [35]. A screw feeder (figure 8) located above the reactor allows introducing the samples at 250 g/hour. The char is collected in a char receiver situated below the tube (figure 9).

The volatiles pass through the metallic filter (figure 9) to remove char particles, dust and soot. The volatiles are further cooled in the water-cooled condenser, where the tar water is condensed. The remaining aerosol is removed in dry ice traps and a cotton filter. The gas composition is analyzed by an on-line programmed gas chromatograph for CO<sub>2</sub>, H<sub>2</sub>, CO, N<sub>2</sub>, CH<sub>4</sub>, and hydrocarbons up to C<sub>7</sub>. The amount of produced gas is measured. The gas chromatograph is equipped with three columns. A porapak Q column 80/100 produces a good separation for carbon dioxide and hydrocarbons such as ethylene, ethane and acetylene. A molecular sieve column (MS5 60/80) is used for separation of hydrogen, oxygen, nitrogen, methane and carbon monoxide. Both columns use helium as carrier gas and are connected to a thermal conductivity detector. A megabore column (bonded phase: DB-1) is used for the separation of high molecular hydrocarbon such as benzene and toluene. The column uses nitrogen as carrier gas and is connected to a flame-ionization detector.

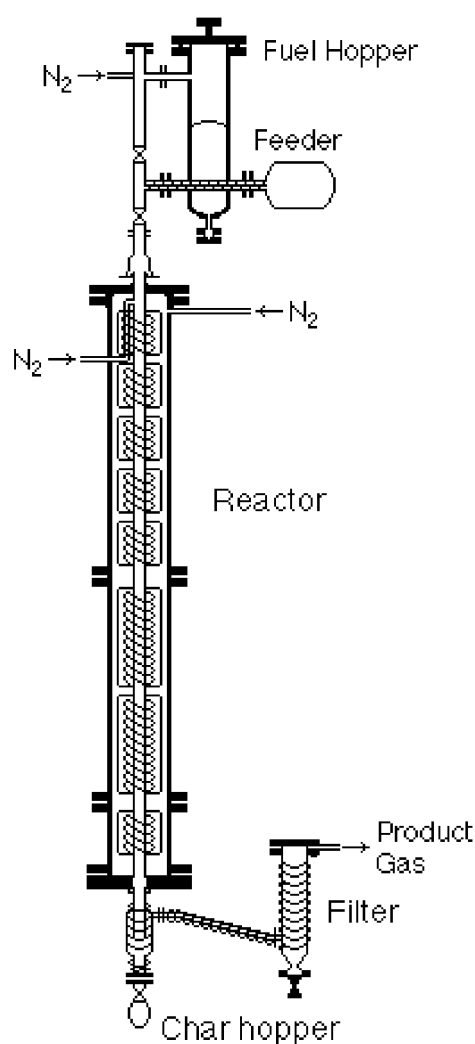


Figure 7. The free fall reactor for fast pyrolysis

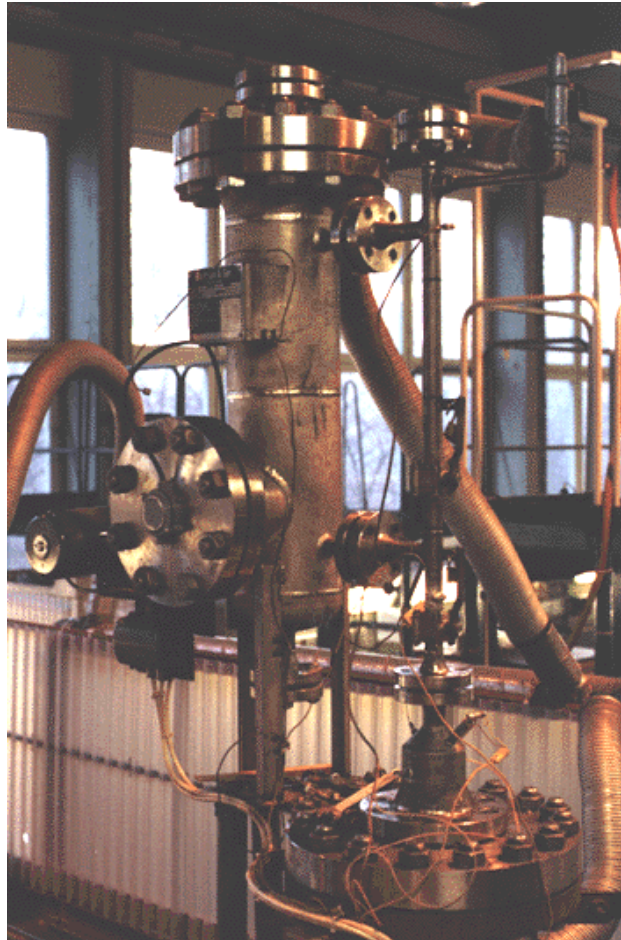


Figure 8. The upper part of the reactor. The feeder

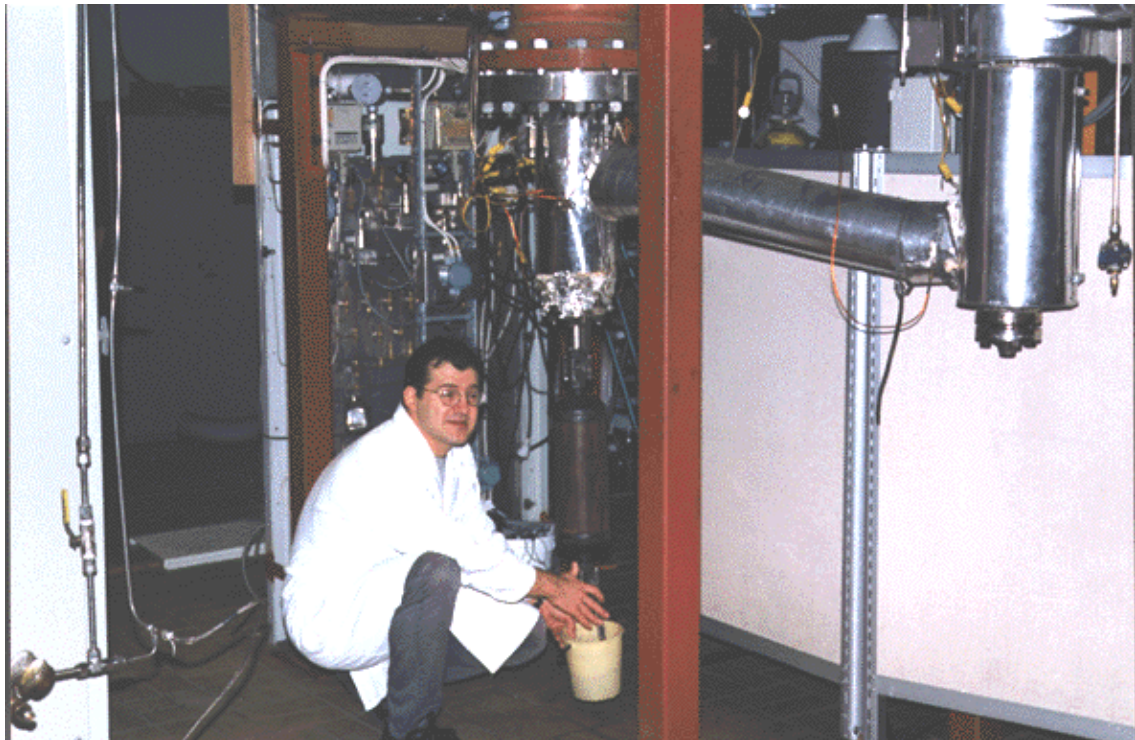


Figure 9. The lower part of the reactor including the char receiver and the filter

The yield of tar was calculated using the total weight of the tar collected in the water-cooled condenser, dry ice traps and cotton filter after the tar water is evaporated. The yield of gas was determined after the condensable part of the volatiles is removed.

The yield of char from biomass was calculated using the ash content in the char and in the wood.

$$\text{Char yield (wt \% maf)} = ((ab/ac) - (ab/100))/(1-(ab/100))$$

where ab is weight % ash in dry biomass, ac is weight % ash in dry char, and maf means moisture and ash free.

The collected char was measured and characterized. The elemental analysis, the calorific value, the ash and moisture content of the obtained chars after the rapid pyrolysis in the free fall reactor were shown in the papers. Bulk densities, surface area and pore volume measurement of both the raw materials and the obtained chars were also presented in paper III. The bulk density is calculated pouring the biomass into a graduated cylinder and determining both the weight and the occupied volume. The surface area is calculated by nitrogen adsorption and desorption isotherms with a Micrometrics Flowsorb II 2300 which uses dynamic flowing technique, providing BET and Langmuir surface area. Surface area was also determined by the adsorption capacity towards iodine [36]. Total pore volume, total pore area and skeletal density were calculated by mercury intrusion analysis with an AutoPore II 9220 Mercury Porosimeter.

The char obtained by the rapid pyrolysis was further pyrolysed under nitrogen in a thermobalance with a slow heating rate (20°C/min) up to 850°C. Heating was continued during 30 minutes in order to reach final pyrolysis. The residual char was further gasified with steam at 750°C in the same thermobalance to determine its reactivity in the gasification reaction. The reactivity presented in this paper is defined by the equation:

$$R = (1/W) * dW/dt$$

dW/dt was calculated between 10% and 50% wt conversion where W is the weight of the ash-free part of the sample at time t [37]. Generally, W was taken as zero when a constant weight was obtained at the end of the gasification run.

## 2.2 Results and Discussion

### 2.2.1 Product distribution

The heating rate has the main influence on the product distribution. A rapid heating increases volatile yields and decreases char yield. A rapid heating leads to a fast depolymerization of the solid material to primary volatiles while the dehydration to more stable anhydrocellulose is too slow to occur. The result is that very small amounts of char are produced in the primary reactions at rapid heating.

The influence of the temperature is studied in papers I, II and III.

The higher treatment temperature has led to more tar cracking resulting in higher yield of gaseous products and lower yields of tar. When the pyrolysis temperature was increased the char yield decreased (figure 10).

At high temperatures both the rate of primary pyrolysis and the rate of thermal cracking of tar to gaseous products are high. The temperature markedly influences the heating rate. The heat flux is proportional to the driving force, the temperature difference between the particle and the environment. At higher temperature, the heat flux and the heating rate are higher. A similar result, a decrease of the char yield and an

increase of the gas yield, was obtained when smaller particles of wood and olive waste were used in the reactor (figure 11). The size of the particles also affects the heating rate. The heat flux and the heating rate are higher in small particles than in large particles. The higher heating rate favours a decrease of the char yield.

Figure 10 shows the influence of temperature on char yield in the selected treatment conditions. After rapid pyrolysis in the free fall reactor, a decrease of char yield of about 18% (from 7.2 wt% maf to 5.9 wt% maf) for particles with size between 0.5-0.7 mm of mixed hardwood (90% birch and 10 % aspen) is reported in paper I when the temperature increases from 750°C to 900°C. A decrease of char yield of about 22% (from 7.2 wt% maf to 5.6 wt% maf) is also reported in the experiments with birch (particle size: 0.7-1.0 mm) when the temperature is increased from 800°C to 1000°C.

The results in paper II with bagasse shows the decrease of the obtained char yield when the temperature is increased from 800°C to 1000°C. The decrease is 18 % (from 5.0 wt% maf to 4.1 wt% maf) for particles with size between 0.5-0.86 mm and 28% for particles with size between 0.86 and 1.0 mm.

The influence of temperature on char yield in experiments with olive waste is presented in paper III. When the pyrolysis temperature is increased from 800°C to 1000°C a decrease of 27% (from 20.0 wt% maf to 14.6 wt% maf) is reported with particles with size between 0.5-0.8 mm while the decrease is 36% (from 27.6 wt% maf to 17.5 wt% maf) when particles of size between 0.8-1.0 mm are used.

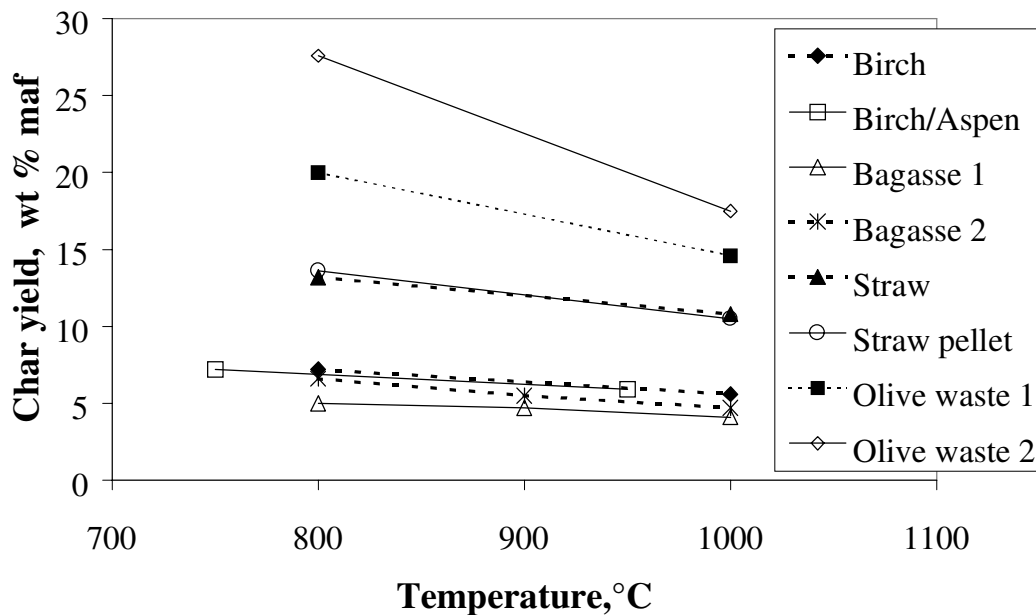


Figure 10. Influence of temperature on char yield

Bagasse 1,  $d_p$ : 0.5-0.86 mm.

Bagasse 2,  $d_p$ : 0.86-1.0 mm.

Olive waste 1,  $d_p$ : 0.5- 0.8mm.

Olive waste 2,  $d_p$ : 0.8-1.0 mm.

$d_p$ : particle size maf: moisture and ash free

The lines connecting the points have only the function of coupling together the points to compare.

Figure 11 shows the influence of particle size on char yield in the conditions selected for the study. In the experiments with birch at 800°C the char yield decreases about 20% (from 7.2 wt% maf to 5.8 wt% maf) when the particle size is reduced from 0.7-1.0 mm to 0.5-0.7 mm. In rapid pyrolysis of bagasse and olive waste also at 800°C the char yield decreases 30% (from 27.6 wt% maf to 20.0 wt% maf for olive waste and from 6.6 wt% maf to 4.6 wt% maf for bagasse) when the particle size is reduced (from 0.8-1.0 mm to 0.5-0.8 mm for olive waste and from 0.86-1.0 mm to 0.3-0.5 mm for bagasse). When the particle size of olive is reduced from 0.8-1.0 mm to 0.5-0.8 mm in the experiments at 1000°C, the char yield is decreased 17% from 17.5 wt% maf to 14.6 wt% maf.

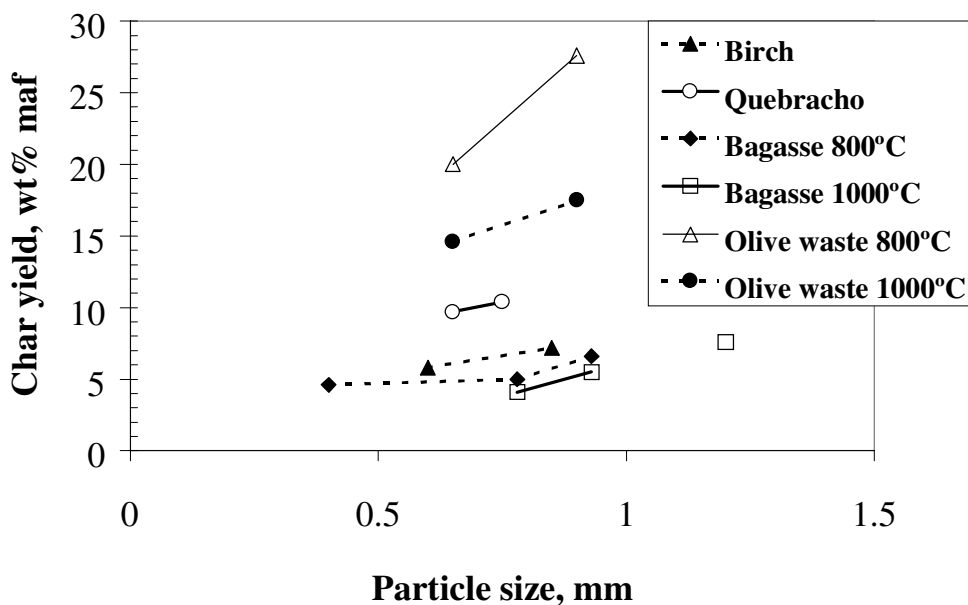


Figure 11. Influence of particle size on char yield  
The lines connecting the points have only the function of coupling together the points to compare.

Rapid pyrolysis of small biomass particles shows that the char yield remains constant above a certain temperature [38,39,40,41]. It seems that for a certain biomass (certain thermal conductivity) and for a certain particle size, a high enough heating rate is reached at a certain temperature. Further increase of heating rate because of an additional increase of temperature does not affect the char yield.

The residence time of the particles in the reactor would influence the char yield. In paper I the influence of the residence is studied by varying the heated length of the reactor. Thus an increase in the residence time of the particles was accompanied by an increase in the residence time of the gas in the reactor. The residence time of the particles was calculated using a computer program described by Nilsson [39]. Part of the model is based on the work of Pyle and Zaror [42]. The shrinkage and change in density of particles were considered in the calculations. In the range of experimental condition used (varying the heated length between 134 cm and 258 cm in the experiments at 800°C and between 78 cm and 196 cm in the experiments at 1000°C) residence time has a limited effect on the yield of pyrolysis products. The char yield obtained in the upper part of the reactor remains constant when the particles are falling in the lower part of the reactor. The char obtained by rapid pyrolysis in the free fall reactor contains a fraction

that can be further volatilized by slow pyrolysis. It seems that pyrolysis proceeds in two steps: an initial fast step followed by a slower step. It was suggested that the primary pyrolysis reactions in the rapid pyrolysis of wood were completed within seconds while the secondary reactions took minutes to be completed. Only the primary pyrolysis reactions have time to take place in the free fall reactor.

Chars from wood produced in the free fall reactor have been pyrolysed to a greater extent than those from agricultural residues. In the experiments at 800°C, 50% of char produced in the free fall reactor is removed in the thermobalance when bagasse and olive waste are used as fuel, 34%-50% using straw, while 20-24% is removed by slow pyrolysis using wood.

The composition of the biomass influences the product distribution. Birch and bagasse gives more volatiles and less char than quebracho, straw and olive waste. The char yield after the rapid pyrolysis in the free fall reactor at 800°C is 5.8-7.2 wt% using birch, 5.0-6.6 wt% using bagasse but 10 wt% using white quebracho, 13 wt% using straw and 20-27 wt% using olive waste. In previous studies, also a higher char yield was observed for agricultural residues because of the presence of large amount of ash that favours the charring reactions [43, 44]. Sugar cane bagasse has a lower ash content (1%) compared with straw and olive waste. The char yield after total pyrolysis is somewhat higher in pyrolysis of pelletised straw than untreated straw. The highest char yield is observed in the tests with olive waste. The higher lignin content in olive waste, in comparison with wheat straw, contributes also to the higher char yield. Higher yields of char are favoured by high carbon content, low oxygen content, low H/C ratio and higher content of coke forming components, such as lignin, in the fuel subject to pyrolysis [45]. The higher yield of char obtained from the wood sample of white quebracho compared to birch may be explained with the chemical composition of the organic material in these samples. Lignin content is higher in white quebracho (35%) than in birch (20%). The low ash content of the wood samples studied here facilitates the prediction of the distribution of products using only the composition of the organic matter in the fuel.

The tests in the free fall reactor using birch and white quebracho were compared with the results obtained using cellulose and lignin, the individual components of biomass.

Table 3. Yield of char produced by rapid pyrolysis of biomass samples with different content of lignin.

	Lignin concentration in wood, wt% mf	Measured char yield wt % maf	Calculated char yield, wt % maf	*
Lignin	100.0	22.0		
Cellulose	0	0.3		
Birch	24.3	5.5	5.57	
White Quebracho	34.8	7.9	7.85	

\* Calculated char yield assuming that the lignin in the biomass yields 22% char while the rest up to 100% yields 0.3% char like cellulose.

maf: moisture ash free, mf: moisture free

The results in table 3 show a relationship between the concentration of lignin in wood and the yield of char obtained from the rapid pyrolysis of wood. Almost the whole sample of cellulose is converted to volatiles.



### 2.2.2 Composition and properties of the obtained char

Results of the elemental analysis (figures 12,13,14) indicate that contents of carbon increase with the pyrolysis temperature while those corresponding to hydrogen and oxygen decrease. Losses in hydrogen and oxygen correspond to the scission of weaker bonds within the char structure favoured by the higher temperature [46].

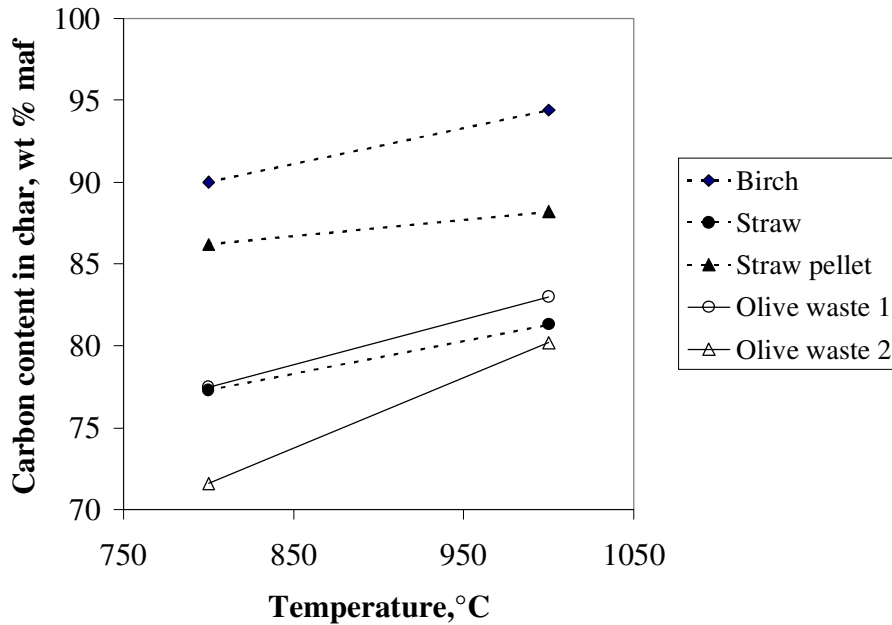


Figure 12. Influence of temperature on content of carbon in char  
olive waste 1,  $d_p$ : 0.5-0.8 mm. olive waste 2,  $d_p$ : 0.8-1.0 mm.  
birch,  $d_p$ : 0.8-1.0 mm. straw,  $d_p$ : 0.5-1.0 mm. straw pellets,  $d_p$ : 0.5-1.0 mm.  
The lines connecting the points have only the function of coupling together the points to compare.

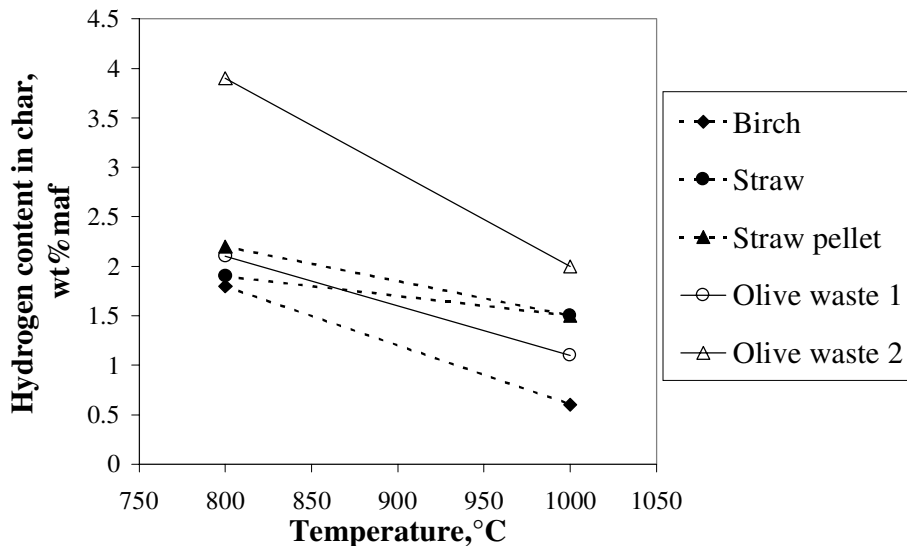


Figure 13. Influence of temperature on content of hydrogen in char  
olive waste 1,  $d_p$ : 0.5-0.8 mm. olive waste 2,  $d_p$ : 0.8-1.0 mm.  
birch,  $d_p$ : 0.8-1.0 mm. straw,  $d_p$ : 0.5-1.0 mm. straw pellets,  $d_p$ : 0.5-1.0 mm.  
The lines connecting the points have only the function of coupling together the points to compare.

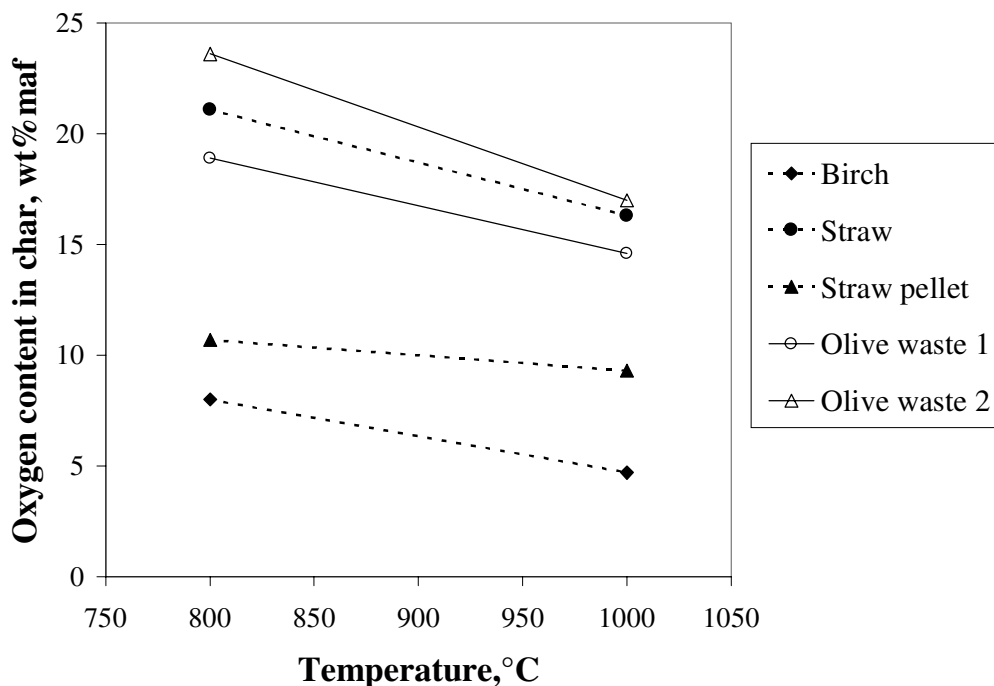


Figure 14. Influence of temperature on content of oxygen in char  
olive waste 1,  $d_p$ : 0.5-0.8 mm. olive waste 2,  $d_p$ : 0.8-1.0 mm.  
birch,  $d_p$ : 0.8-1.0 mm. straw,  $d_p$ : 0.5-1.0 mm. straw pellets,  $d_p$ : 0.5-1.0 mm.  
The lines connecting the points have only the function of coupling together the points to compare.

The part of the char which is volatilized in the thermobalance in order to achieve total pyrolysis is large at lower temperature indicating that the chars produced at 1000°C in the free fall reactor are more pyrolyzed than those obtained at 800°C. This is reflected in the elemental analysis of the chars produced at 800°C and 1000°C.

When smaller particles are used, the contents of carbon in chars, after rapid pyrolysis in the free fall reactor, are higher while those corresponding to hydrogen and oxygen are lower (figures 12,13,14). An increase of temperature has the same effect on the surface area of the char particles as a decrease of the particle size. When large particles are used as raw material, also the fraction of char removed in the thermobalance in order to achieve total pyrolysis is large.

Figure 15 shows the pore size distribution of the chars measured by mercury porosimetry. The char from straw has higher pore volume than chars from wood and olive waste. For all the analysed chars, the major part of the pores has a pore diameter of about 110 microns. A difference can be mentioned between the pore size distribution of wood and agricultural residues. For both agricultural residues, olive waste and straw, a second group of pores with a smaller diameter (0.5 to 1 microns) has been found. In chars from wood no pores with diameter lower than 1 microns has been found with mercury porosimetry. Chars from straw and olive waste even contain some pores with a diameter of 0.1 microns.

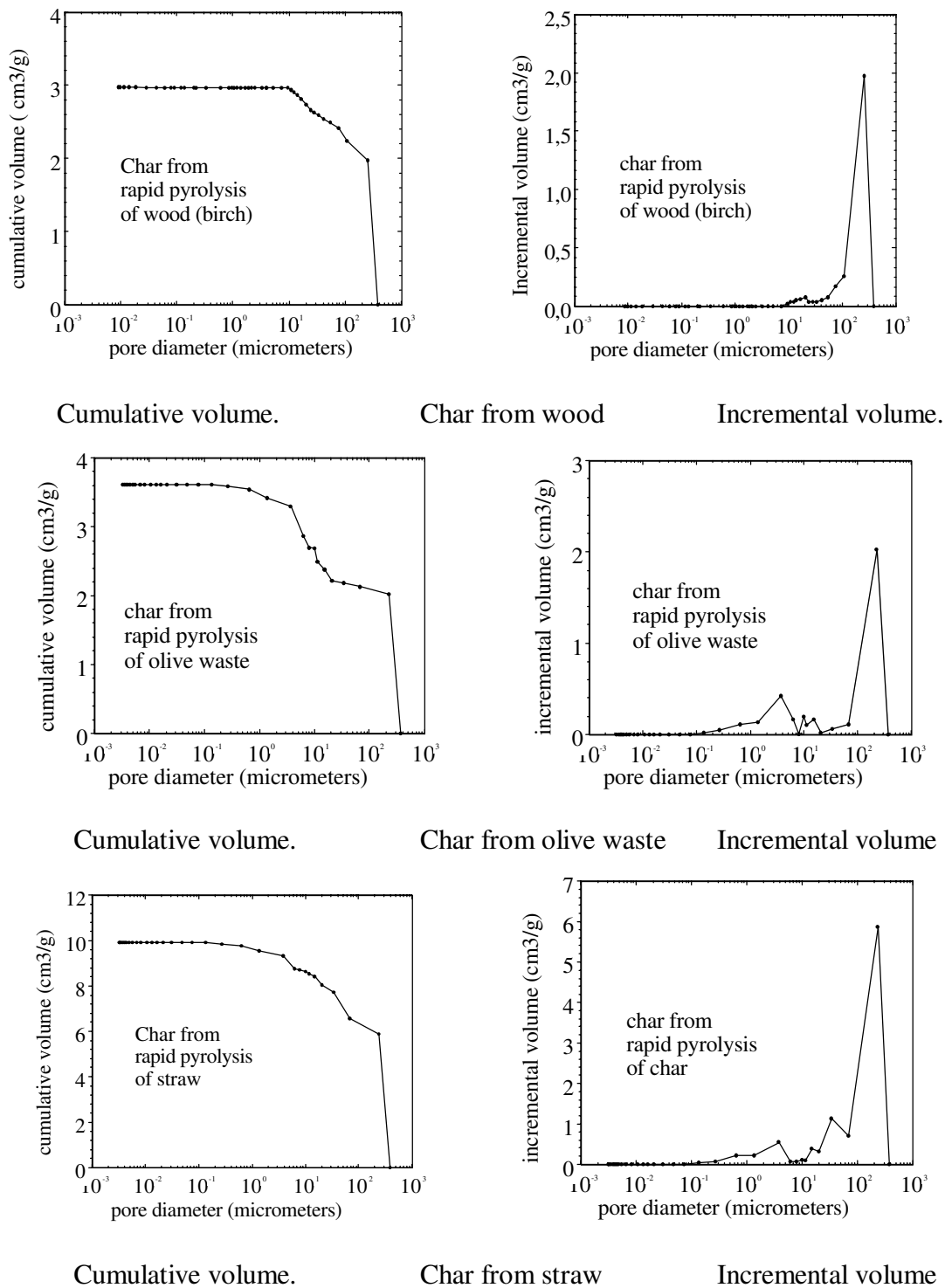


Figure 15. Mercury porosimetry measurements of chars produced by rapid pyrolysis at 1000°C. Pore size distribution

The surface area of the obtained char, characterized by iodine adsorption (DIN 53582) in table 4, is higher at 1000°C than at 800°C. At higher temperature, the heating rate is higher and the devolatilization is more intensive making the char more porous. Depending on the biomass, the influence of increasing the temperature from 800°C to 1000°C on the surface area of the chars is visible above a certain particle size. The chars from straw with a particle size between 0.5-1.0 mm and the chars from olive waste with

a particle size between 0.5-0.8 mm obtained at 800°C and at 1000° have similar surface area. Chars from agricultural residues have a higher surface area than those from wood. In the present experiments the highest surface area has been found in chars from untreated straw.

Table 4. Surface area of the obtained char (characterized by iodine adsorption)

Temperature	Iodine adsorption in mg/g		
	800° C	900° C	1000° C
Birch, dp: 0.5-0.8 mm	23	nd	nd
Birch, dp: 0.8-1.0 mm	21	nd	35
Birch, dp: 1.0-1.35 mm	nd	nd	30
White quebracho, dp: 0.6-0.7mm	18	nd	nd
Straw, dp: 0.5-1.0 mm	105	nd	107
Straw pellets, dp: 0.5-1.0 mm	61	nd	74
Olive waste, dp: 0.5-0.8 mm	74	nd	75
Olive waste, dp: 0.8-1.0 mm	51	nd	67
Bagasse, dp: 0.5-0.86 mm	40	47	60
Bagasse, dp: 0.86-1.0 mm	nd	36	50
Bagasse, dp: 1.0-1.35 mm	nd	nd	45

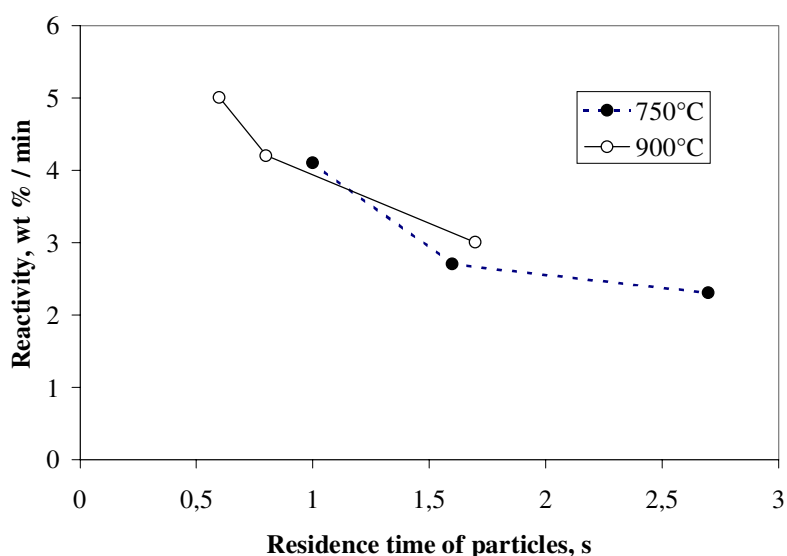


Figure 16. Effect of the residence time on the reactivity of char

Mixture of 10wt% aspen and 90wt% birch. Particle size: 0.5-0.7 mm.

The lines connecting the points have only the function of coupling together the points to compare.

The reactivity of the char, after total pyrolysis, was determined by the reaction of the sample with steam in the thermobalance. The reactivity of the chars reflected the differences in the biomass properties and also the different conditions during the devolatilization when the char is formed.

The residence time of the wood particles in the free-fall reactor affects the reactivity of the char. The results reported in paper I show that the reactivity of the char increases when the residence time in our pyrolysis reactor decreases (figure 16). Longer residence time increases the time for contact between tar and char. The residence time of solids

minus the time for the termination of the primary pyrolysis is the contact time for the tar and the char. Increased contact time between tar and char results in decreased reactivity of the char. The secondary char produced from tar not only covers the primary char but also probably encapsulates the ash and hinders its catalytic effect of the ash [47].

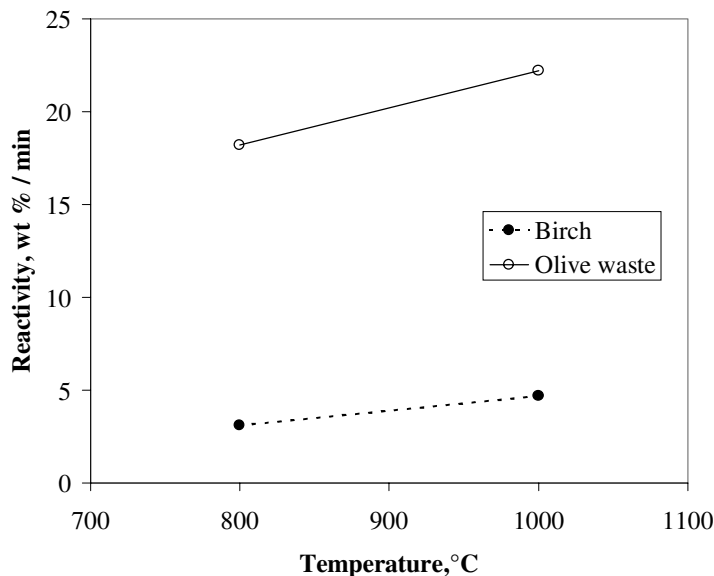


Figure 17. Influence of temperature on the reactivity of char. dp: 0.8-1.0 mm. The lines connecting the points have only the function of coupling together the points to compare.

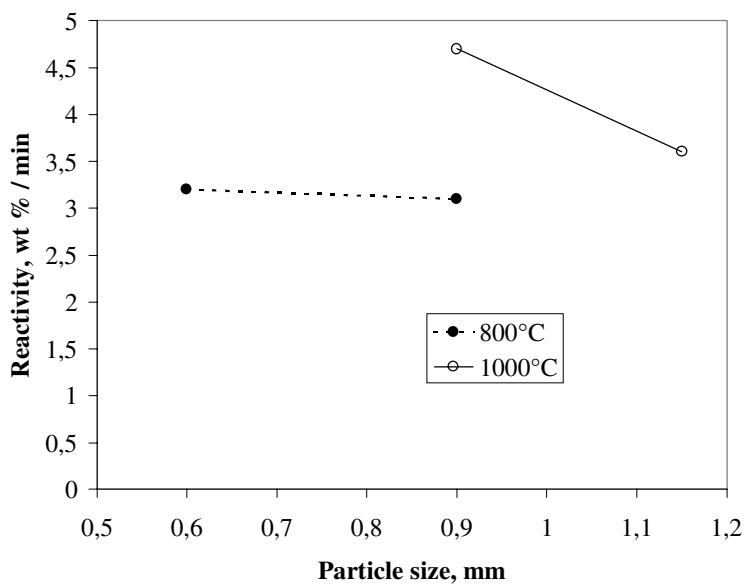


Figure 18. Influence of particle size on reactivity. Birch. The lines connecting the points have only the function of coupling together the points to compare.

The chars from wood (paper I and III) and olive waste (paper III) obtained at 1000°C were more reactive than the chars obtained at 800°C (figure 17). In paper I the reactivity of char is higher when smaller particles are used (figure 18). As mentioned, treatment at a higher temperature and smaller particle size are related to a higher heating rate. During pyrolysis, hydrocarbons are released from the samples as volatiles. Collision of these compounds with pore walls might bring about cracking and carbon deposition, which

decreases the reactivity of the char [48, 49]. At higher heating rate the volatiles are removed faster from the particle. A high char reactivity is favoured by conditions where the volatiles are rapidly removed from the particle, i.e. high heating rate, high temperature and small particles [37]. The reactivity of the samples was also in correlation with the ash content in the char after total pyrolysis. At higher pyrolysis temperatures and using smaller particles, the char yield decreases resulting in a higher ash content in the produced char, favouring a higher reactivity.

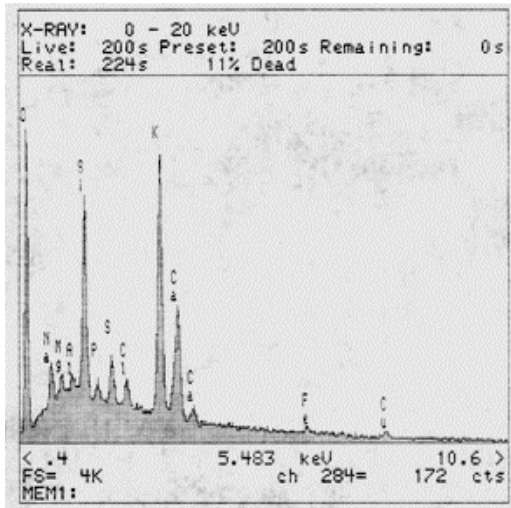
The reactivities of chars from olive waste and straw were higher than those from wood, because of the higher ash content. Chars from untreated straw were more reactive than char from pelletized straw. Chars from olive waste were more reactive than char from straw. The high reactivity of the chars derived from olive waste has been also reported for samples produced by slow heating [50].

Qualitative X-ray microanalysis of the char was made using electron microscope supplied with an energy dispersive spectrometer. The results from the analysis of the char samples (figure 19) show the qualitative ash composition of chars, especially in relation to the components K, Na and Ca, which are recognized to play a catalytic action on heterogeneous reaction rates [51, 52, 53]. The content of K seems to be similar in chars from straw and olive waste, while the content of Ca seems to be higher in chars from olive waste, which could explain the higher reactivity of the chars from olive waste. In chars produced by slow pyrolysis a higher concentration of Na<sub>2</sub>O and CaO has been reported in the ash from olive waste than from straw [50]. The content of K and Ca in chars from sugar cane bagasse seems to be lower than in those from straw. The content of Si is higher in chars from straw and sugar cane bagasse than in those from olive waste and wood.

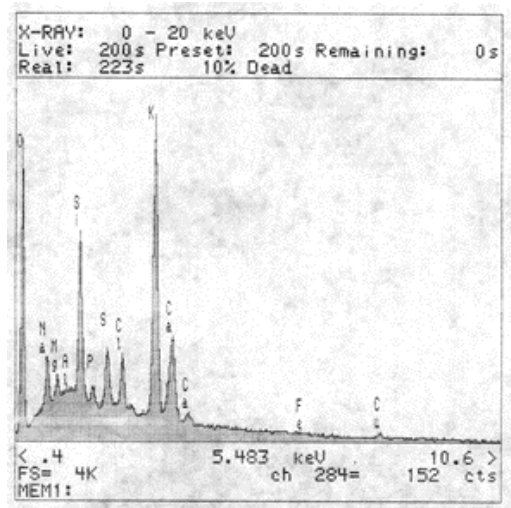
The treatment at high temperatures increases the presence of inorganic elements at the surface. Migration of inorganic constituents from the inner volume to the surface of the particles, as a consequence of thermal conversion processes, has been reported for biomass [54, 55].

The structure of the chars was examined by scanning electron microscope (DSM 940). Figure 20 shows the micrographs of the chars produced by rapid pyrolysis. The rapid pyrolysis at high temperature causes notable changes in the original cellular structure of the biomass. The char obtained by slow pyrolysis retains the fibrous structure (char from birch by slow pyrolysis) while the chars produced by rapid pyrolysis have a porous structure. Removal of cell contents and consequently, the opening-up of cellular structures give rise to a porous network of distinctive features, which evidently depends on the heating rate and the raw material. The influence of the temperature on the porous structure is not very visible in the temperature range, here studied (800°C - 1000°C), while a marked effect of temperature has been reported in the range 600°C - 800°C [55]. The chars from rapid pyrolysis at 800°C - 1000°C present deep cavities and small pores on the walls of the cavities. The light small particles of irregular shape on the surface might be due the presence of inorganic constituents.

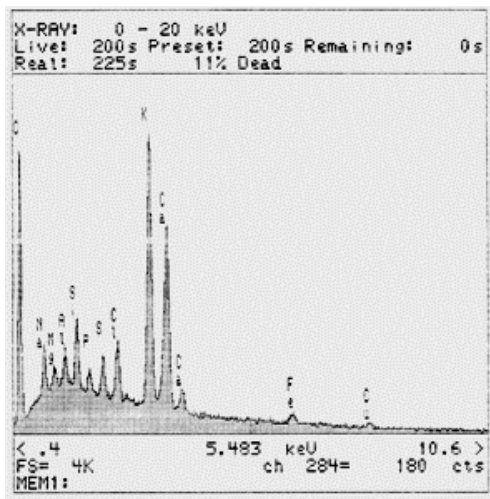
The structure of the chars observed by scanning electron microscope is consistent with the higher total pore volume, determined by mercury porosimetry in paper III, obtained in chars from straw compared which those from olive waste.



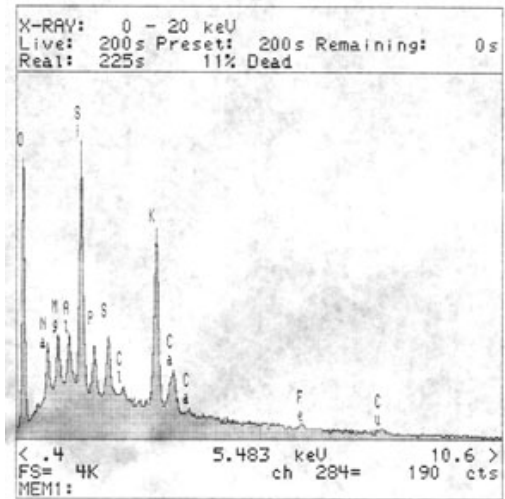
Straw pellets



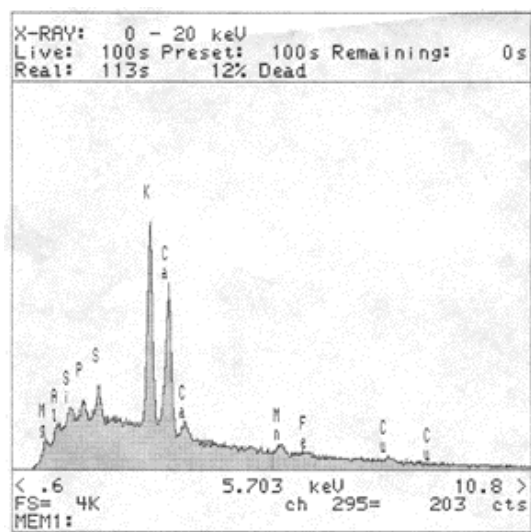
Straw



Olive waste

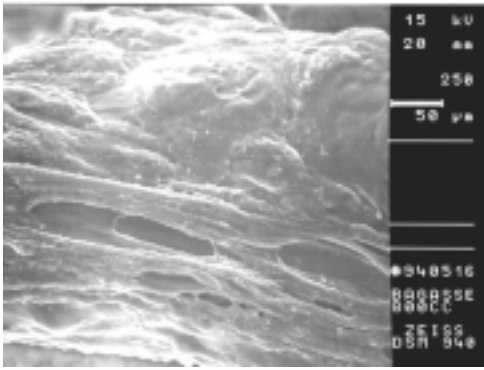


Sugar cane bagasse

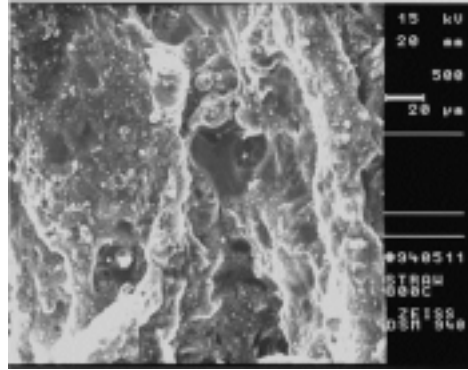


Wood

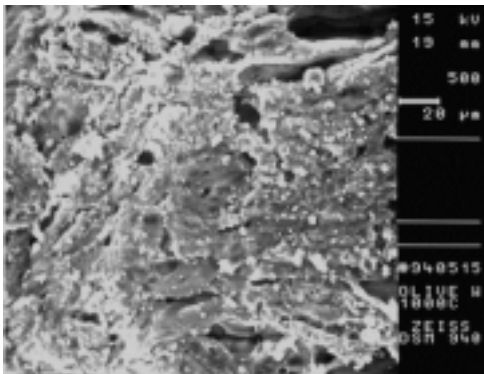
Figure 19: Qualitative energy dispersive X-ray microanalysis of char samples obtained at 1000°C



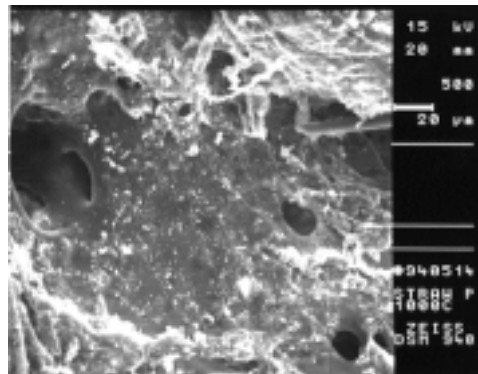
Char from bagasse. 800°C



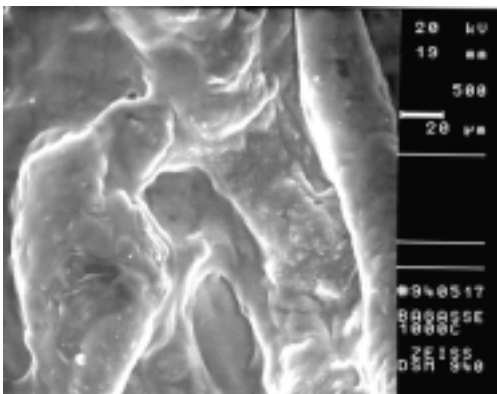
Char from straw. 800°C



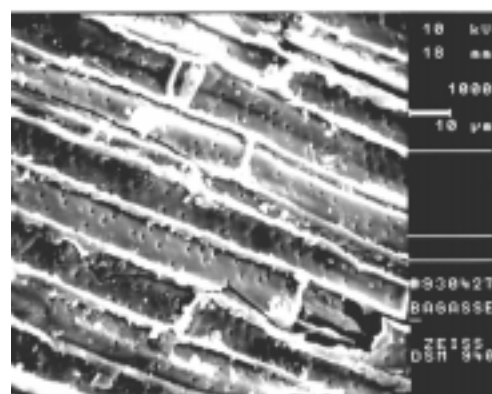
Char from olive waste. 1000°C (x500)



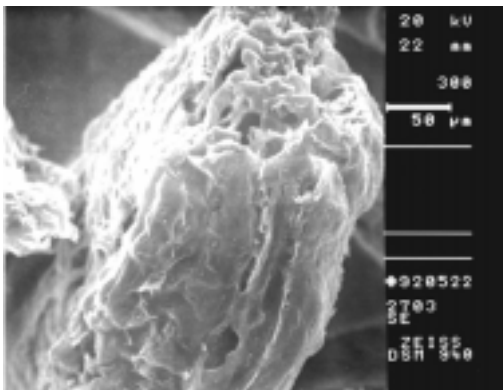
Char from straw pellet. 1000°C (x500)



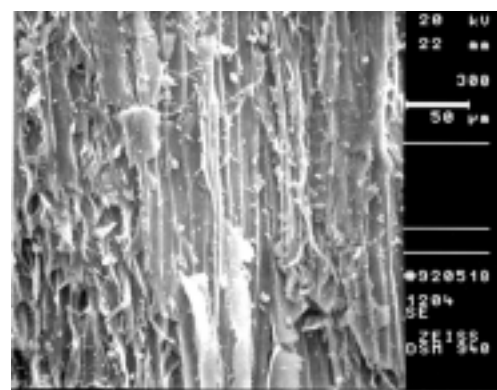
Char from bagasse. 1000 °C (x500)



Bagasse, raw material. (x1000)



Char from birch. 750°C (x300)



Char from birch (slow pyrolysis). 750°C (x300)

Figure 20. Scanning electron microscope images of chars samples



### 2.2.3 Composition of produced gases

The composition of produced gases is expressed in volume % of a nitrogen and oxygen free gas. In the experiments, using a nitrogen flow of 15 l/minutes as carrier gas flow, the concentration of nitrogen in the outgoing gas was around 85-90 vol %.

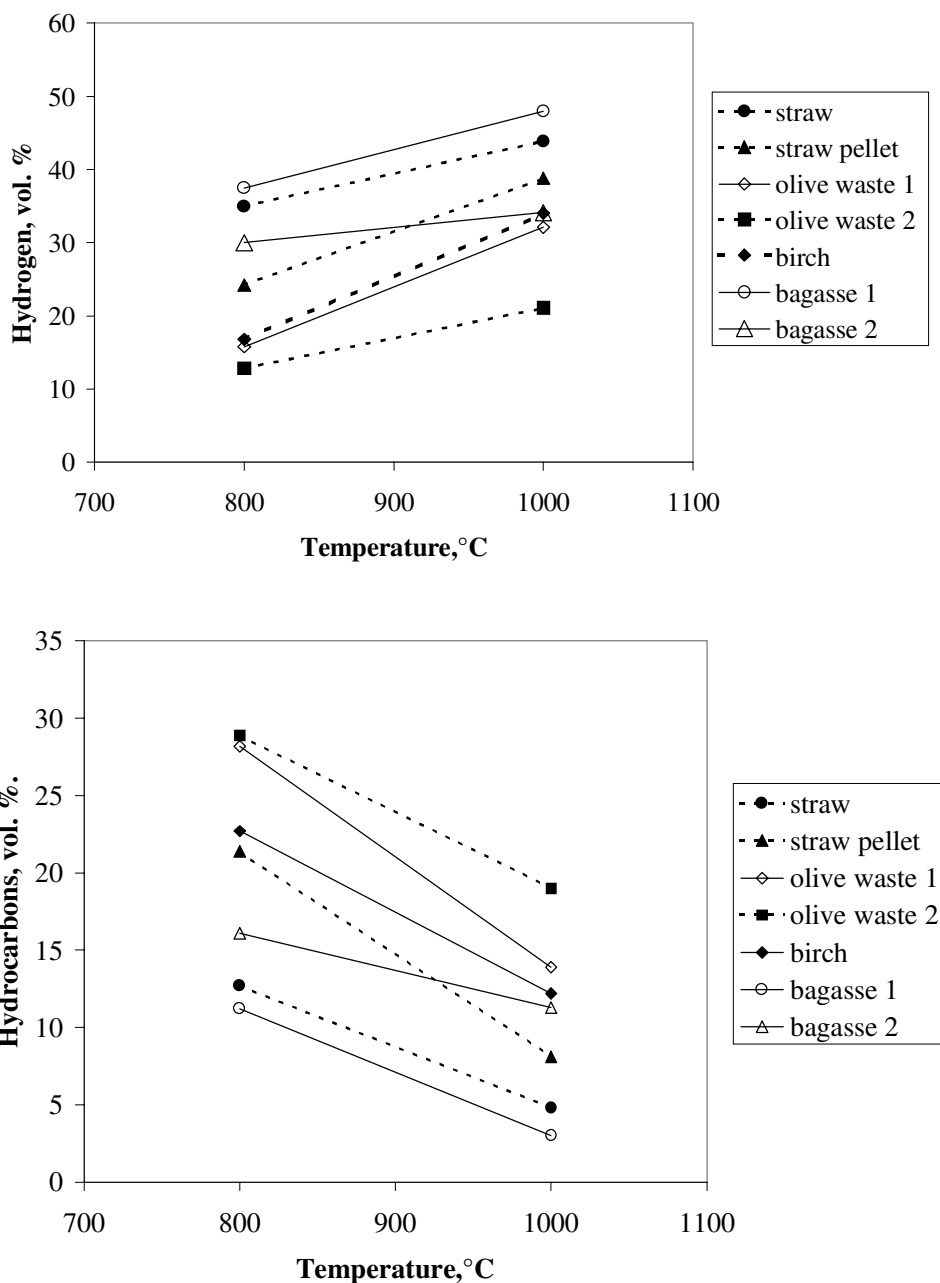


Figure 21. Influence of temperature on the content of H<sub>2</sub> and hydrocarbons (CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>2</sub>)

straw, d <sub>p</sub> : 0.5-1.0 mm.	straw pellet, d <sub>p</sub> : 0.5-1.0 mm.
olive waste 1, d <sub>p</sub> : 0.5-0.8 mm.	olive waste 2, d <sub>p</sub> : 0.8-1.0 mm.
birch, d <sub>p</sub> : 0.8-1.0 mm.	bagasse 1, d <sub>p</sub> : 0.5-0.85 mm.
bagasse 2, d <sub>p</sub> : 0.85-1.0 mm.	

The lines connecting the points have only the function of coupling together the points to compare.

Higher treatment temperatures in pyrolysis favour cracking of the hydrocarbons in the gaseous products and thus increase the yield of hydrogen (figure 21). They have also

decreased the content of CO<sub>2</sub> in the gases and increased the CO content for the agricultural residues (figure 22). Aromatic hydrocarbons (benzene) are products of secondary reactions. At higher temperature benzene was present in the gas.

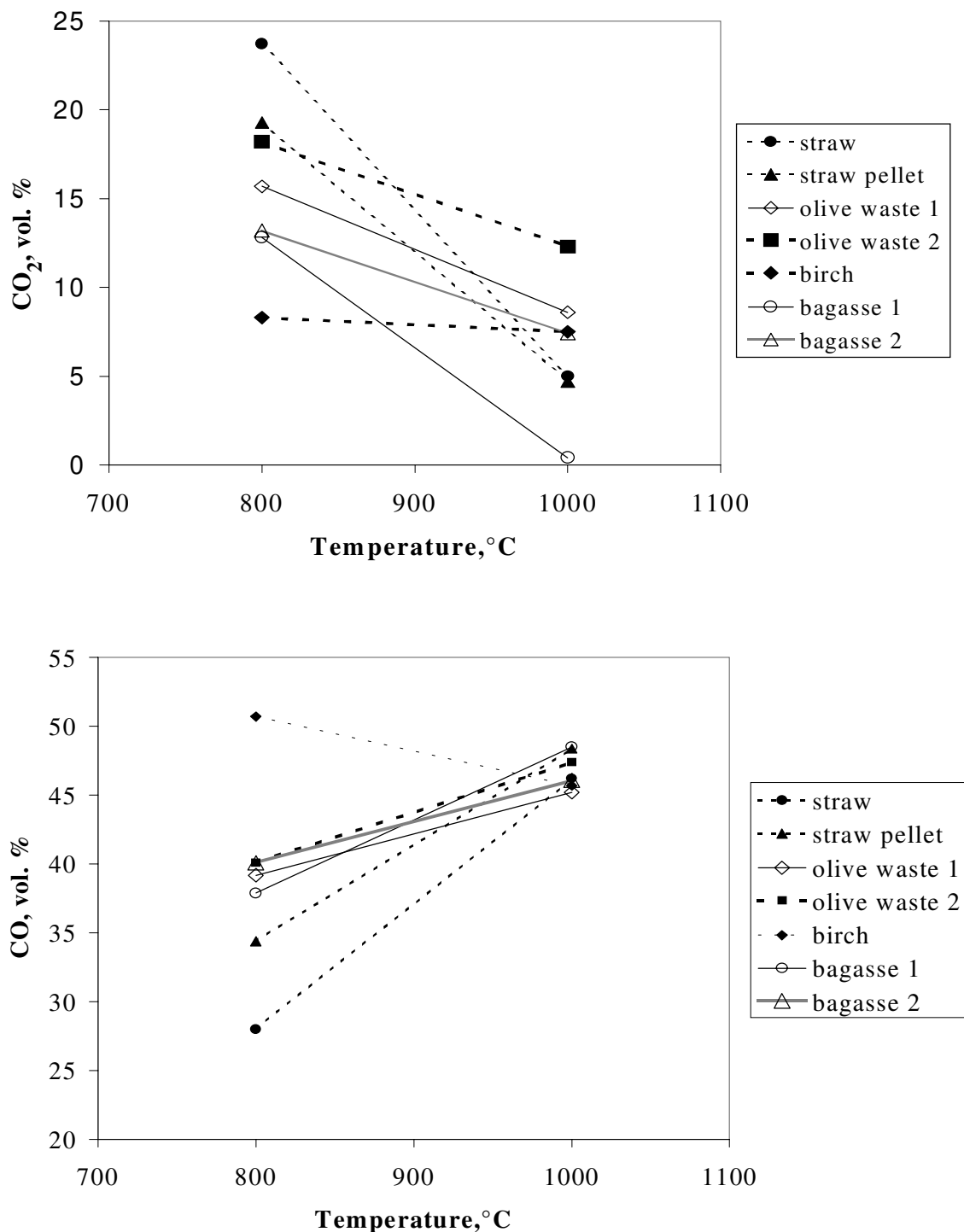


Figure 22. Influence of temperature on the content of CO<sub>2</sub> and CO in the gases  
 straw, d<sub>p</sub>: 0.5-1.0 mm. straw pellet, d<sub>p</sub>: 0.5-1.0 mm;  
 olive waste 1, d<sub>p</sub>: 0.5-0.8 mm. olive waste 2, d<sub>p</sub>: 0.8-1.0 mm.  
 birch, d<sub>p</sub>: 0.8-1.0 mm. bagasse 1, d<sub>p</sub>: 0.5-0.85 mm.  
 bagasse 2, d<sub>p</sub>: 0.85-1.0 mm.  
 The lines connecting the points have only the function of coupling together the points to compare.

The gas residence time determines the secondary reactions in the gaseous phase. Longer residence time of the gaseous products favours the cracking of aliphatic hydrocarbons and the formation of hydrogen (figure 23). It favours the formation of aromatic hydrocarbons (benzene and toluene). This is to be expected since the aromatics are products of secondary gas phase reactions and precursors for coke.

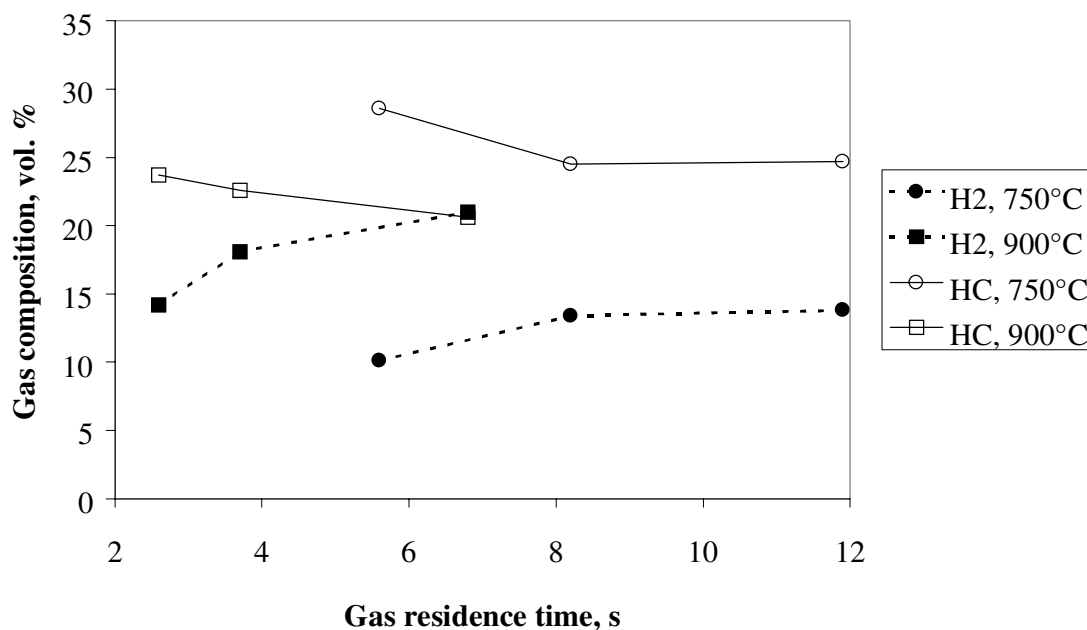


Figure 23. Influence of gas residence time on gas composition.

Hydrogen and hydrocarbons ( $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_2$ ).

Biomass: mixture 90% birch- 10% aspen.  $d_p$ : 0.5-0.7 mm

The lines connecting the points have only the function of coupling together the points to compare.

Smaller particle size has affected also the composition of the gas. It has favoured the cracking of hydrocarbons with an increase of hydrogen yield (figure 24). In smaller particles the produced gas left the particle faster than in large particles. The residence time of the gas outside the particle was longer and cracking was favoured.

In gases from pyrolysis of straw and sugar cane bagasse the concentration of hydrogen was higher and the concentration of hydrocarbons was lower in comparison with the gases from pyrolysis of olive waste and wood. In the test with straw and sugar cane bagasse a higher cracking of hydrocarbons has been reached. A possible reason for the increasing of the cracking reaction in the gaseous products when straw and bagasse are used as raw materials could be that the produced gases have been a longer time outside the particle, in the reactor, facilitating the cracking of the hydrocarbons. Because the density of the straw and bagasse is lower than that of wood and olive waste their falling velocity in the reactor is also lower. When the gases left the particle, the particles have fallen a shorter distance in the reactor using straw and bagasse than using wood or olive waste. Thus, the gases spent a longer time in the reactor in the test with straw. Another reason that could increase the residence time of the gases in the reactor when straw and bagasse are used is the higher porosity of these agricultural residues in comparison with wood and olive waste. The higher porosity of the particle, the faster can the gases leave the particle and spend a longer time in the reactor.

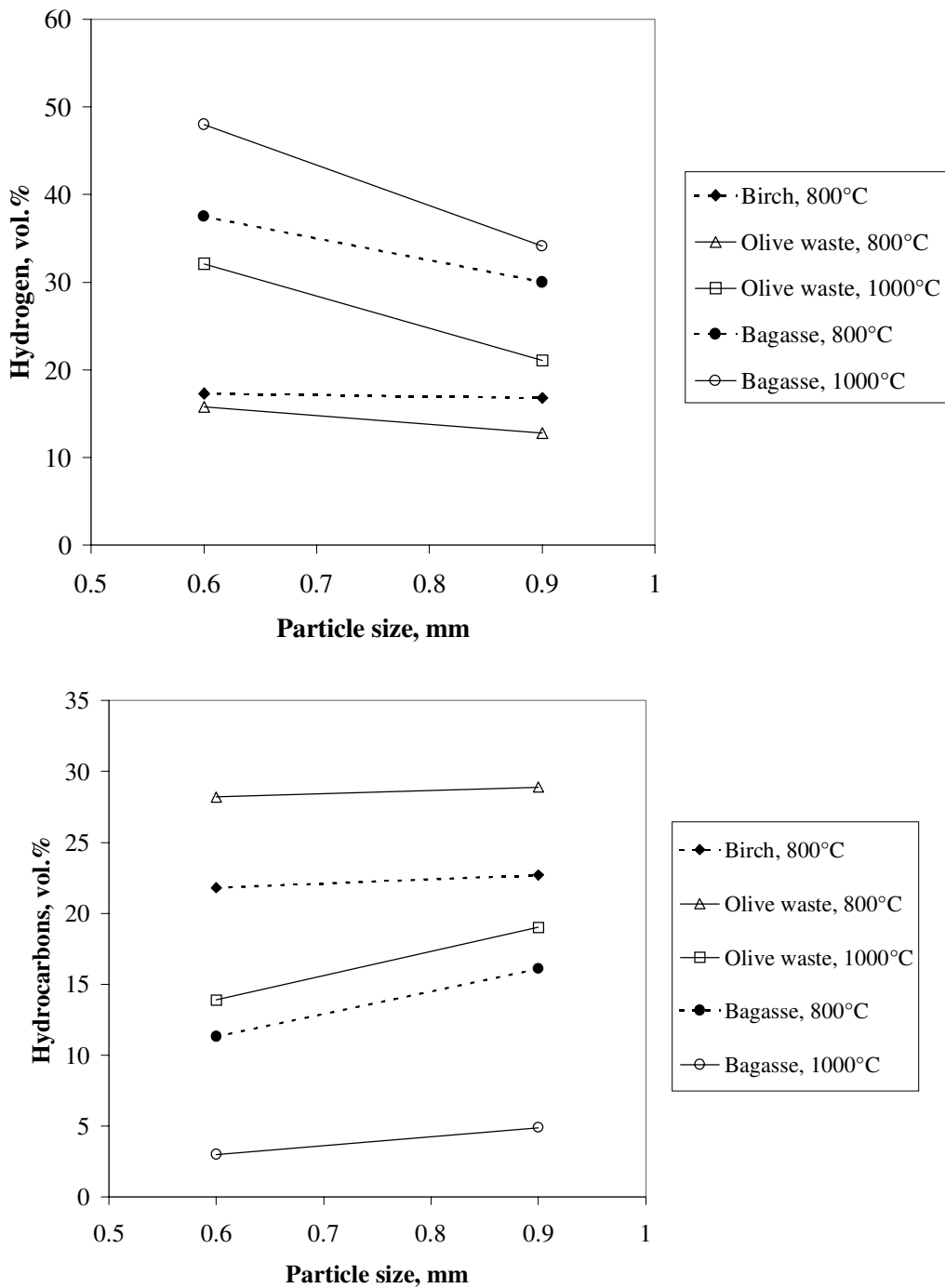


Figure 24. Influence of particle size on produced gas composition. The lines connecting the points have only the function of coupling together the points to compare.

### 2.3. Conclusions

Rapid pyrolysis of wood (birch) and some agricultural residues (olive waste and wheat straw in untreated and in pelletized form) at high temperature (800°C – 1000°C) has been studied in a free fall reactor at pilot scale. The conditions are of interest for gasification in fluidized beds. Because rapid pyrolysis is the first step in gasification and combustion in fluidized bed reactors, knowledge on rapid pyrolysis may contribute to the development of gasification and combustion models in fluidized bed reactors

Both the conditions during the pyrolysis and the composition and properties of the biomass have influenced the product distribution, gas composition and char reactivity.

Higher pyrolysis temperature has led to lower yields of tar and higher yields of gaseous products because of a higher rate of thermal cracking of tar to gaseous products. At higher temperature, the heating rate is higher. The higher heating rate favours also the decrease of char yield. Higher treatment temperatures favour cracking of the hydrocarbons in the gaseous products and the formation of hydrogen.

The size of the particles has significant effect on pyrolysis, because it affects the heating rate of the fuel in the pyrolysis reactor. Increase of the particle size decreases the heating rate and increases the yield of char. Smaller particle sizes favour the cracking of hydrocarbons with an increase of hydrogen yield because the residence time of the volatiles in the reactor is longer when smaller particles are used, favouring the cracking reactions.

The composition of the biomass influenced the product distribution. Birch and bagasse gives more volatiles and less char than quebracho, straw and olive waste. The low ash content of the wood samples studied here facilitates the prediction of the distribution of products using the composition of the organic matter in the fuel. Higher yields of char are favoured by high carbon content, low oxygen content, low H/C ratio and higher content of coke forming components, such as lignin, in the fuel subject to pyrolysis. White quebracho with a higher lignin content than birch produces a higher yield of char when it is submitted to rapid pyrolysis instead of birch. A relation between the concentration of lignin in wood and the yield of char obtained from the rapid pyrolysis of wood is established. Almost the whole amount of cellulose is converted to volatiles. The high ash content in agricultural residues favours the charring reactions, increasing the char yield. The char yield from olive waste was higher than that from straw because of the higher lignin content in olive waste.

The reactivity of the chars reflected the differences in the biomass properties and also the different conditions during the devolatilization when the char is formed.

A high ash content favours the reactivity of the chars. The higher ash content in agricultural residues has led to a more reactive char comparing with char from wood.

Longer residence time in rapid pyrolysis increases the time for contact between tar and char which makes the char less reactive. The secondary char produced from tar not only covers the primary char but probably encapsulates the ash and hinders the catalytic effect of the ash

A high char reactivity is favoured by conditions where the volatiles are rapidly removed from the particle, i.e. high heating rate, high temperature and small particles.

Pyrolysis proceeds in two steps: an initial fast step follow by a slower step including some chemical rearrangement of the char.

### 3. ACTIVE CARBON

#### 3.1 Active carbons, features and characterisation

Active carbons are carbonaceous materials with highly developed internal surface area and porosity, sometimes described as solid sponges. The large surface area results in a high capacity for adsorbing chemicals from gases or liquids.

Active carbons are versatile adsorbents of major importance in a wide range of applications. The adsorptive property stems from the extensive internal pore structure that develops during the activation process. The most widely used commercial active carbons have a specific surface area of the order of 800-1500 m<sup>2</sup>/g [56]. Differences in pore sizes affect the adsorption capacity for molecules of different shapes and sizes, and this is one of the criteria by which carbons are selected for a specific application. Porosity is classified by IUPAC into three different groups of pore sizes [56]:

- Micropores - width less than 2 nm
- Mesopores - width between 2 and 50 nm
- Macropores - width greater than 50 nm

Adsorption takes place in micro- and mesopores with macropores acting as transport channels. Definition and classification of carbons as micro- or mesoporous is not based on exact measurement and does not imply rigid size characterization. Generally, the terms are used to describe adsorption processes as being micro- or mesoporous in nature [57]. Gases are strongly adsorbed at low pressures in micropores, because there is enhancement of adsorption potential due to overlap of the force fields of opposite pore walls. Microporous carbon can exhibit molecular sieve action, i.e., the selective adsorption of small molecules in narrow micropores [58]. In mesopores, capillary condensation with its characteristic hysteresis loop, takes place. In the macropore range, the pores are so wide that it is difficult to obtain the isotherm in detail because the relative pressures are very close to 1. The adsorption isotherm is the relationship, at constant temperature, between the amount of gas adsorbed and the pressure, or relative pressure, respectively. The commonest method used to characterize macropores in carbons is mercury porosimetry [58].

Other important features of active carbons include the presence of surface functional groups, mostly O-containing, that can give the carbon polar, hydrophilic and acidic character [57]. These oxygen complexes can arise from oxidation processes either during heat treatment or during storage after activation [57]. The content of ashes in active carbon can also affect the its properties. Ash content can lead to increased hydrophilicity and can have catalytic effects, causing restructuring processes during regeneration of used active carbons [57].

Two distinct forms of active carbons are commercially recognised: powdered active carbons and granular active carbons. Powdered active carbons, with an average particle size of 15 – 25 μ m, are generally used in liquid media where the small size ensures that diffusion is not the rate limiting step. Granular active carbons are in the form of crushed granules or in pellets. Granular active carbons are generally used in both gases and liquids and sizes vary depending on application. Used granular active carbons are often regenerated as opposed to used powdered active carbons, which are normally discarded after use [59].

### 3.2 Chemical characterisation

Proximate and ultimate analysis methods are often used to determine chemical composition of carbonaceous materials. In the proximate analysis, contents of moisture, volatile material, ashes, and fixed carbon are determined. Ultimate analysis is an elemental analysis employed to determine content of carbon, hydrogen, oxygen and nitrogen. Various spectroscopic methods are also employed to determine the chemical composition of the material. Atomic absorption spectroscopy is used to determine the ash composition and surface analysis with EDAX can be used to determine the content of inorganics. Oxygen complexes on the surface can be detected by multibasic titration.

### 3.3 Textural – morphological characterisation and surface area evaluation

Active carbons are characterised for their adsorption capacity. Surface area is often evaluated through adsorption capacity for N<sub>2</sub> at 77 K or CO<sub>2</sub> at 298 K and application of different models to describe the adsorption isotherms. Frequently used models include the BET method,  $\alpha$  - plot method as well as a method using the Dubinin – Radushkevich equation.

The BET theory was the first to describe successfully multilayer adsorption of gases on a wide range of porous and non porous solids. The BET equation is now accepted as the standard equation for analysing adsorption isotherms to obtain specific surface area of solids. The BET-method was developed and published by Brunauer, Emmett and Teller in 1938. The theory, range of applicability and limitations are discussed further by Gregg & Sing [60]. The equation has serious limitations when applied to microporous solids [58]. Equilibrium was postulated in which the rate at which molecules coming from the gas phase and condensing on the sites is equal to the rate at which molecules evaporate from occupied sites. For multilayers BET makes three assumptions: a) that in all layers except the first the heat of adsorption is equal to the heat of condensation, b) that in all layers except the first the evaporation - condensation conditions are identical, and c) that when  $p=p^{\circ}$  the adsorbate condenses to a bulk liquid on the surface of the solid, that is the number of layers becomes infinite ( $p^{\circ}$ = saturation vapour pressure).

The  $\alpha$ -plot is a method for characterisation of a sample by comparing the shape of the given sample isotherm with the one of a standard isotherm from a reference material [60]. The comparison is made by plotting the liquid volume adsorbed against  $\alpha$ , where  $\alpha$  is a function of relative pressure, expressed, as in equation (1), as the volume adsorbed by the reference carbon at each relative pressure divided by the adsorption at a normal relative pressure. This normal relative pressure is for convenience taken as 0.40 because at higher relative pressures capillary condensation occurs [61].

$$\alpha = \frac{v(x)}{v(0.40)} \quad (1)$$

$v(x)$  - volume adsorbed at relative pressure  $x = P/P_0$

$v(0.40)$  - volume adsorbed at relative pressure  $P/P_0 = 0.40$

The use of Dubinin – Radushkevich equation is another method applied to the adsorption data to evaluate micropore volume. The micropore volume obtained from the DR – equation corresponds to the narrow micropores of the carbon [62].

Scanning electron microscopy may be employed to visualise sample morphology [58]. Pore and fibre structure can be observed and structural changes due to activation can be analysed.

Pore size distribution and pore volume may be determined by mercury porosimetry. Macropores and mesopores wider than 7  $\mu\text{m}$  can be measured and the volumes of meso- and macropores can be evaluated.

### **3.4 Applications of active carbons**

One of the largest uses of active carbons is for water treatment. The carbons are applied to remove compounds that affect taste and odour of the water. Increasing use of active carbon is found in industrial waste water and gas treatment due to the necessity of environmentally friendly processes and also for material recovery purposes. Large numbers of people are exposed to various pollutants in the municipal water and in the air. Active carbon are used as adsorbent for removal of toxic compounds from water (metal ions, organic substances, etc) and air ( $\text{SO}_2$ ,  $\text{NO}$ ,  $\text{Cl}_2$ , etc). The food industry is also a major consumer of active carbons where it is used to remove compounds that adversely affect colour, taste and odour. In the mineral industry, active carbons are used to recover gold from leached liquors. Medicinal uses and the pharmaceutical industry also answer for a large part of the consumption. Catalysis is another area where the structure and features of active carbon are favourable. Oxygen adsorbed on the surface of active carbons enables its use as a catalyst in oxidation of inorganic and organic compounds. With its large surface area, active carbon also makes a good supporting structure for other catalytic materials.

Active carbons are extensively used in air filters for industrial applications as well as in air conditioning. An important industrial use of active carbons is solvent recovery. Volatile organic compounds are used in a wide variety of applications and they create unacceptable environmental problems if vented straight to the atmosphere. In a cyclic adsorption – desorption process, active carbons provide an effective means of recovering the solvent. Active carbons are also used for storage of hydrogen and natural gas as well as material for fuel cells.

### **3.5 Methods for active carbon preparation**

Active carbons can be manufactured from virtually any carbonaceous precursor, but the most commonly used raw materials are wood, coal and coconut shells [63]

The increased use of active carbons has led to an increasing research to ensure safe copious supply of raw materials that fulfil commercial and technological requirements for manufacture. For these reasons, the suitability of agricultural by-products, such as nut shells and fruit stones, waste polymer materials and forestry and petrochemical residues have been investigated. The rapidly increasing use of biomass from fast growing trees as an alternative, renewable fuel source has also led to an interest arising in investigating their possible use as a raw material for active carbons manufacture [63, 64, 65]. This is of particular importance for countries with well developed agriculture as well as for countries rich in forests like the Nordic countries.

The method most frequently used for preparation of active carbons involves pyrolysis of the precursor in an inert atmosphere followed by activation. There are mainly two different methods for activation, namely physical and chemical. The physical activation process comprises treatment of the solid residue obtained in the pyrolysis with some oxidising gas, generally steam or carbon dioxide, at high temperature. In chemical activation, a chemical reactant is



incorporated in the precursor prior to heat treatment. Chemical activation only involves one heat treatment step and activation is achieved at lower temperatures.

In the two-stage physical activation process, the precursor material first undergoes pyrolysis in an oxygen-free atmosphere. The pyrolysis serves to drive off moisture and volatile matter, such as CO, H<sub>2</sub>, CH<sub>4</sub> and other hydrocarbons, to produce a high carbon content solid residue, termed char. The pyrolysis also leads to an initial opening of the precursor carbon structure. The char is then treated in a gas stream at a temperature of 800 – 1200 K. The gases used for the activation step are mainly CO<sub>2</sub> and steam. The gas acts as an oxidising agent and produces a porous structure in the char as it reacts with the carbon in the char to form gaseous reaction products. The activation can be carried out under controlled forms to a desired conversion. The pores thus produced in the char give the active carbon its high surface area and adsorptive properties. The physical activation method sometimes uses chemical additives to increase the rate of the reaction. Alkali salts, such as K<sub>2</sub>CO<sub>3</sub>, are used to catalyse the activation.

A three-step process for the production of active carbons including a carbonization step, an oxidation in air following a stepwise heating from low (ca. 450 K) to high (ca. 660 K) temperatures and finally a heating in an inert environment to a high temperature has also been described. [66, 67]

A simple one-step method for production of active carbons by pyrolysis of solid fuels in the presence of steam has also been developed [68].

In chemical activation, the precursor material is impregnated with a dehydrating and stabilising chemical reactant in order to enhance the development of porous structure upon heat treatment. The most commonly used chemical reactants are phosphoric acid and zinc chloride but alkali compounds, such as KOH and NaOH, as well as sulphuric acid can also be used. Especially the alkali reagents can yield high surface areas in some precursors. The zinc chloride method was the most commonly used chemical activation method up until 1970, but the use has since then decreased in favour of phosphoric acid [57]. The phosphoric acid has an advantage in that it offers an easier extraction process after activation for reagent recovery. Another reason why the phosphoric acid may be preferred is the increased consciousness of the problems with environmental contamination associated with zinc compounds. The chemical activation method employing H<sub>3</sub>PO<sub>4</sub> has been proven to give higher surface areas compared to physical activation for some precursors [69, 70]. The heat treatment temperature used in chemical activation is normally lower than in physical activation[71]. The chemical reactant can be recovered after washing of the resulting active carbon. [57]. A drawback of the chemical activation is the incorporation of impurities in the carbon as a result of the impregnation, which can affect the chemical properties.

Preparation method, type of reactor used, employed conditions and selected precursor material influence the properties of the obtained active carbons. Activation with CO<sub>2</sub> has resulted in carbons with a pore structure consisting mainly of narrow micropores and wide macropores [69]. Introduction of potassium phosphate as a catalyst for the physical activation led to a decrease in macropore volume and diameter, and an increase in micropore diameter. Chemical activation with phosphoric acid produced a carbon with wider micropores and a significant mesoporosity. Hence, depending upon the intended application the preparation method of the active carbon can be an important factor to consider.

Active carbons produced from coconut shells and pine wood wastes have shown good mechanical strength and high adsorption capacities towards various gaseous compounds [73, 74, 75, 76]. Olive stones and almond shells are also suitable raw materials for active carbons with high adsorption capacities, sufficient mechanical strength, and low ash contents. The narrow range of the pore size distribution in these carbons makes them suitable for selective gas adsorption [77]. Active carbons obtained from olive stones and almond shells have high metal ion adsorption capacities [78]. Plum and peach stones have also been used for preparation of active carbons [79]. The carbons from peach stones have also shown narrow pore size distribution and good properties as molecular sieves. The adsorbents prepared from plum stones had a better developed porosity compared to those prepared from peach stones.

### **3.6 Pyrolysis of biomass in presence of steam for preparation of active carbon**

In the present work (papers IV, V and VI) the biomass samples are carbonised and activated in a one-step treatment involving pyrolysis in a flow of steam. The almost simultaneous pyrolysis and gasification of the fuel favour the high reactivity of the solid material and its conversion at milder treatment conditions into active carbon with well developed porous structure and good adsorption capacity [80]. One-step steam pyrolysis is a promising alternative to the conventional processes for production of active carbons and liquid and gaseous fuels [81]. Several simultaneous processes occur in steam pyrolysis: thermal decomposition, multi-component distillation, fast escape and stabilization of the volatiles, mild oxidation, activation of the solid residues and formation of active carbons. The multi - component distillation, which accompanies the pyrolysis in a stream of water vapour, guarantees a 'mild' process and efficient escape of the volatiles from the solid material. The quick removal of the volatiles and stabilization of the radicals in the presence of steam results in increased yields of volatiles and formation of solid products with a highly developed active surface free from organic compounds.

The role of steam and carbon dioxide is not limited only to transport and stabilization of the volatile products, but also to efficient activation of the solid residual materials to transform them into active carbons. The fast removal (steam distillation) of the volatile products out of the high temperature in the pyrolysis zone depresses the secondary pyrolysis reactions.

The results are presented in tables in the annexed papers. In the summary of the papers the results are presented explicitly in figures. In the figures the lines connecting the points have only the function of coupling together the points to compare.

## 4. SUMMARY OF THE PAPERS ON SLOW PYROLYSIS IN PRESENCE OF STEAM FOR PREPARATION OF ACTIVE CARBON

(Papers IV, V and VI)

### 4.1 Experimental

#### 4.1.1 Raw materials

The precursors used in the experiments are birch (wood) and different types of agricultural residues such as sugar cane bagasse, olive waste, miscanthus pellets and straw in untreated and pelletized form. Chemical composition of these materials is shown in papers IV and VI.

#### 4.1.2 The equipment

In paper IV, a horizontal rotating stainless steel reactor is used. The experiments presented in papers V and VI are performed in a stationary reactor. Figure 25 shows the equipment utilized in paper V.

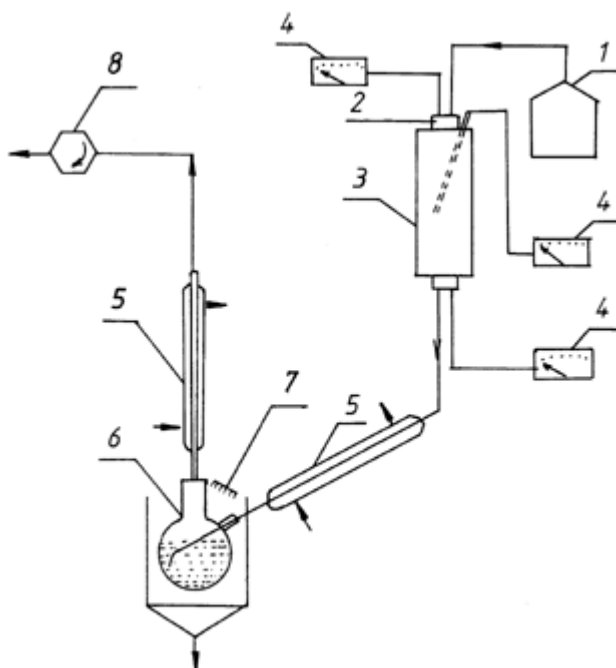


Figure 25. Stationary reactor for pyrolysis of biomass in presence of steam. Paper V.

1. Steam generator; 2. Stationary reactor; 3. Oven; 4. Thermocouple;
5. Cooler; 6. Receiver; 7. Water cooling; 8. Gas counter

Similar equipment is used in the experiments presented in paper VI. It includes also a stationary cylindrical reactor, a steam generator, equipment for removal of the liquid products (water-cooled condenser, ice traps and a column with cotton and phosphorus pentoxide as drying agent) and gas meter. The reactor (figure 26) has a length of 0.5 m and an inner diameter of 0.04 m.

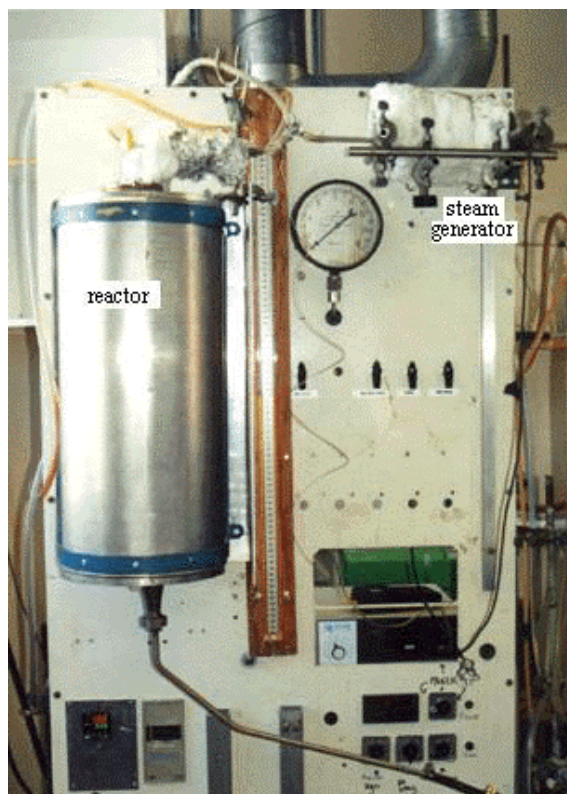


Figure 26. Equipment for production of active carbon. Paper VI.

The activating agent was steam but in paper IV experiments in an inert atmosphere (argon) and in presence of a mixture of carbon dioxide/steam were also performed as comparison. The final temperature was 750°C in paper IV, 700°C, 750°C and 800°C in paper V and 550°C, 650°C and 750°C in paper VI. The treatment time at the final temperature was 120 minutes in paper IV, 60 and 120 minutes in papers V and VI. The heating rate was kept at 10°C/min.

The influence of the steam flow was studied in paper VI.

The adsorption capacity of the produced active carbon was determined towards iodine by the method described in DIN 53582 and the iodine number obtained was related to the surface area. In paper VI the surface area has also been determined by nitrogen adsorption and desorption with a Micromeritics Flowsorb II 2300.

The oxygen-containing functional groups in the solid products (-COOH, =CO and -OH) are determined using the method of Boehm (paper IV). The adsorption properties of the active carbons depend on the surface area, the pore size distribution and the concentration of active sites (e.g. chemical groups containing oxygen or other heteroatoms). The nature of the oxygen functional groups depends strongly on the temperature for the oxidation. The oxygen - containing groups on the surface of carbon may be basic or acidic [82]. Oxidation above 200°C leads mostly to formation of acidic groups, which adsorb predominantly cations. Oxidation above 500°C leads mainly to the formation of oxygen groups with basic character. The oxygen-containing functional groups of different acidity as well as those with basic character are assessed by titration with alkaline solutions of different strength (NaHCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, NaOH and NaOEt) and hydrochloric acid. Thus carboxylic, lactonic, phenolic and carbonylic groups as well as pyrone structures may be identified [83]. Due to relatively high treatment temperature,

the less thermally stable carboxylic and lactonic groups have not been identified in the produced active carbons (reactions with  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$ ) (papers IV and V).

The composition of the liquid products was studied in paper V. After cooling of the volatile products the tar has been separated from the condensed water phase by decantation. In order to isolate maximum amount of water soluble product 100 ml of the condensate was mixed with silica gel (70-230 mesh ASTM) in a quantity sufficient to adsorb the whole liquid. The sample was dried at ambient temperature and eluted with a mixture of - methanol/formic acid (95/5) in a glass column. The solvent was evaporated to dryness under vacuum in a rotary evaporator. Column chromatography was used to separate the organic material into four fractions - aliphatic, aromatic and two polar fractions. The eluents - pentane, toluene, tetrahydrofuran/methanol (85/15) and methanol/formic acid (9/1) have been chosen having in mind the composition of the raw materials and the expected products of the thermochemical treatment.

The gas product was analyzed by a gas chromatograph for  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{N}_2$ ,  $\text{CH}_4$  and hydrocarbons up to  $\text{C}_7$  (paper VI).

## 4.2 Results and Discussion

### 4.2.1 Effect of the raw material.

In paper IV, the chemical composition of the produced active carbon has been compared with the chemical composition of the precursor. As a consequence of the thermochemical treatment the raw materials have been enriched as fuels. The products have similar degrees of carbonisation (similar ratio between the calorific value of the produced active carbon and precursor) and comparable elemental composition of the organic material. The content of carbon has been increased while the content of oxygen has been reduced. The ash content in the solid product has been increased (papers IV, V and VI). The samples obtained from straw present the highest content of inorganic compounds, followed by those from Miscanthus (papers IV, V and VI).

The yield of active carbon obtained in a stationary reactor from straw in pelletized and untreated form is lower than that obtained when birch, salix, olive waste, pelletized miscanthus and bagasse are used (paper VI). In the experiments performed in the stationary reactor shown in figure 26, straw presents a higher reactivity in gasification in comparison with the other used biomasses. The high ash content in straw pellets considerably increases the reactivity of the biomass in the activation stage. Ash may have a catalytic effect in gasification [52, 53]. Untreated straw has a higher porosity than the other used biomasses [84]. Because of the high porosity the volatiles are removed faster from the particles. Even in the experiments at  $650\text{ }^\circ\text{C}$ , in the reactor shown in figure 26, the yield of obtained active carbon was below 5% when pelletized and untreated straw was selected as precursors (paper VI).

In a rotating reactor miscanthus and bagasse were more reactive than straw pellets and they gave lower yields of active carbons (paper IV).

The active carbons with highest surface area were obtained from birch followed by the active carbons produced from salix and sugar cane bagasse (paper VI).

Both in the experiments in a rotating reactor and in a stationary reactor the highest contents of basic groups have been detected on the surfaces of carbons from straw. The pH values of 9.8 of these carbons confirm their basic character. The highest contents of weakly acidic groups are registered for the samples prepared from birch (paper V).

#### 4.2.2 Effect of the activating agent

The yields and adsorption characteristics of the active carbons obtained in a rotating reactor in presence of argon, steam and a mixture of steam and carbon dioxide are compared in paper IV.

The product distribution obtained in pyrolysis in presence of steam at 700°C, 750°C and 800°C has been compared with that obtained with treatment in an inert atmosphere (paper V).

Pyrolysis in inert atmosphere results in a higher yield of the solid product with lower surface area (papers IV and V). The steam has contributed to the formation of solid residues with high surface area and good adsorption capacities. The adsorption capacities of the samples pyrolysed in a flow of steam are much higher compared to the samples pyrolysed in inert atmosphere.

Similar yields and adsorption characteristics of the active carbon are obtained in presence of steam and a mixture of steam and carbon dioxide, with the exception of those from bagasse and olive stones. For these samples activation with only steam results in much lower yield of solid product. For most of the samples, a higher surface area of the active carbon is achieved in presence of a mixture steam/carbon dioxide than in presence of only steam, with the exception of the experiments with miscanthus (paper IV).

Compared to active carbons obtained in presence of inert gas, those obtained in presence of steam or a mixture of steam and carbon dioxide have higher contents of oxygen-containing groups with basic and weakly acidic character (papers IV and V), which are related to active sites. This may be explained with the high oxygen content of the initial raw material and the effect of steam and CO<sub>2</sub> on the pyrolysis.

The water vapour favours quick removal of the volatile compounds from the fuel without substantial change in their structure [80]. Thus the oxygen-rich chemical structures, which are typical for the initial biomass material, are preserved in the volatile products and contribute to formation of polar compounds.

The treatment in a flow of reactive agents (steam and mixture steam/carbon dioxide) favours the escape of the volatiles from the solid material. Thus the amount of liquid products increases considerably. The liquid product obtained in steam is presented in paper V as tar and water-soluble fraction. The largest part of the liquid products from steam pyrolysis is found in the water soluble fractions. This is a serious disadvantage. For all samples the total yield of liquid product obtained in steam pyrolysis is 2 to 4 times higher than in inert atmosphere. The opposite is observed for the gaseous products.

In paper V the liquid products from different raw materials obtained by pyrolysis in presence of steam and inert atmosphere are separated in four fractions (aliphatic, aromatic and two polar fractions). The polar fractions, particularly those eluted with tetrahydrofuran / methanol (85/15) dominate. In the samples from bagasse the contents of both polar fractions are approximately the same. It may also be seen that in the samples obtained in steam pyrolysis the contents of the polar fractions are somewhat higher, while the formation of aliphatic and particularly the aromatic compounds seem to be favoured in inert atmosphere.

### 4.2.3 Influence of the temperature, time of treatment and rate of steam flow in the pyrolysis

The temperature and the time of treatment markedly affect the product distribution. At higher temperatures the reactivity of the carbon in the reaction with steam is higher. Consequently the yield of the active carbon decreases and the gas yield increases.

In paper V the experiments were performed at 700°C (final temperature) under 1 hour activation at this temperature and at 700°C, 750°C and 850°C and 2 hours activation in the reactor showed in figure 25. In the selected experimental conditions increase of the temperature from 700 to 750°C and the duration of treatment from 1 to 2 hours result in decrease of the yield of solid residues and improvement of the adsorption capacities (tables 5 and 6, figures 27 and 28). Further increase of the temperature decreases the yield of solid product without any improvement in the adsorption capacity (figures 27 and 28). At 800°C the gasification reactions are intensified and the solid residues loose both weight and active surface. For all samples treated at 800°C, 2 hours, the adsorption characteristics are worse compared to those obtained at lower temperature. The samples activated 2 hours at 750°C have the best adsorption characteristics. These conditions for activation are used to compare the adsorption capacities of samples obtained by pyrolysis in presence of steam and nitrogen.

Table 5. Influence of time of treatment on the yield of active carbon.  
Temperature: 700 °C

Treatment time	Olive waste yield (wt%)	Straw pellet yield (wt%)	Miscanthus pellet yield (wt%)	Birch yield (wt%)	Bagasse yield (wt%)
1 hour	18.8	20.0	17.7	14.2	18.5
2 hour	16.7	18.2	14.2	12.2	14.5

Table 6. Influence of time of treatment on the surface area of the active carbon characterized by the adsorption capacity towards iodine (I<sub>2</sub> number)  
Temperature: 700 °C

Treatment time	Olive waste I <sub>2</sub> number mg/g	Straw pellet I <sub>2</sub> number mg/g	Miscanthus pellet I <sub>2</sub> number mg/g	Birch I <sub>2</sub> number mg/g	Bagasse I <sub>2</sub> number mg/g
1 hour	790	585	500	645	450
2 hour	875	647	565	694	650

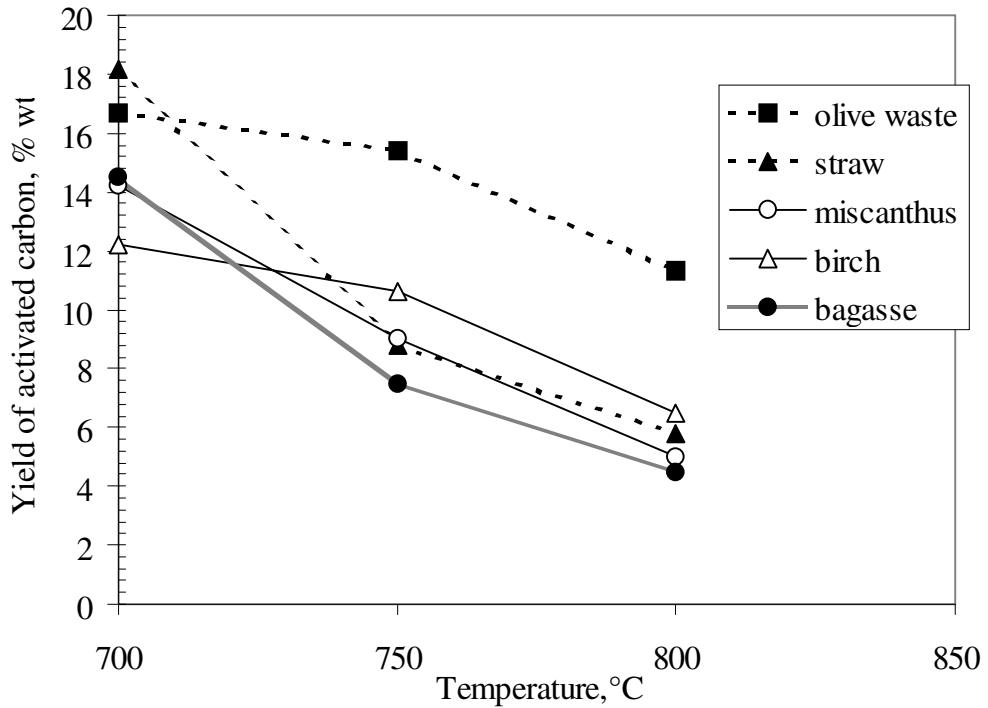


Figure 27. Influence of the final temperature on the yield of active carbon.  
 Time of treatment at the final temperature: 2 hours.  
 The lines connecting the points have only the function of coupling together the points to compare.

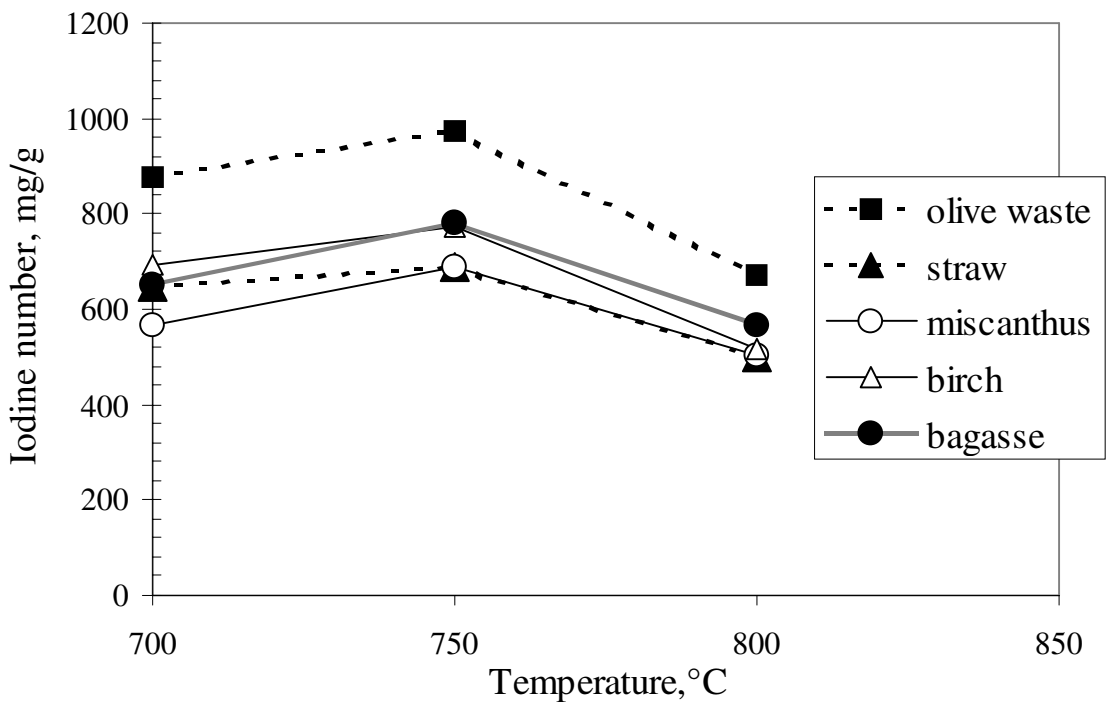


Figure 28. Influence of the final temperature on the surface area of the active carbon.  
 Time of treatment at the final temperature: 2 hours.  
 The lines connecting the points have only the function of coupling together the points to compare.



In paper VI the experiments were performed in the reactor shown in figure 26 at 550°C, 650°C and 750°C (figure 29 and 30). At 550°C the activation rate is lower than at 650°C resulting in higher yield of active carbon with a low surface area. For some samples at 750°C the steam has reacted to a great extent with the biomass destructing also the small pores. In consequence the surface areas of the carbons from these samples produced at 750°C wer lower.

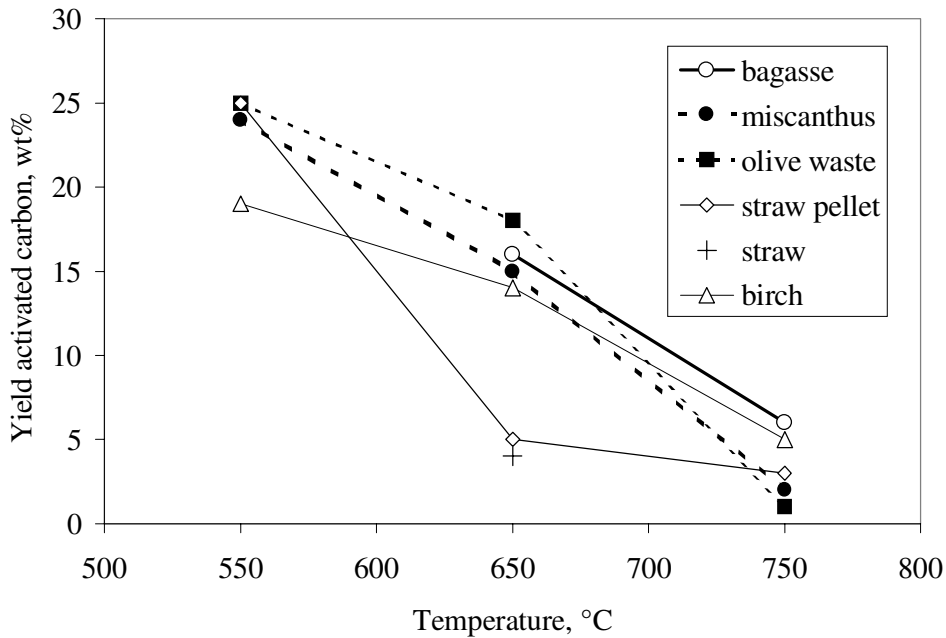


Figure 29. Influence of temperature on the yield of active carbon

Time of treatment at the final temperature: 1 hour

The lines connecting the points have only the function of coupling together the points to compare.

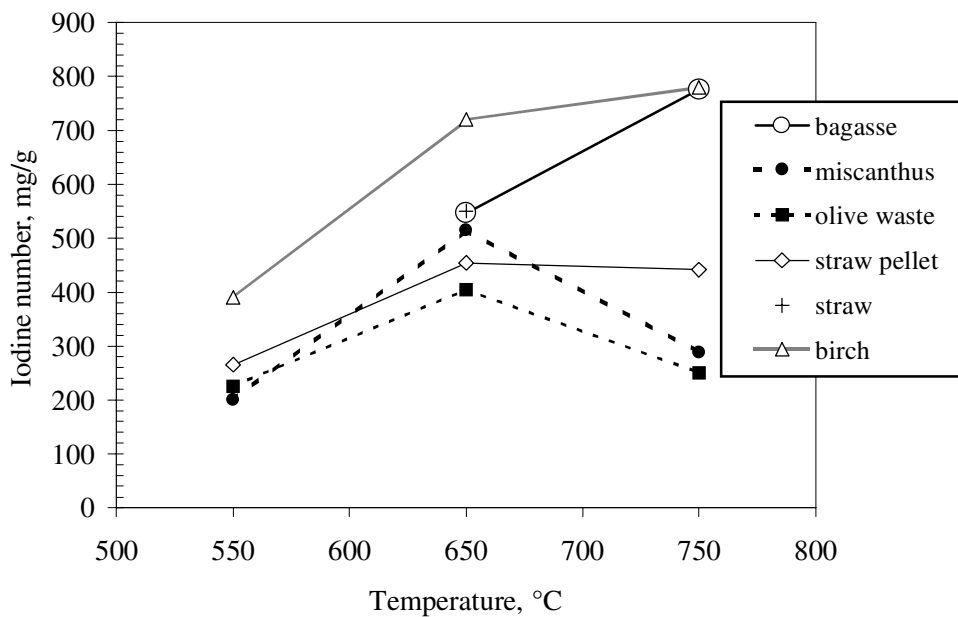


Figure 30. Influence of temperature on surface area of the active carbon

Time of treatment at the final temperature: 1 hour

The lines connecting the points have only the function of coupling together the points to compare.

In the experiments with sugar cane bagasse at 750°C an active carbon was obtained with higher surface area as that produced in the experiments at 650°C. In this experiment the activation time at high temperature (750°C) was reduced from 60 to 45 minutes. Also a high surface area was obtained using birch as precursor when the duration of the treatment at the final temperature (750°C) was 5 minutes. In both cases the increased surface area was at expense of a lower yield of active carbon (5-6%wt). The highest surface area was obtained in active carbons produced from birch at 650°C with an activation time of 2 hours. The prolonged activation time allowed the steam to increase the porosity of the solid product resulting in high surface area.

The composition of the gases obtained in the pyrolysis is also studied in paper VI. The increase of the temperature favours cracking of the hydrocarbons in the gaseous products and thus an increase the yield of hydrogen (figures 31 and 32). It has also decreased the content of CO<sub>2</sub> and CO in the gases. Aromatic hydrocarbons (benzene) are products of secondary pyrolysis reactions. The increase of the temperature from 650 °C to 750 °C has not affected significantly the composition of the produced gas with exception of the result with bagasse. In the experiments with sugar cane bagasse the hydrogen yield increased more significantly while the hydrocarbon yield in the gases decreased when the temperature was increased from 650 °C to 750 °C.

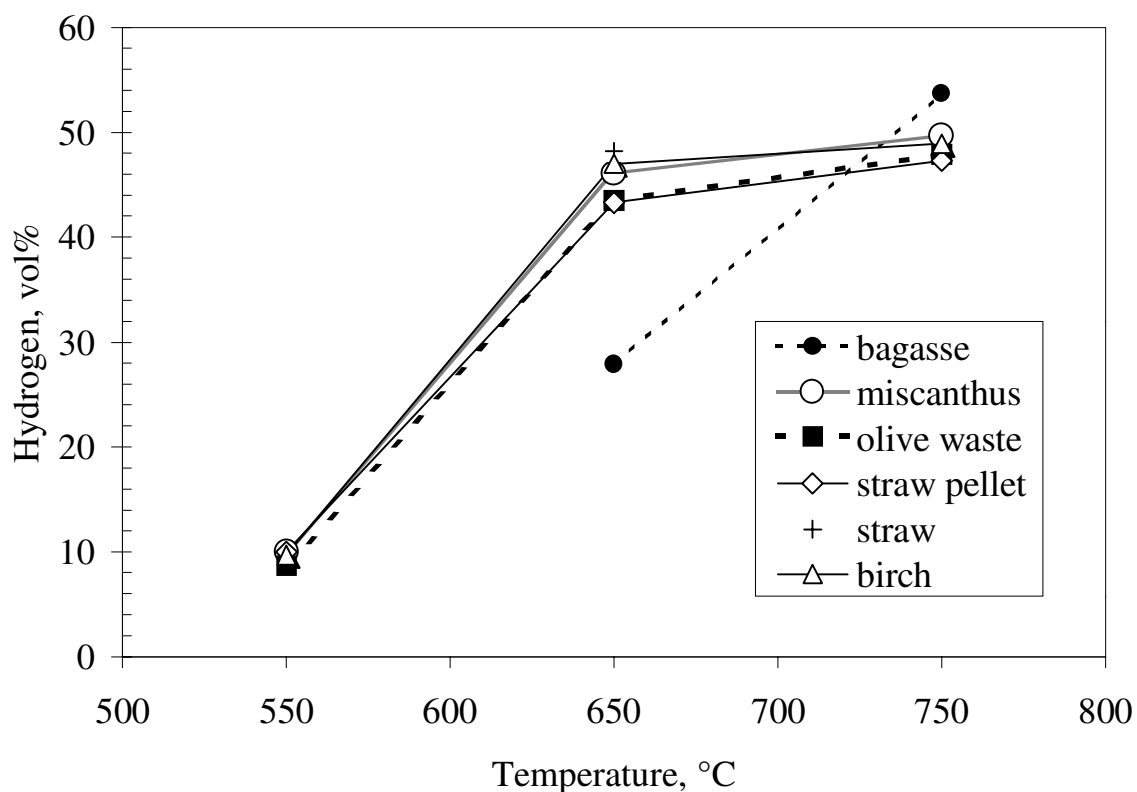


Figure 31. Influence of temperature on H<sub>2</sub> concentration in the produced gas.

Time of treatment at the final temperature: 1 hour

The lines connecting the points have only the function of coupling together the points to compare.

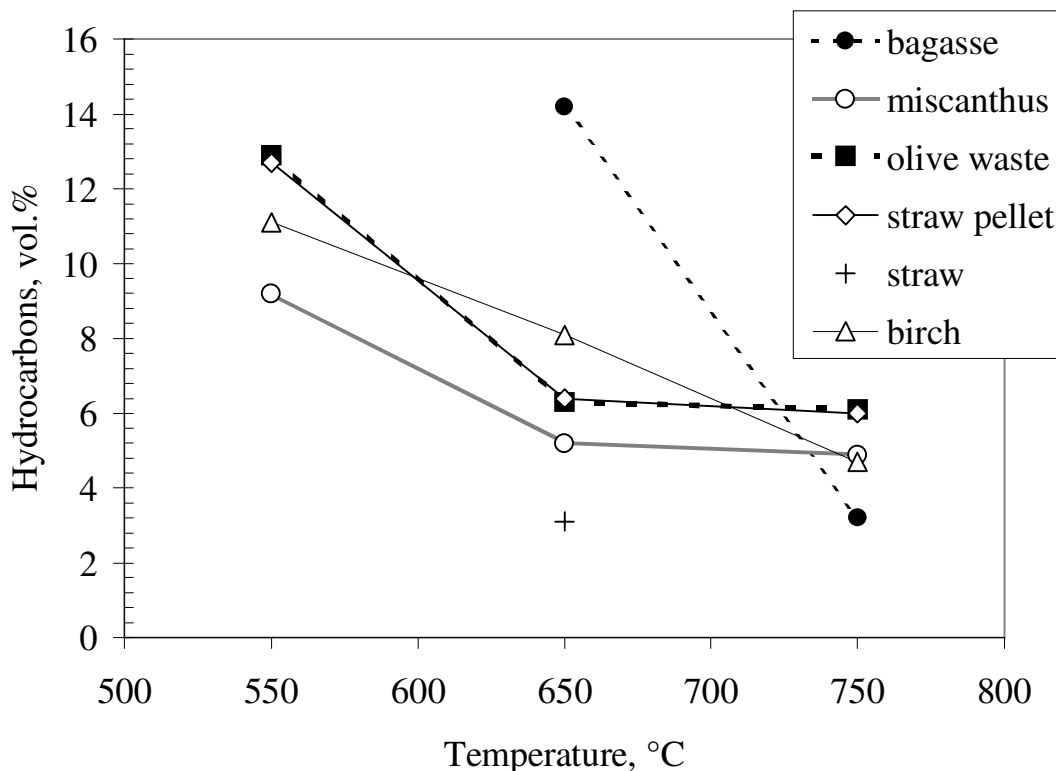


Figure 32. Influence of temperature on concentration of hydrocarbons in the produced gas.

Time of treatment at the final temperature: 1 hour

The lines connecting the points have only the function of coupling together the points to compare.

The rate of steam flow influences the product distribution. In the experiments with birch (paper VI) the yield of liquid products was reduced from 50 wt% to 25 wt% and the gas yield was increased from 33 wt% to 69% wt% when the steam flow was reduced from 500 ml/h to 250 ml/h. This result is of interest because it shows that optimisation of the process may improve significantly the distribution of products.

#### 4.2.4 Rotating versus stationary reactor

In paper IV the results obtained using a rotating reactor have been compared with those using a stationary reactor (from paper V). The rotating reactor seems to favour the production of energy-rich gases. The yields of gaseous products are 60-70 wt% in the rotating reactor, while in the stationary reactor they are less than 40 wt%. The yields of liquid products obtained in the rotary reactor are less than 10 wt% while the yields of liquid products in the stationary reactor are above 40 wt%. This result is of practical interest.

### 4.3 Conclusions

Active carbons with high surface area and good adsorption capacities may be produced from biomass samples using a one-step preparation method using simultaneous pyrolysis and steam activation of the precursors.

The results from the pyrolysis of biomass in presence of steam are compared with those obtained in inert atmosphere of nitrogen. The steam contributes to the formation of solid residues with high surface area and good adsorption capacities. The presence of steam favours efficient removal of the volatile products from the carbonising material and formation of solid product with increased surface area. The yield of liquid pyrolysis products increases significantly at the expense of the gaseous and solid products. It is found that, without any optimisation, the liquid products consist predominantly of water soluble polar compounds. Large parts of the volatiles are found in the water phase condensed along with the tar. The yield of liquid products may be decreased significantly if the rate of steam is decreased.

The type of biomass, the type of reactor and the treatment conditions, mainly temperature and activation time, determine the properties and the yield of active carbon obtained by steam pyrolysis.

In comparison to the stationary fixed bed reactor, the rotary reactor increases the production of energy-rich gases at the expense of liquid products. In the selected experimental conditions the surface areas of the solid products obtained in the rotary reactor are lower than those obtained in a stationary reactor.

The raw materials have strong effect on the yield and the properties of the pyrolysis products. High yields of solid residues with good adsorption characteristics were obtained from olive wastes, birch, salix, bagasse and miscanthus. Using a stationary reactor and straw as precursor, lower yield of active carbon has been obtained. A high ash content in pelletized straw has increased the activation rate, because of the catalytic effect of the ash in gasification. The active carbons with highest surface area were obtained from birch followed by salix and sugar cane bagasse.

At equal time of treatment an increase of the temperature results in a decrease of the yield of solid residues and improvement of the adsorption capacities of the carbons until the highest surface area is reached. Further increase of the temperature decreases the yield of solid product without any improvement in the adsorption capacity.

Due to the high reactivity of straw it may be treated at milder treatment conditions, lower temperature and shorter residence time. In general agricultural residues are more reactive in comparison with wood.

The rate of steam flow influences the product distribution. The yield of liquid products increased while the gas yield decreased when the steam flow was increased.

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## **APPENDIX-1**

### **PAPER I**

**Rapid high-temperature pyrolysis of biomass in a free-fall reactor,**

Zanzi, R., Sjöström, K. and Björnbom, E.

*Fuel*, 1996, 75 (5), 545-550.

# Rapid high-temperature pyrolysis of biomass in a free-fall reactor

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Rapid pyrolysis of biomass, wood and agricultural residues was studied using a free-fall reactor with which the effects of heating rate, temperature, particle size and residence time on the product distribution, gas composition and char reactivity could be determined. Interest was focused on the effect of the rapid pyrolysis conditions on the reactivity of the char. Formation of low yields of char with high reactivity is desirable in both gasification and combustion. The reactivity of char obtained in pyrolysis of biomass is very strongly influenced by the treatment conditions and may be significantly increased by using high heating rates, small particle size of the fuel and short residence time at higher temperature. Copyright © 1996 Elsevier Science Ltd.

(Keywords: biomass; rapid pyrolysis; char reactivity)

Renewable biomass fuels are a feasible alternative to fossil fuels for heat and energy supply. Utilization of biomass residues is an attractive option in the efforts to develop fuel processes which do not contribute to the greenhouse effect. There are two main reasons for the recent interest in using biomass for energy: the net contribution of carbon dioxide to atmospheric pollution is considered to be nil, and cheap forest and agricultural residues are widely available in many world areas.

The present paper deals with rapid pyrolysis of biomass in a free-fall reactor. Interest is focused on the yield and the reactivity of the char obtained in the pyrolysis. Rapid pyrolysis at high temperature plays an important role as a first step in combustion and gasification. It is well known that the pyrolysis conditions strongly determine the yield of char and its reactivity in combustion and gasification<sup>1,2</sup>. In both combustion and gasification, a low char yield (volatilization of the major part of the fuel) and a high char reactivity are important for the capacity of the reactors. Better understanding of the effect of the treatment conditions, such as temperature, heating rate, residence time and particle size, on both the primary pyrolysis and the secondary reactions is needed in order to develop combustion and gasification models that can predict yields, compositions and rates of formation of products.

## EXPERIMENTAL

### Raw materials

The chemical composition of the fuels used in the pyrolysis is shown in *Table 1*. The biomass samples selected for the study included wood and agricultural residues. Two types of wood, birch (*Betula pubescens*) and white quebracho (*Aspidosperma quebracho*), and

three types of agricultural residues (straw pellets, bagasse and sugar cane agricultural residue, SCAR) were used. Bagasse is mostly composed of the fibrous residue that remains after the milling of sugar cane. Sugar cane agricultural residue (SCAR) is composed of sugar cane leaves.

A single sample of coal (Daw Mill) was also used as a raw material for comparison with the biomass.

### Equipment

Rapid pyrolysis was conducted in a free-fall reactor with a maximum operating pressure of 5.0 MPa and a maximum operating temperature of 1100°C. A 1 kg h<sup>-1</sup> screw feeder was situated above the reactor. The heating rates of the particles in the reactor were selected to be of the same magnitude as those obtained in fluidized bed reactors<sup>3</sup>. The free-fall tubular reactor had a heated length of 2.9 m and an i.d. of 40 mm. The reactor tube was heated by eight independent electrical heaters. The carrier gas was preheated before it entered the reactor.

### Procedure

The solid fuels were milled, sieved and pneumatically classified to obtain fractions of uniform particle size. For every run, the heated length of the reactor was selected so that the residence time was at least long enough for almost complete pyrolysis of the fuel. *Rapid pyrolysis* took place when the biomass particles passed through the hot zone of the free-fall reactor. The char was collected in a char receiver. The volatiles passed through a metallic filter to remove char particles, dust and soot. The volatiles were further cooled in a water-cooled condenser, where the tar water was condensed. The remaining aerosol was removed in dry-ice traps and a cotton filter. The gas composition was analysed by an

**Table 1** Raw materials used for pyrolysis

	Wood		Agricultural residues			Coal
	Birch	White quebracho	Straw pellets	Bagasse	SCAR	(Daw Mill)
C (wt% daf)	48.4	50.7	47.0	47.2	43.8	78.7
H (wt% daf)	5.6	6.3	6.2	6.2	5.8	5.3
N (wt% daf)	0.2	0.65	1.0	0.4	0.4	1.2
O (wt% daf) (diff.)	45.8	42.4	45.8	46.2	50.0	14.8
Ash (wt% db)	0.3	0.75	4.6	1.2	6.8	7.0
Moisture (wt%)	5.0	7.2	7.4	5.1	6.8	2.0

on-line programmed gas chromatograph, which took a sample every 9 min. The concentrations of CO<sub>2</sub>, H<sub>2</sub>, CO, N<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>–C<sub>5</sub> hydrocarbons and aromatic hydrocarbons (benzene and toluene) were determined.

The char from the rapid pyrolysis was further treated in a thermobalance with slow heating (20 K min<sup>-1</sup>) in nitrogen to 850°C. The heating was continued to constant weight of the char to achieve *final pyrolysis*.

The reactivity of the char in gasification was determined by reaction with steam in the same thermobalance. The reactivity was calculated as the rate of weight loss of the char during the reaction between 10 and 50 wt% conversion. For the char from coal, the reactivity was determined at 850°C because such char is much less reactive than char from biomass.

The yield of tar was calculated from the total weight of the tar collected in the water-cooled condenser, the dry-ice traps and the cotton filter after the tar liquor had been evaporated. The yield of gas was determined after the condensable part of the volatiles had been removed.

The yield of char was calculated from the ash yields of the char and biomass:

$$\text{Char yield (wt\% daf)} = \frac{a_b/a_c - a_b/100}{1 - a_b/100} \times 100$$

where  $a_b$  is wt% ash in the dry biomass and  $a_c$  is wt% ash in the dry char. The yield of char from coal was determined directly as total weight of the material from the char receiver, material from the walls and the filter.

The balance to 100 wt% was tar liquor plus losses.

#### Residence time of the particles

The residence time of the particles and the gas in the free-fall reactor was varied by changing the number of electrical heaters used around the reactor. Thus an increase in the residence time of the particles was accompanied by an increase in the residence time of the

gas in the reactor. The residence time of the particles was calculated using a computer program described by Nilsson<sup>4</sup>. Part of the model is based on the work of Pyle and Zaror<sup>5</sup>. The shrinkage and change in density of the particles in the process were considered in the calculation.

## RESULTS AND DISCUSSION

### Effect of heating rate on yield and reactivity of char

Table 2 compares the yield and reactivity in steam gasification reaction of char produced by slow and rapid pyrolysis of different biomass samples. A single result obtained with coal is also presented. As expected, rapid heating resulted in less char formation than that obtained in slow heating. Heating rate has a much greater effect on the pyrolysis of biomass than on that of coal.

Table 2 also shows that chars produced by rapid pyrolysis are more reactive in gasification than those produced by slow pyrolysis. The quick devolatilization of the fuel in rapid pyrolysis favours the formation of char with high porosity and high reactivity. The apparent density of the char from birch measured by water displacement was 750 kg m<sup>-3</sup> for slow pyrolysis and 250 kg m<sup>-3</sup> for rapid pyrolysis.

The data in Table 2 are affected by the inevitable differences in the experimental conditions of slow pyrolysis in the thermobalance and rapid pyrolysis in the free-fall reactor. The slow removal of the volatiles from the bed of the fuel particles in the thermobalance facilitates secondary pyrolysis reactions between the volatiles and the char, which favours the formation of char. In the free-fall reactor, on the contrary, the removal of volatiles from the solids is facilitated because the fuel moves as a stream of individual particles. Hence secondary pyrolysis is limited. Though the conditions in the free-fall reactor and the thermobalance are thus not completely comparable, the large differences in the

**Table 2** Yield and reactivity of char produced by slow and rapid pyrolysis

	Wood		Agricultural residues		Coal
	Birch	White quebracho	Straw pellets	Bagasse	(Daw Mill)
Yield after slow pyrolysis (wt% daf)	15.0	20.0	16.0	10.0	67.0
Reactivity at 750°C (wt% min <sup>-1</sup> )	1.3	0.6	2.3	1.0	0.7 <sup>a</sup>
Yield after fast pyrolysis (wt% daf)	5.5	8.2	11.0	4.3	57.1
Reactivity at 750°C (wt% min <sup>-1</sup> )	3.1	2.0	3.7	1.6	1.3 <sup>a</sup>

<sup>a</sup> Reactivity at 850°C

results may be attributed mostly to the difference in heating rate.

The stronger effect of the heating rate on the formation of char from biomass than from coal may be attributed to the high cellulose content of the biomass. It is known that heating rate has a significant effect on the pyrolysis of cellulose. The dehydration of cellulose to a more stable anhydrocellulose, which gives higher char yield, is the dominant reaction at temperatures  $<300^{\circ}\text{C}$ <sup>6</sup>. At temperatures  $>300^{\circ}\text{C}$ , cellulose depolymerizes, producing volatiles. If the heating rate is very high, the residence time of the biomass at temperatures  $<300^{\circ}\text{C}$  is insignificant. Thus a high heating rate provides a shorter time for the dehydration reactions and the formation of less reactive anhydrocellulose, which gives higher yield of char. The result is that the rapid heating of the fuel favours the depolymerization of cellulose and the formation of volatiles and suppresses the dehydration to anhydrocellulose and char formation<sup>7,8</sup>. Hence the effect of heating rate is stronger in the pyrolysis of biomass than in that of coal.

#### Effect of fuel type

The results in *Table 3* show the effect of the composition of the fuel on the yields of pyrolysis products. Compared with coal, the biomass samples produced much larger amounts of volatile fractions and

lower yields of char even though, due to the difference in reactivity of biomass and coal, the biomass samples were pyrolysed at lower temperatures.

Biomass also produced char which is more reactive to steam.

Owing to the intrinsic properties of the biomass samples used, the particle sizes and residence times for some of the experiments represented in *Table 3* were not the same. However, it has been shown that changes in these variables within the limits for the experiments have relatively little effect on the distribution of products obtained in pyrolysis<sup>9</sup>. The differences due to the effect of the nature of the fuel are much stronger. However, it is shown below that some of the above-mentioned variables may have an effect on the reactivity of char in gasification.

The chemical composition of the biomass samples influenced the distribution of the pyrolysis products. The difference in the distribution of products from the wood samples (birch and white quebracho) seems to be in good accord with the difference in the chemical composition of these two samples. Higher yields of char are favoured by high carbon content, low oxygen content, low H/C ratio and high content of coke-forming components, such as lignin, in the fuel subjected to pyrolysis<sup>10-12</sup>. Comparison of the data for the birch and quebracho in *Table 3* shows that the higher yield of char obtained from white quebracho may be explained by the chemical composition of the organic material in these samples. The low ash

**Table 3** Effect of the raw material on yield and properties of products obtained in rapid pyrolysis

	Wood		Agricultural residues			Coal
	Birch	White quebracho	Straw pellets	Bagasse	SCAR	(Daw Mill)
Carbon content (wt% daf)	48.4	50.7	47.0	47.2	43.8	78.7
Oxygen content (wt% daf)	45.8	42.4	45.8	46.2	50.0	14.8
H/C ratio	0.12	0.12	0.13	0.13	0.13	0.07
Lignin content (wt% daf)	24	35	25	24	27	n.d. <sup>a</sup>
Ash (wt% db)	0.3	0.75	4.6	1.2	6.8	7.0
Rapid pyrolysis						
Particle size (mm)	0.7-1.0	0.7-0.8	0.5-0.9	0.5-0.9	0.5-0.9	0.6-0.8
Temperature ( $^{\circ}\text{C}$ )	800	800	800	850	850	1000
Particle residence time (s)	1.4	1.4	1.4	3.4	3.4	1.0
Gas yield (wt% daf)	71.2	66.9	56.2	72.6	61.0	26.1
Tar yield (wt% daf)	1.1	1.3	1.0	0.4	0.8	0.5
Char yield (wt% daf)	7.2	10.4	16.6	5.0	11.4	62.0
Reactivity at $750^{\circ}\text{C}$ (wt% min <sup>-1</sup> )	3.1	2.0	3.7	1.6	0.7	1.3 <sup>b</sup>
Final slow pyrolysis						
Char yield after total pyrolysis (wt% daf)	5.5	8.2	11.0	4.3	9.8	57.1
Fraction of char removed by slow pyrolysis (% daf)	23.6	21.1	33.6	13.7	13.7	7.9
Composition of gaseous products (vol. % db)						
H <sub>2</sub>	16.8	16.2	13.2	15.7	12.7	52.2
CH <sub>4</sub>	16.2	17.5	18.2	12.0	14.5	19.9
C <sub>2</sub> H <sub>2</sub> , C <sub>2</sub> H <sub>4</sub>	6.2	5.3	6.3	4.8	5.9	1.3
C <sub>2</sub> H <sub>6</sub>	0.3	0.3	0.6	0.2	0.2	0.1
Benzene	1.2	1.6	1.4	1.6	1.0	0.6
Toluene	0.2	0.4	0.3	0.3	0.3	n.d. <sup>a</sup>
CO <sub>2</sub>	8.3	9.0	13.6	9.0	12.4	4.6
CO	50.7	49.7	46.3	56.2	53.0	21.3

<sup>a</sup> Not determined

<sup>b</sup> Reactivity at  $850^{\circ}\text{C}$

**Table 4** Effect of temperature on yield and properties of products obtained in rapid pyrolysis

		Birch	Mixture of 90% birch and 10% aspen	
Rapid pyrolysis				
Particle size (mm)	0.7–1.0	0.7–1.0	0.5–0.7	0.5–0.7
Temperature (°C)	800	1000	750	900
Particle residence time(s)	1.4	1.4	1.6	1.7
Gas yield (wt% daf)	71.2	83.0	73.0	81.1
Tar yield (wt% daf)	1.1	0.2	1.2	1.1
Char yield (wt% daf)	7.2	5.6	7.2	5.9
Reactivity at 750°C (wt% min <sup>-1</sup> )	3.1	4.7	2.7	3.0
Final slow pyrolysis				
Char yield after total pyrolysis (wt% daf)	5.5	4.95	5.5	4.4
Fraction of char removed by slow pyrolysis (% daf)	23.6	11.6	23.9	24.6
Composition of gaseous products (vol.% db)				
H <sub>2</sub>	16.8	34.0	13.4	21.0
CH <sub>4</sub>	16.2	11.7	16.8	16.0
C <sub>2</sub> H <sub>2</sub> , C <sub>2</sub> H <sub>4</sub>	6.2	0.5	6.2	4.4
C <sub>2</sub> H <sub>6</sub>	0.3	n.d. <sup>a</sup>	1.5	0.2
Benzene	1.2	0.6	0.4	0.4
Toluene	0.2	n.d. <sup>a</sup>	0.1	n.d. <sup>a</sup>
CO <sub>2</sub>	8.3	7.5	9.4	8.2
CO	50.7	45.7	51.8	49.8

<sup>a</sup> Not detected

of the wood samples studied facilitates prediction of the distribution of products from the composition of the organic matter in the fuel.

The distribution of pyrolysis products obtained from the agricultural residues (straw pellets, bagasse and SCAR) is more difficult to predict from the chemical composition of the organic matter, due to the high content of inorganic matter in some of these samples.

The reactivities of the agricultural residues studied are lower than those of the wood samples. The higher yield of solid residue obtained in pyrolysis of straw pellets may be explained by the negative effect of the pelletization on the reactivity. Untreated straw gives more volatiles than straw pellets<sup>9</sup>.

Though the treatment temperature for bagasse and SCAR was somewhat higher than that for the wood samples (850 instead of 800°C), the distribution of products from bagasse is comparable with that from wood, while the devolatilization of the SCAR is even lower. The high ash of the agricultural residues may have a significant effect on the pyrolysis results. The longer residence time for bagasse and SCAR may also have a negative effect on the reactivity.

The higher content of hydrogen in the gaseous product obtained from coal may be explained by the more intense cracking reactions of the tar and the hydrocarbons in the gas phase at the higher temperature of pyrolysis.

#### Effect of pyrolysis temperature

Table 4 shows the effect of temperature on yield of products obtained in rapid pyrolysis of wood (birch and a mixture of 90 wt% birch and 10 wt% aspen). For both samples the higher treatment temperature resulted in lower yields of char and tar and higher yields of gaseous products. The temperature markedly influences the heating rate. The heat flux is proportional to the driving force, the temperature difference between the particle and the environment. At higher temperature, the heat

flux and the heating rate are higher. The higher heating rate results in decreased char yield. This result is in accord with previous results obtained for rapid pyrolysis of biomass, which showed that the char yield remains constant above a certain treatment temperature<sup>7,8,13,14</sup>. It seems that for a certain biomass (certain thermal conductivity) and for a certain particle size, a high enough heating rate is reached at a certain temperature. Further increase of heating rate because of an additional increase of temperature does not affect the char yield.

The char samples obtained by rapid pyrolysis at higher temperatures are more reactive in steam gasification than those obtained at lower pyrolysis temperatures. This result is of practical interest for utilization of biomass as a raw material for gasification.

Higher pyrolysis temperatures affect the composition of the gaseous product. A higher temperature caused cracking of tar and of the hydrocarbons in the gaseous phase and thus it increased the total yield of gas and the proportion of hydrogen.

#### Influence of particle size

Table 5 shows the effect of biomass particle size on the pyrolysis. The results follow the trends described by Chan *et al.*<sup>15</sup>.

The reactivity of char is higher when smaller fuel particles are subjected to pyrolysis, a point that is of interest for the utilization of biomass for gasification and combustion.

An increase in particle diameter from 0.5–0.7 to 0.7–1.0 mm for birch at 800°C increases the solid residue from 4.6 to 5.5 wt% after total pyrolysis, i.e. a ~20% increase in amount of char.

In Table 5 the difference in the particle size of the biomass from white quebracho is too small to influence significantly the pyrolysis results. Though the trend in the results obtained with white quebracho is in agreement with that for birch, these two experiments illustrate the reproducibility of the experimental results rather

**Table 5** Effect of particle size of fuel on rapid pyrolysis

	Birch				White quebracho	
	0.5–0.7	0.7–1.0	0.7–1.0	1.0–1.3	0.6–0.7	0.7–0.8
Rapid pyrolysis						
Particle size (mm)	0.5–0.7	0.7–1.0	0.7–1.0	1.0–1.3	0.6–0.7	0.7–0.8
Temperature (°C)	800	800	1000	1000	800	800
Gas yield (wt% daf)	72.2	71.2	83.0	78.4	67.7	66.9
Tar yield (wt% daf)	1.1	1.1	0.2	0.4	1.3	1.3
Char yield (wt% daf)	5.8	7.2	5.6	6.8	9.7	10.4
Reactivity at 750°C (wt% min <sup>-1</sup> )	3.2	3.1	4.7	3.6	2.0	2.0
Final slow pyrolysis						
Char yield after total pyrolysis (wt% daf)	4.6	5.5	5.0	5.9	7.9	8.2

than the effect of the experimental conditions on the pyrolysis.

The effect of particle size on the char yield is most pronounced for fuels with low char yield. In pyrolysis of coal, with a higher yield of char, this effect is less pronounced. In rapid pyrolysis of coal at 1000°C an increase in particle size of the fuel from 0.3–0.6 to 0.6–0.8 mm increased the amount of char by only 4–5%<sup>9</sup>.

Under the experimental conditions used, the composition of the pyrolysis gas (not shown in the table) was not significantly influenced by the change in the particle size.

#### Influence of residence time

The residence time affects the yield and the properties of the pyrolysis products. The yields of pyrolysis products obtained at different residence times of the wood particles (0.5–0.7 mm of a mixture of 10 wt% aspen and 90 wt% birch) in the free fall-reactor are given in Table 6. The moisture content of the biomass was 7.8 wt% and the ash of the dry wood was 0.42 wt%.

In the range of experimental conditions studied,

residence time had a limited effect on the yield of pyrolysis products. As regards the yield of char at 900°C, longer residence time at 900°C favours the secondary pyrolysis reactions which result in higher yields of char and also influences the composition of the gaseous products.

A longer residence time in rapid pyrolysis results in the formation of char of lower reactivity. This may be seen both in the gasification tests and in the tests on final pyrolysis of the char. The reactivity of the char in steam gasification increased when the residence time in rapid pyrolysis decreased.

The char obtained at longer residence time in rapid pyrolysis also appears to be more stable in final slow pyrolysis using the thermobalance. The longer the residence time in the rapid pyrolysis, the lower the fraction of the volatiles obtained in final slow pyrolysis in the thermobalance.

#### Final pyrolysis

The results in Tables 3–6 show that the char obtained

**Table 6** Effect of residence time on rapid pyrolysis of wood

Temperature (°C)	750			900		
Particle residence time (s)	1.0	1.6	2.7	0.6	0.8	1.7
Pressure (kPa)	280	270	300	260	270	270
Heated tube length (cm)	134	196	258	78	106	196
Gas yield (wt% daf)	73.2	73.0	73.5	81.6	81.3	81.1
Tar yield (wt% daf)	1.7	1.2	1.1	1.2	1.1	1.1
Char yield (wt% daf)	7.2	7.2	7.2	5.2	5.5	5.9
Reactivity at 750°C (wt% min <sup>-1</sup> )	4.1	2.7	2.3	5.0	4.2	3.0
Char yield after total pyrolysis (wt% daf)	5.1	5.5	5.8	3.6	3.8	4.4
Fraction of char removed by slow pyrolysis (% daf)	29.5	23.9	19.3	31.1	30.7	24.6
Gas residence time(s)	5.6	8.2	11.9	2.6	3.7	6.8
Composition of gaseous products (vol.% db)						
H <sub>2</sub>	10.1	13.4	13.8	14.2	18.1	21.0
CH <sub>4</sub>	19.8	16.8	17.2	16.2	16.0	16.0
C <sub>2</sub> H <sub>2</sub> , C <sub>2</sub> H <sub>4</sub>	6.5	6.2	6.2	6.5	6.2	4.4
C <sub>2</sub> H <sub>6</sub>	2.3	1.5	1.3	1.0	0.4	0.2
Butane	0.3	0.3	0.1	0.2	n.d. <sup>a</sup>	n.d. <sup>a</sup>
Pentane	0.1	0.1	0.1	n.d. <sup>a</sup>	n.d. <sup>a</sup>	n.d. <sup>a</sup>
Benzene	0.4	0.4	0.5	0.3	0.3	0.4
Toluene	0.1	0.1	0.2	0.1	0.1	n.d. <sup>a</sup>
CO <sub>2</sub>	13.4	9.4	9.5	8.9	8.1	8.2
CO	47.0	51.8	51.2	52.6	50.8	49.8

<sup>a</sup> Not detected



by rapid pyrolysis contains a fraction that can be volatilized further by slow pyrolysis. Thus pyrolysis proceeds in two steps: an initial fast step followed by a slower step including some chemical rearrangement of the char. The results suggest that the primary pyrolysis reactions in the rapid pyrolysis of wood are completed within seconds. The secondary reactions take minutes to be completed. The residence time of the wood particles in the free-fall reactor is not sufficient for final pyrolysis. Pyrolysis is completed in the further slow heating in the thermobalance. The fraction of char removed by the final slow pyrolysis is greater than for char samples from biomass than from coal<sup>9</sup>.

#### ACKNOWLEDGEMENTS

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## **APPENDIX-2**

### **PAPER II**

#### **Rapid pyrolysis of bagasse at high temperature,**

Zanzi, R., Sjöström, K. and Björnbom, E.

in *Proceedings of the third Asian-Pacific international symposium on combustion and energy utilization,*

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Proceeding of the symposium, Vol 1, pp. 211-215, 1995.

## **Rapid Pyrolysis of Bagasse at High Temperature**

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### **Abstract**

Rapid pyrolysis of bagasse is performed in a free-fall reactor. Contribution to the development of thermochemical processes such as gasification and combustion in fluidized beds is aimed. The effect of heating rate, temperature, particle size on the product distribution, gas composition and char reactivity is studied. The low amounts of a highly porous char and the high yield of gaseous products obtained in rapid pyrolysis of bagasse at high temperature are similar to those produced in rapid pyrolysis of wood.

**Keywords:** rapid pyrolysis, biomass, bagasse, agricultural residues, char, tar, reactivity, product distribution.

### **INTRODUCTION**

Third World Countries face serious problems in meeting the energy demands. Sugar cane plays an important role in the economy of many developing countries. Gasification of bagasse for electricity production can be one of the solutions to meet energy demands with a favourable effect on the environment.

Pyrolysis consists in heating solid biomass in absence of air to produce solid, liquid or gaseous fuels. Depending on the conditions the solid, liquid or gaseous products are maximized. Rapid pyrolysis at high temperature is the first step in gasification and combustion in fluidized bed reactors. The treatment conditions in pyrolysis determine the char yield and its reactivity in gasification <sup>[1,2]</sup>. Char yield and char reactivity are important for the capacity of the gasifier. Reaching the lowest char yield and the highest char reactivity in pyrolysis is

advantageous for combustion and gasification.

The present paper concerns a study on rapid pyrolysis of bagasse in a free-fall reactor.

This study was financially supported by SAREC (Swedish Agency for Research Cooperation with Developing Countries).

### **EXPERIMENTAL**

The rapid pyrolysis of the fuel is conducted in the free-fall reactor shown in figure 1. The free-fall tubular reactor has a heated length of 2.9 m and an inner diameter of 0.04 m. The carrier gas is preheated before it enters the reactor. The reactor tube is heated by eight independent electric heaters. The char is collected in a char receiver situated below the tube. The gas passes a metallic filter. It is further cleaned in a tar condenser, dry ice traps and a cotton filter. The cleaned gas is analysed in a chromatograph for CO<sub>2</sub>, H<sub>2</sub>,

CO, N<sub>2</sub>, CH<sub>4</sub>, saturated hydrocarbons (C<sub>1</sub>-C<sub>5</sub>) and aromatic hydrocarbons (benzene and toluene).

The char from the rapid pyrolysis is further pyrolyzed in nitrogen atmosphere in a thermobalance with a slow heating rate (20°C/min) up to 850°C [3]. The heating is continued for a period of 30 minutes. Then the temperature is reduced to 750°C and the reactivity of the char is determined by reaction with steam in the same thermobalance. The reactivity is calculated as the rate of the weight loss of the char during the reaction between 10% and 50% conversion.

The slow pyrolysis of biomass is also performed in the thermobalance up to 850°C.

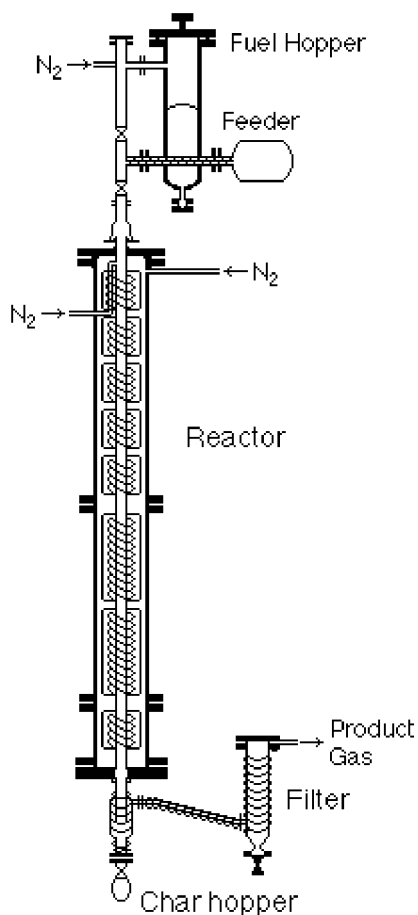


Figure 1. Free-fall reactor

## Raw material

Bagasse is primarily composed of the fibrous residue that remains after the milling of sugar cane.

Before the pyrolysis the bagasse is milled, sieved and wind classified to obtain 4 fractions of uniform particle size.

The chemical composition of the bagasse used in the pyrolysis is shown in table 1. Table 2 shows the ash and moisture content in the samples

The properties of de 4 fractions of bagasse are not similar. Further studies in order to make the influence of these properties in thermochemical processes clear may be useful.

Probably the separation by milling, sieving and wind classifying makes that the material contained in the fractions comes of different places in the sugar cane bagasse.

Table 1. Chemical composition of bagasse (in wt % maf, moisture and ash free).

bagasse d <sub>p</sub> in mm	C	H	N	O by diff.
0.3-0.5	46.8	6.2	0.3	46.7
0.86-1.0	47.3	6.2	0.3	46.2

Table 2. Ash (in wt % mf, moisture free) and moisture (in wt %) content in bagasse.

d <sub>p</sub> in mm	Ash	Moisture
0.30-0.50	2.4	6.8
0.50-0.86	1.0	6.9
0.86-1.00	0.9	7.0
1.00-1.35	1.5	6.9

## RESULTS AND DISCUSSION

### Effect of the heating rate

Table 3 compares the yields and the reactivities of chars produced by slow pyrolysis in thermobalance and rapid pyrolysis in free fall reactor. As expected rapid heating rate has resulted in less char formation than this obtained at slow heating rate.

Table 3 shows also that chars produced by rapid pyrolysis are more reactive in gasification than those produced by slow pyrolysis. The quick devolatilization of biomass in rapid pyrolysis results in formation of char with high porosity and high reactivity.

Table 3. Yield and reactivity of char produced by slow and rapid pyrolysis of bagasse (fraction with  $d_p$ : 0.86-1.0 mm)

<b>Slow Pyrolysis</b>	
Char yield (wt % maf)	10.0
Reactivity in gasification wt. % loss/min	0.7
<b>Rapid Pyrolysis</b>	
Char yield (wt % maf)	2.4
Reactivity in gasification wt. % loss/min	3.4

The data in Table 3 are affected also by the inevitable differences in the experimental conditions for slow pyrolysis in the thermobalance and for rapid pyrolysis in the free fall reactor.

The slow removal of the volatiles from the bed of the fuel particles in the thermobalance facilitates the secondary pyrolysis reactions between the volatiles and the char, which favours the formation of char. In the free-fall reactor, on the contrary, the removal of

volatiles from the solids is facilitated because the fuel particles move in a stream of individual particles. Hence the secondary pyrolysis is limited. Though the conditions in the free-fall reactor and in the thermobalance are thus not completely comparable the big differences in the results may be attributed mostly on the effect of the differences in the heating rates in the slow and fast pyrolysis.

### Effect of the pyrolysis temperature.

Table 4 shows the effect of temperature on the yield of products obtained in rapid pyrolysis of two samples of bagasse of different size.

For both samples the higher treatment temperature has resulted in formation of lower yields of char and tar and higher yields of gaseous products. The char yield decreases when temperature is increased from 800°C to 1000°C.

The low yield of char and the high yield of gaseous products obtained in rapid pyrolysis of bagasse at high temperature are similar to those produced in rapid pyrolysis of wood<sup>[2]</sup>.

The temperature influences also the heating rate. At higher temperature the heating rates are higher. The higher heating rate results in decreased char yield.

The char obtained by rapid pyrolysis contains a fraction that can be further volatilized by slow pyrolysis. The residence time of the particles in the free fall reactor is not enough for the final pyrolysis. The fraction of char removed by slow pyrolysis is larger in char samples from bagasse (40%-50%) compared to wood (20%)<sup>[2]</sup>.

Table 4. Effect of temperature on the yield of products obtained in rapid pyrolysis of bagasse in a free-fall reactor

Particle size, mm	0.5-0.86			0.86-1.0		
Temperature, °C	800	900	1000	800	900	1000
Gas yield, wt % maf	81.5	83.8	87.5	79.1	81.2	87.0
Tar yield, wt % maf	0.5	0.5	0.3	0.4	0.3	0.2
Char yield, wt % maf	5.0	4.7	4.1	6.6	5.5	4.7
<b>Final slow pyrolysis</b>						
Char yield after total pyrolysis, wt % maf	2.6	3.3	2.6	2.8	2.4	2.3
Char removed by slow pyrolysis, wt % maf	49	30	37	57	56	51
Reactivity, wt loss %/min	1.8	1.5	1.8	3.1	3.4	3.0
<b>Composition of the gaseous products, vol. %, mf</b>						
H <sub>2</sub>	37.5	37.8	48.0	30.0	34.1	45.0
CH <sub>4</sub>	7.6	7.0	3.0	11.2	9.7	4.9
C <sub>2</sub> H <sub>2</sub> , C <sub>2</sub> H <sub>4</sub>	3.6	1.1	bdl	4.9	1.6	bdl
C <sub>2</sub> H <sub>6</sub>	0.1	bdl	bdl	bdl	bdl	bdl
Benzene	0.4	0.5	0.1	0.3	0.7	0.2
CO <sub>2</sub>	12.8	8.5	0.4	13.2	7.4	0.8
CO	37.9	45.0	48.5	40.1	46.4	49.0

bdl: below detection limit, maf: moisture and ash free mf: moisture free

The final pyrolysis of char from bagasse is not achieved in 30 minutes at 850°C in the thermobalance. The slope indicating the weight loss shows that the pyrolysis could continue and the fraction removed by slow pyrolysis could be larger. Especially in the test with particle size 0.5-0.86 mm at 900°C the data from the analysis in the thermobalance show clearly that the pyrolysis could continue and the fraction removed by slow pyrolysis would be larger. In test with wood, the final pyrolysis of char was achieved after treatment at 850 °C in the thermobalance <sup>[2]</sup>.

Higher treatment temperatures favour cracking of the hydrocarbons in the gaseous products and thus increase the yield of hydrogen. Aromatic hydrocarbons (benzene) are products of secondary reactions. At

higher temperature benzene is present in the gas. It means that both the formation and the cracking of benzene have increased.

### Effect of particle size

Table 4 and 5 shows the effect of particle size on rapid pyrolysis of bagasse at 800°C 900°C and 1000°C.

In the selected experimental conditions smaller particle size has favoured the devolatilisation of the bagasse in the pyrolysis. It is worth mentioning that the ash is not the same in all the samples (2.4% in the smaller, 1.5 in the bigger and 1% in the middle fractions). The different amount of inorganics may also affect the results. The char yield decreases when smaller particles are used.

Table 5. Effect of particle size of bagasse in rapid pyrolysis in a free-fall reactor

Temperature, °C	800°C			1000°C		
Particle size, mm	0.3-0.5	0.5-0.86	0.86-1.0	0.5-0.86	0.86-1.0	1.0-1.35
Gas yield, wt % maf	82.0	81.5	79.1	87.5	81.2	81.1
Tar yield, wt % maf	0.4	0.5	0.4	0.3	0.3	0.3
Char yield, wt % maf	4.6	5.0	6.6	4.1	5.5	7.6
<b>Final slow pyrolysis</b>						
Char yield after total pyrolysis, wt % maf	3.6	2.6	2.8	2.6	2.3	4.8
Char removed by slow pyrolysis, wt % maf	21	49	57	37	51	37
Reactivity, wt loss %/min	1.6	1.8	3.1	1.8	3.0	3.1
<b>Composition of the gaseous products</b> (vol. %, nitrogen and water-free basis)						
H <sub>2</sub>	35.3	37.5	30.0	48.0	34.1	35.8
CH <sub>4</sub>	8.1	7.6	11.2	3.0	9.7	7.6
C <sub>2</sub> H <sub>2</sub> ,C <sub>2</sub> H <sub>4</sub>	3.7	3.6	4.9	bdl	1.6	0.4
C <sub>2</sub> H <sub>6</sub>	0.1	0.1	bdl	bdl	bdl	bdl
Benzene	0.4	0.4	0.3	0.1	0.7	0.5
CO <sub>2</sub>	16.8	12.8	13.2	0.4	7.4	9.7
CO	35.9	37.9	40.1	48.5	46.4	46.1

bdl:below detection limit, maf: moisture and ash free mf: moisture free

The size of the particles affects the heating rate. The heat flux and the heating rate are higher in small particles than in large particles. The higher heating rate decreases the char yield. These results follow the trends concerning the influence of the heat flux and pellet length on the product yields described by Chan <sup>[4]</sup>.

The results concerning the reactivity of the char determined at 750°C show a big difference between chars from the samples with a particle size of 0.50-0.86 mm and those from samples with a particle size of 0.86-1.0 mm. The differences can not be explained by differences in particle size or ash content but they probably depend on the composition and structure of the char.

The high ash content in the samples with a particle size of 0.3-0.5 may have affected the reactivity of the char.

Smaller particle size has affected also the composition of the gas. It has favoured the cracking of hydrocarbons with an increase of hydrogen yield. In smaller particle the produced gas leaves the particle faster than large particles, the residence time of the gas in the reactor increases and the cracking is favoured.

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## **APPENDIX-3**

### **PAPER III**

**Rapid pyrolysis of agricultural residues at high temperatures,**

Zanzi, R., Sjöström, K. and Björnbom, E.

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## Rapid pyrolysis of agricultural residues at high temperatures

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### Abstract

This paper deals with rapid pyrolysis of agricultural residues such as olive waste and straw at high temperature (800°C-1000°C) in a free fall reactor at pilot scale. The conditions are of interest for gasification in fluidized beds where rapid pyrolysis plays an important role as first stage.

The objective of the work is to study the effect of the treatment conditions such as heating rate, temperature and particle size on the product distribution, gas composition and char reactivity. A higher temperature and smaller particles increase the heating rate resulting in a decreased char yield. The cracking of the hydrocarbons with an increasing of the hydrogen content is favoured by a higher temperature and by using smaller particles. Wood gives more volatiles and less char than straw and olive waste. The higher ash content in agricultural residues favours the charring reactions. The higher lignin content in olive waste results in a higher char yield in comparison with straw. Chars from olive wastes and straw are more reactive in gasification than chars from birch because of the higher ash content.

*Keywords:* agricultural residues, rapid pyrolysis, biomass, straw, olive waste, wood, product distribution

### 1. Introduction

Gasification of agricultural residues in combined gas turbine/steam processes for electricity and heat production from agricultural residues could increase the amount of energy produced with a decrease of the carbon dioxide emissions [1,2,3]. Heat and electricity coproduction would improve the economics of agricultural industries involving socio-economic benefits.

Fluidized bed reactors constitute the most promising type of reactors for large-scale gasification of biomass because of their high heat and mass transfer rates, and their flexibility towards feedstock.

Rapid pyrolysis at high temperature is the first step in gasification in fluidized bed reactors. The distribution of products depends on the heating rate, residence time, surrounding atmosphere and temperature. In addition, the type of biomass also affects both biomass devolatilization and char conversion. The rate-limiting step in steam gasification is the reaction between the char and the reactive gases, oxygen or/and steam. It is well known also that the conditions under the pyrolysis determine the char yield and its reactivity [4,5]. Char yield and char reactivity are important for the capacity of the gasifier. Reaching the lowest char yield and the highest char reactivity in pyrolysis is advantageous for combustion and gasification. The pyrolysis of biomass in a fluidized bed is a rapid process, which produces reduced yield of char with high reactivity in gasification.

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Better quantitative understanding of the effects of temperature, heating rate, residence time, pressure and particle size on both primary pyrolysis and secondary reactions is needed in order to develop gasifier models that can predict yields, compositions and rates of formation of products [6-11].

Because the devolatilization stage plays an important role in the conversion processes numerous studies have been carried out in order to determine product distribution and gas, and sometimes liquid, composition. Several studies concern slow pyrolysis of biomass related to charcoal production. Low final temperature maximizes the solid char yield. The method have been practiced for many years and actual studies aim at increasing the yields of charcoal by using elevated pressure [6]. Studies on slow pyrolysis at higher temperatures up to 1000°C aim to investigate the importance devolatilization stage as the initial stage in gasification in fast bed reactors [7,8,9,10]. Many studies on rapid pyrolysis have been performed at temperatures around 500°C where the liquid product is of main interest [11].

This work presents a study concerning the rapid pyrolysis of agricultural residues at high temperature (800°C-1000°C) performed in a free fall reactor at pilot scale. These conditions are of interest for gasification in fluidized beds. Of main interest are the gas and char production, the gas composition and the reactivity of the char in gasification.

## 2. Experimental

The biomass samples selected for the study included wood (birch) and three different types of agricultural residues. The used agricultural residues were olive wastes from oil production (composed by a crushed mixture of kernel and pulp) and wheat straw in untreated and in pelletised form. The chemical compositions of these materials are shown in Table 1.

Biomass samples were milled, sieved and separated in fractions. One fraction of particle diameter 0.5-1.0 was selected in the experiments with straw in untreated and in pelletised form. In the experiments with olive waste and wood (birch) two fractions of 0.5-0.8 mm and 0.8-1.0 mm were used in order to study the influence of the particle size. The experiments with all the selected materials were performed at 800 and 1000°C in order to study the influence of the temperature.

The rapid pyrolysis was conducted in the free-fall reactor shown in Figure 1. The free-fall tubular reactor has a heated length of 2.9 m and an inner diameter of 0.04 m. The carrier gas, nitrogen, was preheated before it enters the reactor. The nitrogen flow was 15 l/min. The reactor tube was heated by eight independent electric heaters. The heating rate in the equipment was about 500°C/s. A screw feeder located above the reactor allowed introducing the samples at 250 g/hour. The low bulk density of the straw was a problem when feeding into the reactor. The char was collected in a char receiver situated below the tube.

The evolved gas passed through a metallic filter. It was further cleaned in a tar condenser, dry ice traps and a cotton filter. The amount of tar separated in the tar condenser, dry ice traps and cotton filter was measured. The composition of the cleaned gas was determined using an on-line GC-chromatograph for CO<sub>2</sub>, H<sub>2</sub>, CO, N<sub>2</sub>, CH<sub>4</sub>, and hydrocarbons up to C<sub>7</sub>. The amount of produced gas was measured.

The collected char was measured and characterized. The surface area was determined by nitrogen adsorption and desorption isotherms with a Micromeritics Flowsorb II 2300 which uses dynamic flowing technique, providing BET and Langmuir surface area. Surface area was also characterized by the adsorption capacity towards iodine [12]. Total pore volume, total

pore area and skeletal density were calculated by mercury intrusion analysis with an AutoPore II 9220 Mercury Porosimeter.

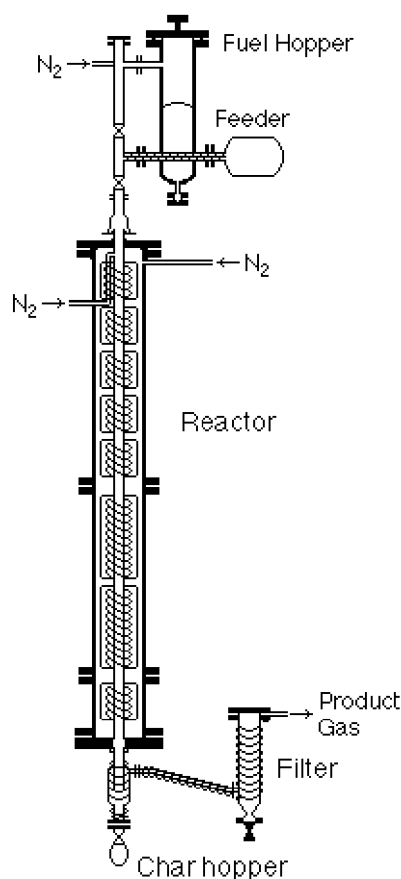
The char obtained by the rapid pyrolysis was further pyrolysed under nitrogen in a thermobalance with a slow heating rate (20°C/min) up to 850°C. Heating was continued during 30 minutes in order to reach final pyrolysis. The residual char was further gasified with steam at 750°C in the same thermobalance to determine its reactivity in the gasification reaction. The reactivity presented in this paper is defined by the equation:

$$R = (1/W) \cdot dW/dt$$

In the reactivity presented in table 4,  $dW/dt$  was calculated between 10% and 50% wt conversion. Where  $W$  is the weight of the ash-free sample at time  $t$  [13]. Generally,  $W$  was taken as zero when a constant weight was obtained at the end of the gasification run.

The high heating value (HHV) in table 1 was calculated as:

$$\text{HHV} = 0.34 \%C + 1.40 \%H - 0.16 \%O$$



**Figure 1.** Free fall reactor.

### 3. Results and discussion

Table 2 shows the elemental analysis, the calorific value, the ash and moisture content of the obtained chars after the rapid pyrolysis in the free fall reactor. Bulk densities, surface area and pore volume measurement of the raw materials and the chars are compared in table 3.

Table 4 shows the yield of products obtained in rapid pyrolysis of wood and agricultural residues in a free fall reactor.

Table 1: Chemical composition of the raw materials used for pyrolysis

Raw materials	Chemical composition in wt % maf				HHV MJ/kg maf <sup>a</sup>	Extracti- ves wt % mf <sup>b</sup>	Hemi- Cellulose wt % mf	Cellulose wt % mf	Lignin wt % mf	Ash wt % mf	Moisture wt %
	C	H	N	O by diff.							
Olive waste, d <sub>p</sub> = 0.5-0.8 mm	52.3	6.4	0.7	40.6	20.25	n.d. <sup>c</sup>	n.d.	n.d.	n.d.	4.7	7.1
Olive waste, d <sub>p</sub> = 0.8-1.0 mm	50.9	6.5	0.5	42.1	19.67	8.7	18.5	18.5	28.0	2.8	10.6
Untreated wheat straw	48.0	6.5	0.5	44.6	18.28	7.4	27.3	27.3	21.7	3.2	7.1
Pelletised wheat straw	48.9	6.4	0.5	44.2	18.51	n.d.	n.d.	n.d.	n.d.	3.9	6.8
Wood: Birch	48.6	5.6	0.2	45.6	17.07	4.6	31.8	31.8	21.0	0.3	5.0

<sup>a</sup>maf: moisture and ash free      <sup>b</sup>mf: moisture free      <sup>c</sup>n.d.: not determined      HHV : high heating value

Table 2: Elemental analysis of chars after rapid pyrolysis in a free fall reactor.

Raw materials	Pyrolysis Temp. °C	Composition in wt % maf <sup>a</sup>				HHV MJ/kg	Ash wt % mf <sup>b</sup>	Moisture wt %
		C	H	N	O <sup>c</sup>			
Olive waste, d <sub>p</sub> : 0.5-0.8 mm	800	77.5	2.1	1.5	18.9	26.3	20.0	3.8
Olive waste, d <sub>p</sub> : 0.5-0.8 mm	1000	83.0	1.1	1.3	14.6	27.4	25.4	0.3
Olive waste, d <sub>p</sub> : 0.8-1.0 mm	800	71.6	3.9	0.9	23.6	26.0	9.4	4.1
Olive waste, d <sub>p</sub> : 0.8-1.0 mm	1000	80.2	2.0	0.8	17.0	27.3	14.1	1.9
Untreated wheat straw	800	77.3	1.9	0.7	20.1	25.7	20.0	6.7
Untreated wheat straw	1000	81.3	1.5	0.9	16.3	27.1	21.6	5.6
Pelletised wheat straw	800	86.2	2.2	0.9	10.7	30.7	23.0	4.8
Pelletised wheat straw	1000	88.2	1.5	1.0	9.3	30.6	27.8	1.3
Wood, d <sub>p</sub> : 0.5-0.8 mm	800	90.5	1.7	0.2	7.6	31.9	4.9	2.7
Wood, d <sub>p</sub> : 0.8-1.0 mm	800	90.0	1.8	0.2	8.0	31.8	4.0	2.5
Wood, d <sub>p</sub> : 0.8-1.0 mm	1000	94.4	0.6	0.3	4.7	32.2	5.1	1.6

<sup>a</sup>maf: moisture and ash free      <sup>b</sup>mf: moisture free      <sup>c</sup>: by difference

Table 3: Properties of the raw materials and the chars produced at 1000 °C.

	straw	Straw pellets	Olive waste d <sub>p</sub> : 0.8-1 mm	Wood: Birch d <sub>p</sub> : 0.8-1 mm
Raw material				
Bulk density (g/cm <sup>3</sup> )	0.1	0.3	1.3	0.3
Surface Area (m <sup>2</sup> /g)	0.7	0.4	0.3	0.2
Char obtained by rapid pyrolysis at 1000 °C				
Bulk density (g/cm <sup>3</sup> )	0.05	0.1	0.4	0.1
Surface Area (m <sup>2</sup> /g) <sup>a</sup>	68.7	5.4	3.1	0.7
Adsorption of iodine (mg/g)	107	74	49	33
Total pore volume (cm <sup>3</sup> /g)	9.9	n.d. <sup>b</sup>	3.6	2.9
Total pore area (m <sup>2</sup> /g)	7.3	n.d.	3.5	3.1
Skeletal density	1.1	n.d.	1.0	0.6

<sup>a</sup> determined by nitrogen adsorption and desorption. <sup>b</sup>n.d.: not determined

Table 4: Yield of products obtained in rapid pyrolysis in a free fall reactor

Biomass	Straw		Straw pellets		Olive waste				Wood: Birch		
	0.5-1.0		0.5-1.0		0.5-0.8	0.8-1.0	0.5-0.8	0.8-1.0			
Particle size, mm	0.5-1.0		0.5-1.0		0.5-0.8	0.8-1.0	0.5-0.8	0.8-1.0			
Temperature, °C	800 1000		800 1000		800 1000	800 1000	800 1000	800 1000	800 1000		
Gas yield, wt % maf <sup>a</sup>	75.8 86.0		75.4 85.5		61.0 75.3	51.8 70.8	81.1 77.7	87.0			
Tar yield, wt % maf	0.9 0.1		0.8 0.1		1.1 0.2	0.9 0.2	1.1 1.1	0.2			
Char yield, wt % maf	13.2 10.8		13.6 10.5		20.0 14.6	27.6 17.5	5.8 7.2	5.6			
Water and losses, wt % maf	10.1 3.1		10.2 3.9		17.9 9.9	19.7 11.5	12.0 14	7.2			
Char surface area <sup>b</sup> , m <sup>2</sup> /g	105 107		61 74		74 75	51 67	23 21	33			
Further pyrolysis in thermobalance and reactivity measurement											
Char removed by slow pyrolysis, wt%maf	75.2 31.8		55.8 36.0		n.d. <sup>c</sup> n.d.	53.5 49.0	n.d. 24.0	12.0			
Char yield after total pyrolysis, wt % maf	3.3 7.3		6.0 6.7		n.d. n.d.	12.8 8.9	n.d. 5.5	5.0			
Ash content, wt%	50.2 31.0		40.3 37.6		n.d. n.d.	18.2 24.3	n.d. 5.2	11.4			
Reactivity, wt % / min	50.0 10.6		9.3 4.8		n.d. n.d.	18.2 22.2	n.d. 3.1	4.7			

<sup>a</sup>maf: moisture and ash free

<sup>b</sup>determined by adsorption of iodine

<sup>c</sup>n.d.: not determined

The higher treatment temperature has favoured tar cracking resulting in higher yield of gaseous products and lower yields of tar. When the pyrolysis temperature was increased from 800°C to 1000°C the char yield decreased. The temperature influences the heating rate. At higher temperature the heating rate are higher. A similar result, a decrease of the char yield and an increase of the gas yield, was obtained when smaller particles of wood and olive waste were used in the reactor. The heating rate for the smaller particles also decreases the yield of char. The char yield is affected by the influence of the temperature and particle size on heating rate.

Results of the elemental analysis (Table 2) indicate that contents of carbon increase with the pyrolysis temperature while those corresponding to hydrogen and oxygen decrease. Losses in hydrogen and oxygen correspond to the scission of weaker bonds within the char structure favoured by the higher temperature [14]. The part of the char that was volatilized in the thermobalance in order to achieve total pyrolysis was larger for the char obtained at the lower temperature (800°C) and larger particles. The elemental analysis of the chars also reflects the higher conversion at 1000°C (table 2).

The surface area of the char, characterized by iodine adsorption (DIN 53582) (table 4) is higher at 1000° C than at 800°C. At higher temperature, the heating rate is higher and the devolatilization is more intensive making the char more porous. Depending on the biomass, the influence of increasing the temperature from 800°C to 1000°C on the surface area of the chars was visible above a certain particle size. The chars from straw with a particle size between 0.5-1.0 mm and the chars from olive waste with a particle size between 0.5-0.8 mm obtained at 800°C and at 1000° had similar surface area.

The composition of the biomass influenced the product distribution. Wood gave more volatiles and less char than the studied agricultural residues. The char yield after the rapid pyrolysis in the free fall reactor at 800°C was 7.2 wt% using wood but 13 wt% using straw and 20-27 wt% using olive waste. In previous studies, also a higher char yield was observed for agricultural residues because of the presence of large amount of ash, which favours the charring reactions [7,15]. The char yield after total pyrolysis was somewhat higher in pyrolysis of pelletised straw than untreated straw. The highest char yield was observed in the tests with olive waste. The higher lignin content in olive waste, in comparison with the wheat straw, contributed also to the higher char yield. Higher yields of char are favoured by high carbon content, low oxygen content, low H/C ratio and higher content of coke forming components, such as lignin, in the fuel subject to pyrolysis [16].

The residence time of the particles in the free fall reactor is not enough for the final pyrolysis. Previous experiments in the same reactor with wood changing the number of the used electrical showed that the char yield obtained in the upper part of the reactor remain constant when the particles were falling in the lower part of the reactor [5]. It seems that pyrolysis proceeds in two steps: an initial fast step followed by a slower step. It was suggested that the primary pyrolysis reactions in the rapid pyrolysis of wood were completed within seconds while the secondary reactions took minutes to be completed. Only the primary pyrolysis reactions have time to take place in the free fall reactor. For this reason, the char obtained by rapid pyrolysis contains a fraction that can be further volatilized by slow pyrolysis. After rapid pyrolysis in the free fall reactor, the fraction of char removed by slow pyrolysis in the thermobalance was larger in char samples from agricultural residues compared to wood.

The reactivity of the char was determined by the reaction of the sample, after total pyrolysis, with steam in the thermobalance. The reactivity of the chars reflected the differences in the biomass properties and also the different conditions during the pyrolysis. The chars from wood and olive waste obtained at 1000°C were more reactive than the chars obtained at 800°C. As mentioned, treatment at a higher temperature is related to a higher heating rate. High char reactivity is favoured by high heating rate [13]. The reactivity of the samples was also in correlation with the ash content in the char after total pyrolysis. At higher temperatures the char yield decreases and the ash content in the produced char increases. Thus, the char produced at higher temperatures has a higher ash content favouring a higher reactivity.

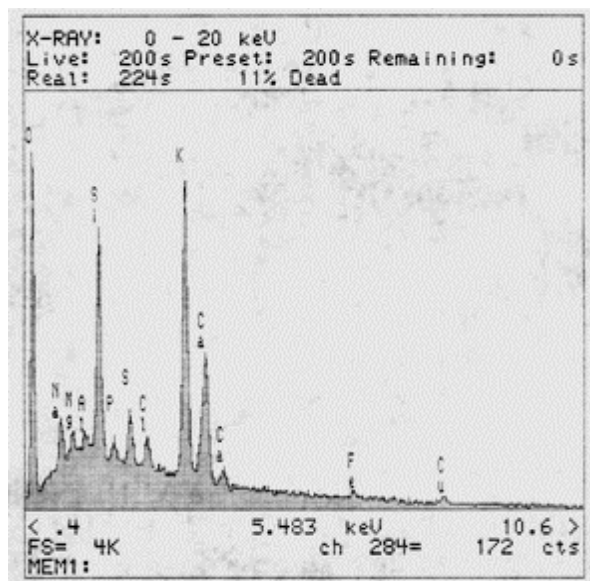
In test with straw in untreated and pelletised form, the fraction of char removed by slow pyrolysis in the thermobalance, before the reactivity measurements, was much higher for chars obtained at 800°C than for chars obtained at 1000°C (table 4). The char yield after total pyrolysis was lower for straw pyrolysed at 800°C compared to 1000°C. Thus, the ash content after total pyrolysis was higher in the samples pyrolysed at 800°C, increasing the reactivity of the char (table 4).

The reactivities of chars from agricultural residues were higher than those from wood, because of the higher ash content. Chars from untreated straw were more reactive than char from pelletized straw. Chars from olive waste were more reactive than char from straw. The high reactivity of the chars derived from olive waste has been also reported for samples produced by slow heating [17].

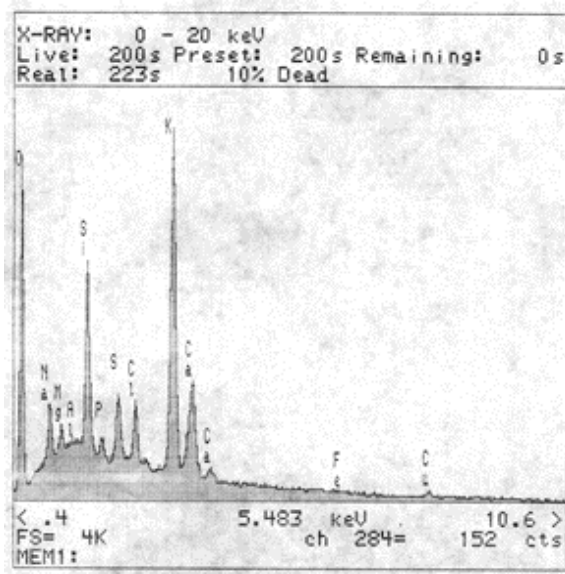
Qualitative X-ray microanalysis of the char samples were made using electron microscope supplied with an energy dispersive spectrometer. The results (figure 2) showed the qualitative ash composition, especially in relation to the components K, Na and Ca, which are recognized to play a catalytic action on the gasification reaction [18,19,20]. The content of K, seems to be similar in chars from straw and olive waste, while the content of Ca seems to be higher in chars from olive waste, which could explain the higher reactivity of the chars from olive wastes. In chars produced by slow pyrolysis have been reported higher concentrations of Na<sub>2</sub>O and CaO in the ash from olive waste than from straw [17].

The porosity and surface area of the chars are presented in table 3. Chars from agricultural residues have a higher surface area than those from wood. Char from untreated straw presented the highest surface area. Figure 3 shows the pore size distribution of the chars measured by mercury porosimetry. The char from straw has higher pore volume than wood and olive waste. For all the analysed chars, the major part of the pores has a pore diameter of about 110 microns. A difference can be mentioned between the pore size distribution of wood and agricultural residues. For both agricultural residues, olive waste and straw, a second group of pores with a smaller diameter (0.5 to 1 microns) has been found. In chars from wood no pores with diameter lower than 1 microns has been found with mercury porosimetry. Chars from straw and olive wastes even contain some pores with a diameter of 0.1 microns.

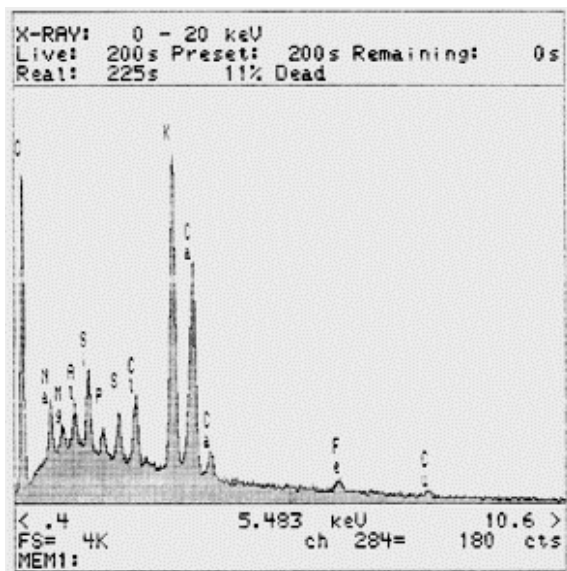




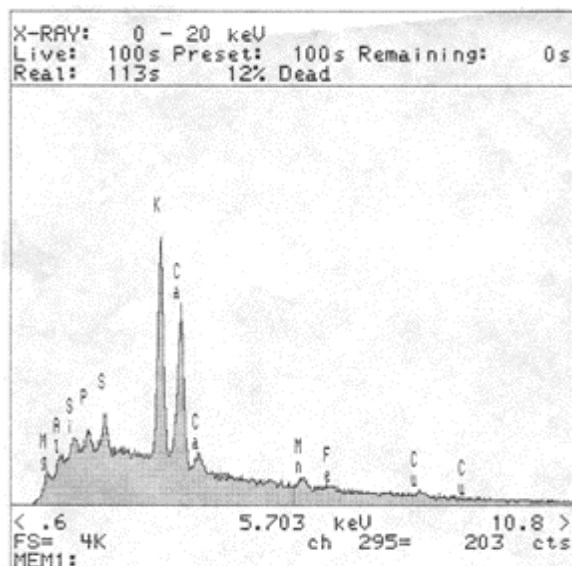
Straw pellets



Straw



Olive waste



Wood

Figure 2: Qualitative energy dispersive X-ray microanalysis of char samples obtained at 1000°C.

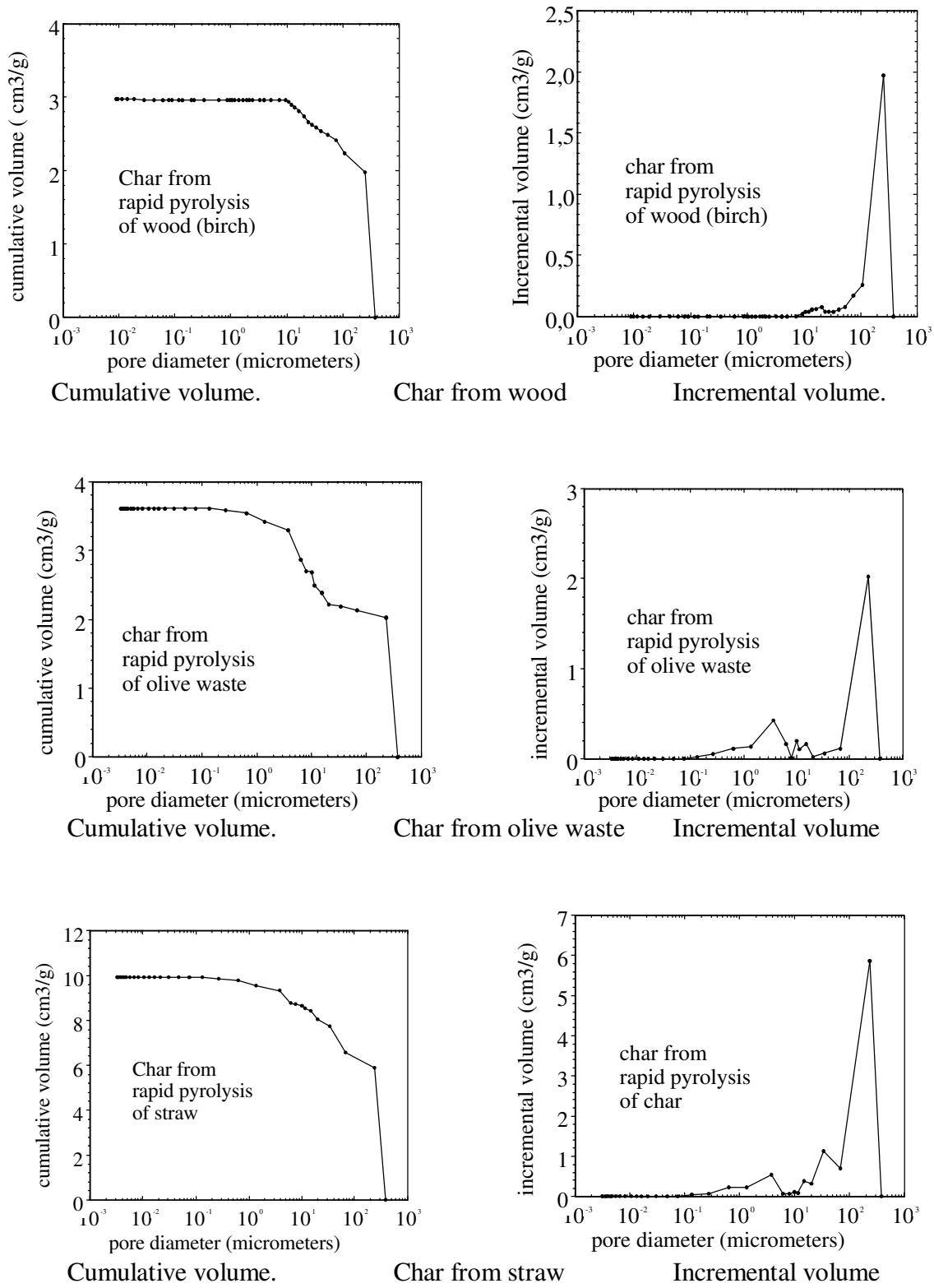


Figure 3: Mercury porosimetry measurements of chars produced by rapid pyrolysis at 1000°C. Pore size distribution.

Table 5 shows the composition of the gaseous products obtained in rapid pyrolysis of wood and agricultural residues in a free fall reactor.

Table 5: Composition of the gaseous products (vol. %. Nitrogen and waterfree basis)

Biomass	Straw		Straw pellets		Olive waste				Wood: Birch		
	0.5-1.0		0.5-1.0		0.5-0.8		0.8-1.0		0.5-0.8	0.8-1.0	
Temperature, °C	800	1000	800	1000	800	1000	800	1000	800	800	1000
H <sub>2</sub>	35.0	43.9	24.2	38.8	15.8	32.1	12.8	21.1	17.3	16.8	34.0
CH <sub>4</sub>	9.5	4.8	16.2	8.0	24.1	13.5	24.1	18.3	15.7	16.2	11.7
C <sub>2</sub> H <sub>2</sub> , C <sub>2</sub> H <sub>4</sub>	3.1	bdl <sup>a</sup>	4.7	0.1	3.4	0.3	3.9	0.5	5.8	6.2	0.5
C <sub>2</sub> H <sub>6</sub>	0.1	bdl	0.5	bdl	0.7	0.1	0.9	0.2	0.3	0.3	bdl
Benzene	0.6	0.1	0.7	bdl	0.6	0.2	0.5	0.2	1.2	1.2	0.6
CO <sub>2</sub>	23.7	5.0	19.3	4.7	15.7	8.6	18.2	12.3	9.6	8.3	7.5
CO	28.0	46.2	34.4	48.4	39.2	45.2	40.1	47.4	50.0	50.7	45.7

<sup>a</sup>bdl: below detection limit

A higher treatment temperature favoured cracking of the hydrocarbons in the gaseous products and thus increased the yield of hydrogen. It has also decreased the content of CO<sub>2</sub> in the gases and increased the CO content for the agricultural residues. Aromatic hydrocarbons (benzene) are products of secondary reactions. At higher temperature benzene was present in the gas.

Smaller particle size has affected also the composition of the gas. It has favoured the cracking of hydrocarbons with an increase of hydrogen yield. In smaller particles the produced gas left the particle faster than in large particles. The residence time of the gas outside the particle was longer and cracking was favoured.

In gases from pyrolysis of straw the concentration of hydrogen was higher and the concentration of hydrocarbons was lower in comparison with the gases from pyrolysis of olive waste and wood. In the test with straw a higher cracking of hydrocarbons has been reached. A possible reason for the increasing of the cracking reaction in the gaseous products when straw is used as raw materials could be that the produced gases have been a longer time outside the particle, in the reactor, facilitating the cracking of the hydrocarbons. Because the density of the straw is lower than that of wood and olive waste the falling velocity in the reactor is also lower. When the gases left the particle, the particles have fallen a shorter distance in the reactor using straw than using wood or olive waste. Thus, the volatiles spent a longer time in the reactor in the test with straw. Another reason that could increase the residence time of the gases in the reactor when straw is used is the higher porosity of this biomass. The porosity of both the raw material and its char is higher for straw in comparison with wood and olive waste. The higher porosity of the particle, the faster can the gases leave the particle and spend a longer time in the reactor.

#### **4. Conclusions**

Rapid pyrolysis of wood (birch) and three agricultural residues (sugar cane bagasse, olive waste and wheat straw in untreated and in pelletized form) at high temperature (800°C – 1000°C) has been studied in a free fall reactor at pilot scale. The conditions are of interest for gasification in fluidized beds. Because rapid pyrolysis is the first step in gasification and combustion in fluidized bed reactors, knowledge on rapid pyrolysis may contribute to the development of gasification and combustion models in fluidized bed reactors

Both the conditions during the pyrolysis and the composition and properties of the biomass have influence the product distribution, gas composition and char reactivity.

The higher treatment temperature has led to lower yields of tar and higher yields of gaseous products. At higher temperature, the heating rate is higher. The higher heating rate favours also the decrease of char yield. Higher treatment temperatures favour cracking of the hydrocarbons in the gaseous products and thus increase the yield of hydrogen.

The size of the particles affects the heating rate. When small particles are used the heating rate is higher and the char yield decreases. Smaller particle sizes favour the cracking of hydrocarbons with an increase of hydrogen yield because the residence time of the volatiles in the reactor is longer when smaller particles are used, favouring the cracking reactions.

A high ash content favours the reactivity of the chars. The higher ash content in agricultural residues has led to a more reactive char comparing with char from wood.

Wood gives more volatiles and less char than straw and olive waste. The high ash content in agricultural residues favours the charring reactions, increasing the char yield. The char yield from olive waste was higher than that from straw because of the higher lignin content in olive waste.

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## **APPENDIX-IV**

### **PAPER IV**

#### **Thermochemical treatment of biomass in a flow of steam or in a mixture of steam and carbon dioxide,**

Minkova, V., Marinov, S.P., Zanzi, R., Björnbom, E., Budinova, T., Stefanova, M. and Lakov, L.

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# Thermochemical treatment of biomass in a flow of steam or in a mixture of steam and carbon dioxide

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## Abstract

Simultaneous pyrolysis and gasification of biomass samples of different origin is performed in a flow of steam or in a mixture of steam and carbon dioxide. Wastes from birch wood, olive stones, bagasse, and pellets from straw and Miscanthus are used as feedstock. The raw materials are heated with 10°C/min to 750°C at atmospheric pressure and kept for a period of 2 h at this temperature. Laboratory experimental equipment with a horizontal rotating stainless steel reactor is used. The oxygen-containing functional groups in the solid products (–COOH, =CO and –OH) are determined using the method of Boehm. The results are compared with those obtained in treatment in inert atmosphere as well as with those obtained in a stationary reactor. The rotating pyrolysis reactor seems suitable for production of energy-rich gaseous products and activated carbons. © 2000 Published by Elsevier Science B.V. All rights reserved.

*Keywords:* Activated carbon; Biomass; Carbon dioxide; Gasification; Steam pyrolysis

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## 1. Introduction

Pyrolysis of biomass in the presence of reactive agents may produce activated carbons and energy-rich gaseous and liquid products [1–4]. This one-step process is a promising alternative to the expensive conventional processes for production of activated carbons and upgraded fuels. It also offers efficient utilisation of biomass, which is

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of particular importance for agricultural countries with vastly available biomass by-products as well as for countries rich in forest like the Nordic countries in Europe [5].

The nature of the activating agent (hydrogen, steam or carbon dioxide) and the way the contact between the agent and the fuel occurs, may influence significantly the yield and the quality of the products [6]. The temperature, which also has an important role in preparation of activated carbons [2,7], is kept in the range 600–800°C in the one-step treatment.

The aim of the present work is to study one-step pyrolysis and gasification of biomass wastes in flow of steam or mixtures of steam and carbon dioxide in a horizontal-rotating reactor. Birch wood, bagasse, olive stones, and two types of pellets, straw and Miscanthus, are used as raw materials. The temperature and the duration of the treatment are the same as those previously used in a stationary reactor [2,7] to allow comparing the results in these two reactors.

## 2. Experimental

The biomass samples are pyrolysed and activated in a one-step treatment, employing a laboratory equipment supplied with a horizontal rotating stainless steel reactor (1.3 l), situated in an electrically heated oven. The inner volume of the reactor can be regulated by a moving barrier. The treatment is conducted at 750°C for a period of 2 h. The temperature ramp is 10°C/min. The volatile products are swept out of the carbonised material by the reactive agents, steam or mixture of steam and carbon dioxide, or by argon. The degree of carbonisation is assessed as a ratio between the calorific value of the solid product and the calorific value of the initial sample of biomass ( $CV_p/CV_b$ ). The calorific values are calculated using the elemental composition of the samples [8]:

$$CV = 0.34\%C + 1.40\%H - 0.16\%O$$

where %C, %H and %O are wt.% in daf sample.

The energy recovered in the solid product ( $E_r$ ) is determined as a ratio between the energy content of the solid product and the energy content of the raw material. They are calculated using the amounts and the calorific values of the product and the feed.

The surface of the solid product is characterised by determination of the oxygen functional groups [9], and the adsorption capacity towards iodine [10]. The samples are agitated for at least 16 h with 0.05 M solutions of four bases with different strength:  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{CO}_3$ , NaOH and NaOEt, as well as with 0.05 M HCl. Thus, carboxylic, lactonic, phenolic, and carbonylic functional groups as well as pyrone structures may be identified.

## 3. Results and discussion

### 3.1. Effect of the raw material on the chemical composition of the solid product

The raw materials used in the study are presented in Table 1. The effects of the raw material on the chemical composition of the solid products obtained in pyrolysis in the



Table 1  
Chemical composition of the raw materials

Raw materials	Elemental composition (wt.% maf <sup>a</sup> )				H/C	O/C	Ash (wt.% mf <sup>b</sup> )	Moisture (wt.%)
	C	H	N	O diff <sup>c</sup>				
Birch wood	48.4	5.6	0.2	45.8	0.12	0.95	0.2	6.6
Bagasse	47.3	6.2	0.3	46.2	0.13	0.98	1.6	6.0
Olive wastes	49.5	6.3	0.5	43.7	0.13	0.88	2.1	7.7
Miscanthus pellets	48.9	4.6	0.4	46.7	0.09	0.96	2.4	12.1
Straw pellets	47.0	6.1	0.5	46.4	0.13	0.99	6.2	7.0

<sup>a</sup> maf: moisture and ash-free material.

<sup>b</sup> mf: moisture-free material.

<sup>c</sup> O diff: the oxygen is assessed by difference.

presence of inert atmosphere or reactive agents, steam or a mixture of steam and carbon dioxide, are shown in Tables 2–4.

All raw materials are enriched as fuels in the thermochemical treatment. The contents of carbon are increased, while the contents of oxygen are decreased. The products have similar degrees of carbonisation ( $CV_p/CV_b$ ), and comparable composition of the organic material. The contents of inorganic material vary a lot. The removal of volatile organic compounds in the thermal treatment results in enrichment of the inorganic material in the solid residues. Among the selected samples, the highest content of inorganic compounds is observed for the samples obtained from straw, followed by those from Miscanthus. The ash contents of the solid products depend strongly on the raw materials.

### 3.2. Effect of the reactive agents on the chemical composition of the solid product

Table 5 compares the chemical compositions of the products obtained in the presence of the activation agents, steam or a mixture of steam and carbon dioxide, with those obtained in an inert atmosphere of argon. In the selected experimental conditions, the highest degree of carbonisation (highest content of carbon and lowest content of oxygen)

Table 2  
Effect of the raw material on the chemical composition of the solid product obtained in inert atmosphere of argon

Raw materials	Elemental composition (wt.% maf <sup>a</sup> )				$CV_p/CV_b^c$	Ash (wt.% mf <sup>a</sup> )
	C	H	O diff <sup>b</sup>	O/C		
Birch wood	76.3	5.3	18.4	0.24	1.5	1.4
Bagasse	82.4	3.1	14.5	0.18	1.7	11.8
Olive wastes	78.6	3.9	17.5	0.22	1.6	3.9
Miscanthus pellets	82.2	3.3	14.5	0.18	1.9	20
Straw pellets	75.2	3.9	20.9	0.28	1.6	31

<sup>a</sup> maf and mf are the same as in Table 1.

<sup>b</sup> O diff — the oxygen assessed by difference. The nitrogen is neglected.

<sup>c</sup>  $CV_p$  — calorific value of the solid product,  $CV_b$  — calorific value of the initial sample of biomass.

Table 3

Effect of the raw material on the chemical composition of the solid product obtained in a flow of a mixture of steam and carbon dioxide

Raw materials	Elemental composition (wt.% maf <sup>a</sup> )				CV <sub>p</sub> /CV <sub>b</sub> <sup>a</sup>	Ash (wt.% mf <sup>a</sup> )
	C	H	O diff <sup>a</sup>	O/C		
Birch wood	89.3	3.1	7.6	0.08	2.0	5.6
Bagasse	86.9	2.8	10.3	0.12	1.8	12.7
Olive wastes	83.0	3.7	13.0	0.16	1.7	8.7
Miscanthus pellets	82.7	3.1	14.2	0.17	1.9	17.6
Straw pellets	80.0	2.9	17.1	0.21	1.7	29

<sup>a</sup> maf, mf, O diff, CV<sub>p</sub> and CV<sub>b</sub> are the same as in Tables 1 and 2.

is obtained in the presence of a mixture of steam and carbon dioxide. As expected, the ash yields increase with the degree of carbonisation. Thus, the treatments in the presence of reactive agents result in products with higher ash contents. Table 5 includes only samples with lower ash contents, because the dominating effect of large amounts of inorganic compounds may confuse the interpretation of the results pertaining to effects of the reactive agents.

### 3.3. Yield and adsorption capacity of the solid product

The yields and the adsorption characteristics of the solid products obtained in the presence of different activating agents or in an inert atmosphere of argon are presented in Table 6. The results show the effect both of the feed and of the reactive agents.

In pyrolysis in the presence of reactive agents, a significant quantity of the organic materials is liberated as volatiles and hence, the yield of solid residue is less than in the case of argon. For all biomass samples, the highest yield of solid product is obtained in the presence of inert atmosphere of Ar.

The lower yields of solid products obtained in the presence of reactive agents depend also in gasification reactions, which occur during the treatment. The results obtained in the presence of steam or a mixture of steam and carbon dioxide are similar, with the

Table 4

Effect of the raw material on the chemical composition of the solid product obtained in a flow of steam

Raw materials	Elemental composition (wt.% maf <sup>a</sup> )				CV <sub>p</sub> /CV <sub>b</sub> <sup>a</sup>	Ash (wt.% mf <sup>a</sup> )
	C	H	O diff <sup>a</sup>	O/C		
Birch wood	81.9	2.6	15.5	0.19	1.7	4.1
Bagasse	74.7	3.2	22.1	0.30	1.5	3.1
Olive wastes	82.4	3.0	14.6	0.18	1.6	6.3
Miscanthus pellets	78.9	2.7	18.4	0.23	1.8	13.4
Straw pellets	76.4	3.3	20.3	0.27	1.6	47.6

<sup>a</sup> maf, mf, O diff, CV<sub>p</sub> and CV<sub>b</sub> are the same as in Tables 1 and 2.

Table 5

Effect of the gaseous atmosphere in the pyrolysis on the chemical composition of the solid product

Raw materials and treatment	Elemental composition (wt.% maf <sup>a</sup> )			CV <sub>p</sub> /CV <sub>b</sub> <sup>a</sup>	Ash (wt.% mf <sup>a</sup> )
	C	H	O diff <sup>a</sup>		
<i>Birch wood</i>					
CO <sub>2</sub> + H <sub>2</sub> O	89.3	3.1	7.6	1.97	5.6
H <sub>2</sub> O	81.9	2.6	15.5	1.71	4.1
Ar	76.3	5.3	18.4	1.49	1.4
<i>Olive wastes</i>					
CO <sub>2</sub> + H <sub>2</sub> O	83.0	3.7	13.0	1.67	8.7
H <sub>2</sub> O	82.4	3.0	14.6	1.60	6.3
Ar	78.6	3.9	17.5	1.56	3.9

<sup>a</sup> maf, mf, O diff, CV<sub>p</sub> and CV<sub>b</sub> are the same as in Tables 1 and 2.

exception of those for bagasse and olive stones. For these samples activation with only steam results in much lower yield of solid product.

The multi-component distillation, which accompanies the pyrolysis in a flow of reactive agents, favours the escape of the volatiles from the solid material. The quick

Table 6

Effect of the raw material and the gaseous atmosphere on the yield and the adsorption properties of the solid product (values obtained in a stationary reactor within parentheses)

Raw materials and treatment	Yield (wt.%)	E <sub>r</sub> (%)	Iodine adsorption (mg/g)
<i>Birch wood</i>			
CO <sub>2</sub> + H <sub>2</sub> O	17	32	360
H <sub>2</sub> O	21 (10.6)	34	310 (770)
Ar	30	53	150
<i>Bagasse</i>			
CO <sub>2</sub> + H <sub>2</sub> O	19	31	565
H <sub>2</sub> O	5 (7.5)	7	440 (780)
Ar	35	54	133
<i>Olive wastes</i>			
CO <sub>2</sub> + H <sub>2</sub> O	25	39	345
H <sub>2</sub> O	15 (15.4)	23	310 (975)
Ar	34	53	126
<i>Miscanthus</i>			
CO <sub>2</sub> + H <sub>2</sub> O	11	18	266
H <sub>2</sub> O	13 (9.0)	20	355 (690)
Ar	42	67	140
<i>Straw pellets</i>			
CO <sub>2</sub> + H <sub>2</sub> O	25	32	340
H <sub>2</sub> O	26 (8.8)	23	325 (690)
Ar	32.5	39	178

removal of the volatiles and their stabilisation in the presence of reactive agents result in increased yields of volatiles. Compared to the experiments in argon, the yields and the energy recovered in the solid products are lower in the presence of reactive agents (Table 6). Thus, using reactive agents, a significant part of the feed may be converted into energy-rich liquid and gaseous products.

The reactive agents contribute also to the activation of the solid residual material to transform it into activated carbon with well-developed surface area. The adsorption capacity of the solid products are assessed by their iodine adsorption [11]. The adsorption properties depend strongly both on the initial material and on the presence and type of the activating agent (Table 6). For most of the samples, the highest activities are achieved by treatment in the presence of the mixture of CO<sub>2</sub> and H<sub>2</sub>O. The results for Miscanthus are an exception — the treatment in the presence of steam alone leads to the highest adsorption capacity. As expected, the adsorption capacities obtained in the presence of inert gas are much lower than to those obtained in the presence of activating agents. The increased adsorption capacities of the solid products obtained in the presence of the activating agents suggest the feasibility of using these products as adsorbents.

### *3.4. Rotating vs. stationary reactor*

Table 6 includes also some results pertaining to experiments performed with the same temperature and duration of the treatment using a stationary reactor. These results are shown in parentheses. In the selected experimental conditions, the treatment in the stationary reactor has resulted in solid products with much higher adsorption capacities towards iodine.

The rotating reactor seems to favour the gasification reactions. The yields of gaseous products in the present study are 60–70 wt.% (not shown in the table), while in the stationary reactor, they are less than 40 wt.% [12]. The yields of liquid products obtained in the rotary reactor are less than 10 wt.%, while the yields of liquid products in the stationary reactor are above 40 wt.% [12].

### *3.5. Oxygen-containing functional groups on the surface of the solid products*

The adsorption properties of the activated carbons depend on the concentration of active sites (e.g., chemical groups containing oxygen or other heteroatoms). The nature of the oxygen functional groups depends strongly on the temperature for the oxidation. The oxygen-containing groups on the surface of carbon may be basic or acidic [13]. Oxidation above 200°C leads mostly to formation of acidic groups, which adsorb predominantly cations. Oxidation above 500°C leads mainly to the formation of oxygen groups with basic character.

The oxygen-containing functional groups of different acidity as well as those with basic character are assessed by titration with alkaline solutions of different strength (NaHCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, NaOH and NaOEt) and hydrochloric acid. Thus, carboxylic,

lactonic, phenolic and carbonylic groups as well pyrone structures may be identified [9]. Significant amounts of oxygen functional groups, both with basic and with acidic character, are detected on the surfaces of the activated carbons prepared in this study (Table 7). Groups with weaker acidic and basic characters are predominant on the surface of the carbons. No groups that react with  $\text{NaHCO}_3$  or  $\text{Na}_2\text{CO}_3$  have been detected. Compared to the samples treated in the presence of inert gas, the samples treated with  $(\text{CO}_2 + \text{H}_2\text{O})$  have higher contents of oxygen-containing groups with basic and weakly acidic character.

Materials without carboxylic and lactonic groups have better thermal resistance. According to Papier et al. [14] and Boehm [15], the basic groups on the surface of the activated carbon are probably of pyrone structures, which may be formed by thermal decomposition of the acidic groups at temperatures above  $600^\circ\text{C}$  and re-arrangement of the residual active sites or reactions of these sites with the reactive agents.

The highest contents of basic groups have been detected on the surfaces of carbons from straw. The pH values of 9.8 of these carbons confirm their basic character. This result is in agreement with the pH determined for activated carbons prepared in a stream of water vapour in a stationary fix-bed reactor. The highest contents of weakly acidic groups are registered for the samples prepared from birch.

Table 7  
Acid–base neutralisation capacity

Raw materials and treatment	Base uptake (mmol/g)		Acid uptake (mmol/g)
	NaOH	EtONa	HCl
<i>Birch</i>			
$\text{CO}_2 + \text{H}_2\text{O}$	0.14	2.83	1.78
$\text{H}_2\text{O}$	0.17	1.50	0.80
Ar	0.14	1.62	1.08
<i>Bagasse</i>			
$\text{CO}_2 + \text{H}_2\text{O}$	0.30	2.07	1.53
Ar	0.30	2.02	1.33
<i>Olive wastes</i>			
$\text{CO}_2 + \text{H}_2\text{O}$	0.20	2.49	1.48
$\text{H}_2\text{O}$	0.17	2.31	1.00
Ar	0.20	1.84	1.18
<i>Mischantus</i>			
$\text{CO}_2 + \text{H}_2\text{O}$	0.30	2.40	1.83
$\text{H}_2\text{O}$	–	1.74	2.57
Ar	0.30	2.14	1.23
<i>Straw pellets</i>			
$\text{CO}_2 + \text{H}_2\text{O}$	0.10	1.77	2.03
$\text{H}_2\text{O}$	0.06	1.50	2.37
Ar	0.10	1.67	1.88

## 4. Conclusions

Compared to treatment under argon, pyrolysis of biomass in a flow of reactive agents, steam or a mixture of steam and carbon dioxide, favours efficient removal of the volatile products from the carbonising material and formation of solid product with increased surface area. The feed has strong effect both on the distribution and the quality of the products.

The rotary reactor used in this study contributes to the faster escape of the volatiles from the carbonising material as well as to the gasification reactions and formation of gaseous products at the expense of solid and liquid products.

Rotary pyrolysis reactors seem suitable for processes, which aim at both energy-rich gaseous products and activated carbons. In the selected experimental conditions, the surface areas of the solid products obtained in the rotary reactor are lower than those obtained in a stationary reactor.

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## **APPENDIX-V**

### **PAPER V**

**Effect of water vapour and biomass nature on the yield and quality of the pyrolysis products from biomass,**

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## Effect of water vapour and biomass nature on the yield and quality of the pyrolysis products from biomass

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### Abstract

Slow pyrolysis/activation of biomass in a flow of steam is studied in laboratory equipment supplied with a fixed bed reactor. Forestry and agricultural residues of different origin are selected as raw materials (birch wood, olive stones, bagasse, pelletised straw and miscanthus). The final pyrolysis temperature is varied in the range 700–800°C and the duration of the activation is 1 or 2 h. The effect of both the nature of the investigated biomass samples and the presence of water vapour on the quality of the pyrolysis products is in the focus of interest of this work. Column chromatography is used to characterize the liquid products. The surface area and the acid–base neutralization capacity of the solid products are determined by the adsorption capacity towards iodine and reactions with EtONa and HCl. The results are compared with those obtained in pyrolysis in inert atmosphere of nitrogen. It is shown that the presence of steam has strong effect on the yield and properties of the products. Significant part of the liquid product is found dissolved in the water phase obtained after condensation of the volatiles. The solid products obtained in the presence of steam have the properties of activated carbons. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Pyrolysis; Biomass; Steam; Nitrogen atmosphere; Activated carbon; Liquid products

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## 1. Introduction

Most of the scenarios for future energy supply suggest that renewable biomass energy will play significant role in the 21st century [1]. Converted to liquid or gaseous fuels, biomass has a great potential as an energy carrier. Increased use of biomass is an attractive alternative to the utilization of fossil fuels. As a carbon dioxide-neutral fuel, biomass provides important environmental benefits.

Numerous studies have been devoted on the preparation of high quality carbon adsorbents from biomass [2–4]. Activated carbon is a well-known versatile product used in many applications. It is employed to remove pollutants from gaseous and liquid streams, for purification and separation in several industrial processes. In the last years, special emphasis on the preparation of activated carbons from agricultural by-products has been given due to the growing interest in low-cost activated carbons from renewable safe copious supplies, especially for applications concerning treatment of drinking water and wastewater. Pyrolysis of biomass in a flow of steam is a promising method for simultaneous production of activated carbon, liquid and gaseous fuels and valuable chemicals. Presence of steam in the pyrolysis favours the formation of high yield of liquid products [5–7], while the almost simultaneous pyrolysis and gasification of the fuel results in formation of solid product with high surface area and well-developed porous structure [8,9]. Steam is used as a reactive agent alone or in mixtures with carbon dioxide [10].

The aim of the present work is to study the effect of steam flow and the nature of the investigated biomass samples on the yield and the quality of the products obtained in pyrolysis/activation of samples of agricultural and forestry wastes.

## 2. Experimental

The biomass samples are pyrolysed and activated in one-step thermochemical treatment in presence of steam. The samples are heated with a heating rate of 10°C/min to a final temperature of 700°C, 750°C or 800°C and kept 1 or 2 h at this temperature in the flow of steam. For comparison, the samples are treated also in inert atmosphere of nitrogen. The laboratory equipment with a fixed bed pyrolysis reactor and the experimental procedure are previously described [5]. The selected agricultural and forestry wastes used as raw materials are presented in Table 1.

After the activation, the tar is separated from the condensed water phase by decantation and the amount of water-soluble product is determined as previously described [11].

Column chromatography is used to separate the tars into four fractions—aliphatics, aromatics and two polar fractions. The respective solvents pentane, toluene, tetrahydrofuran/methanol (85:15) and methanol/formic acid (9:1) have been selected having in mind the composition of the raw materials and the products of their thermal decomposition [7,12].

The adsorption capacity of the solid material towards iodine is determined by the method described in DIN 53582.

Table 1  
Chemical composition of the raw materials

Sample	C (wt.% maf)	H (wt.% maf)	N (wt.% maf)	O diff	Ash (wt.% mf)	Moisture (wt.%)
Olive wastes	49.5	6.3	0.5	43.7	2.1	7.7
Miscanthus pellets	48.9	4.6	0.4	46.1	2.4	12.1
Straw pellets	47.0	6.1	0.5	46.4	6.2	7.0
Birch wood	48.4	5.6	0.2	45.8	0.2	6.6
Bagasse	47.3	6.2	0.3	46.2	1.6	6.0

maf—Moisture- and ash-free material; mf—moisture-free material; O diff—the oxygen is assessed by difference.

The base neutralisation capacities of the solid residues are determined by the method of Boehm [13] and the acid neutralization capacities with hydrochloric acid [14].

The sulphur content of the solid residues was determined by method of IR absorption in the stream of O<sub>2</sub> at 1300°C on SC-132, Lego—USA.

### 3. Results and discussion

#### 3.1. Yield of pyrolysis products

The yields of solid, liquid and gaseous products obtained in pyrolysis/activation of the selected biomass samples are shown in Fig. 1. The results obtained in presence of

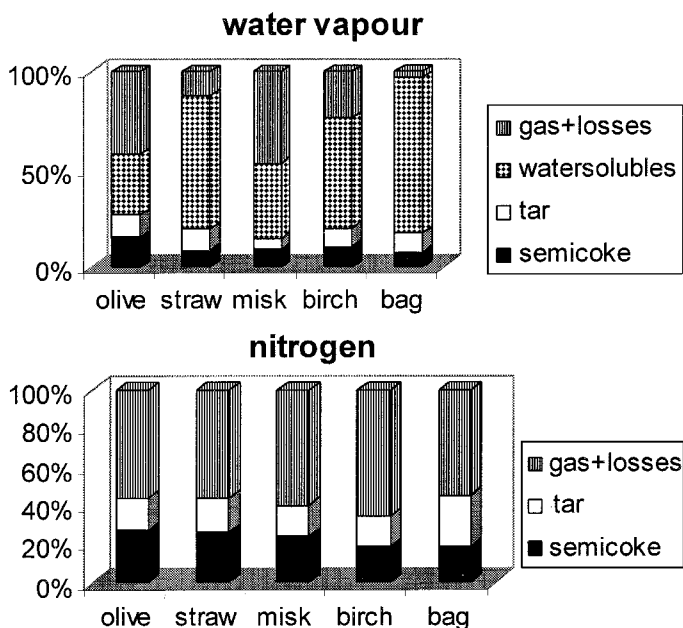


Fig. 1. Yield of products obtained in pyrolysis of the selected raw materials in stream of water vapour and nitrogen. Final treatment temperature: 750°C; time of treatment at this temperature: 2 h.

water vapour are compared with those obtained in inert atmosphere. The water vapour has strongly influenced the distribution of products. In a flow of steam, the yields of liquid products have dramatically increased at the expense of gaseous and solid products. The liquid product obtained in steam is presented as tar and water-soluble fraction. The largest part of the liquid products from steam pyrolysis is found in the water-soluble fractions. For all samples, the total yield of liquid product obtained in steam pyrolysis is 2–4 times higher than this in inert atmosphere. The opposite is observed for the gaseous products.

The lower yield of solid residue and the higher yield of volatiles obtained in pyrolysis under a flow of steam are related to the ability of the water vapour to penetrate the solid material and to help desorption, distillation and efficient removal of the volatile products from it. During pyrolysis in a flow of nitrogen, some of the pores in the solid material may be blocked by deposition of carbonaceous material and this contributes also to higher yield of the solid residue [5].

The water vapour is not only a “vehicle” for the volatiles. It is also a reactive agent, which reacts with the pyrolysis products. It may stabilise the radicals obtained in the thermal decomposition of the fuel increasing the yield of volatiles. The increased content of hydrogen and oxygen as well as the decreased content of carbon in the solid pyrolysis residues compared with those obtained in inert atmosphere support the chemical reactions between the steam and the fuel (Table 2).

The presence of large amount of water condensate in the steam pyrolysis contributes to extraction of water-soluble compounds from the tar and the gaseous phase into the water phase and thus, additional decrease of tar and gaseous products.

### 3.2. Effect of the raw material

Fig. 1 shows that the distribution of products depends strongly on the raw materials submitted to pyrolysis. In the selected experimental conditions, the highest yields of liquid products are obtained from the samples of straw, birch and bagasse. The yields of gaseous and solid products vary also among the samples.

### 3.3. Composition of the liquid products

Column chromatography has been used to separate the liquid products (without the water-soluble part) into four fractions: aliphatic, aromatic and two polar fractions, eluted respectively with pentane, toluene, tetrahydrofurane/methanol (85:15) and methanol/formic acid (9:1). The results are presented in Fig. 2, which compares the products from different raw materials obtained by pyrolysis in presence of steam or inert atmosphere. The polar fractions, particularly those eluted with tetrahydrofurane/methanol (85:15) dominate. In the samples from bagasse, the contents of both polar fractions are approximately the same. It may also be seen that in the samples obtain in steam pyrolysis the contents of the polar fractions are somewhat higher, while the formation of aliphatic and particularly the aromatic compounds seem to be favoured in inert atmosphere.

Table 2  
Analyses of the solid residues from pyrolysis in the stream of steam and nitrogen (N<sub>2</sub>)

Raw material	C (wt.% maf)	ΔC (wt.% maf)	H (wt.% maf)	ΔH (wt.% maf)	O diff (wt.% maf)	ΔO diff (wt.% maf)	S total (wt.% maf)	Ash (wt.% mf)
Olive (steam)	82.4	+ 32.9	3.0	− 3.3	14.6	− 29.1	–	6.3
Olive (N <sub>2</sub> )	86.0	+ 36.5	2.5	− 3.8	11.5	− 32.2	–	3.9
Straw (steam)	79.0	+ 32.0	3.3	− 2.8	17.7	− 28.7	0.008	47.6
Straw (N <sub>2</sub> )	82.0	+ 35.4	2.3	− 3.8	15.6	− 30.7	–	31.0
Birch (steam)	81.9	+ 33.5	2.6	− 3.0	15.5	− 30.3	0.005	4.1
Birch (N <sub>2</sub> )	85.3	+ 36.9	2.4	− 3.2	12.3	− 33.5	–	1.4
Bagasse (steam)	74.7	+ 27.4	3.2	− 3.0	22.1	− 24.1	0.040	3.4
Bagasse (N <sub>2</sub> )	82.9	+ 35.6	2.2	− 4.0	11.8	− 34.4	–	11.8
Miscanthus (steam)	78.9	+ 30.0	2.7	− 1.9	18.4	− 28.3	–	13.4
Miscanthus (N <sub>2</sub> )	81.1	+ 32.2	2.2	− 2.4	16.7	− 30.0	–	20.0

maf—Moisture- and ash-free material; mf—moisture-free material; O diff—the oxygen is assessed by difference; ΔC, ΔH, ΔO—changes in contents of carbon, hydrogen and oxygen during the treatment.

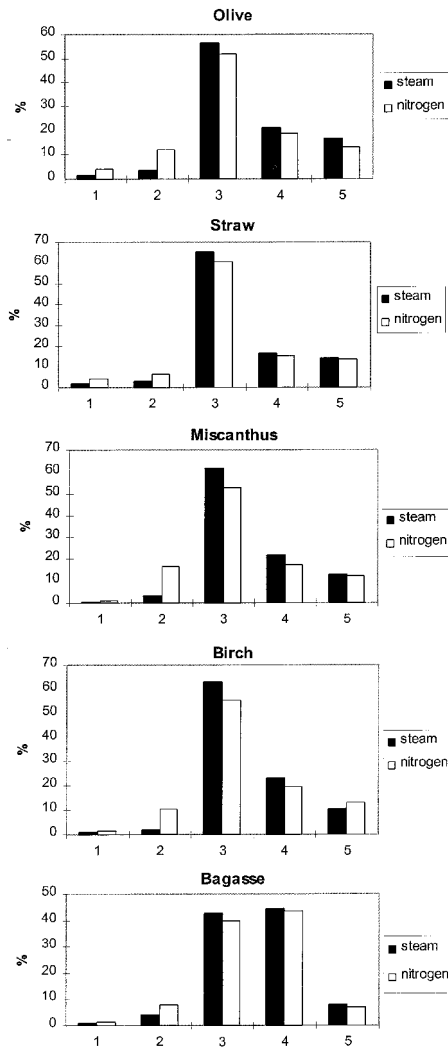


Fig. 2. Yield of fractions obtained by column chromatography of tar obtained in pyrolysis in a flow of steam or nitrogen. Final treatment temperature: 750°C; time of treatment at this temperature: 2 h. Fractions eluted with: pentane (1), toluene (2), tetrahydrofurane/methanol (85:15) (3), and methanol/formic acid (9:1) (4); Losses (5).

The total yield of oxygen-rich polar compounds obtained in pyrolysis of biomass in presence of steam is much higher than those obtained in inert atmosphere (see also the water-soluble fractions in Fig. 1). This may be explained with the high oxygen content of the initial raw material and the effect of steam on the pyrolysis. The water vapour favours quick removal of the volatile compounds from the fuel without substantial change in their structure [5]. Thus, the oxygen rich chemical structures, which are typical

for the initial biomass material, are preserved in the volatile products and contribute to formation of polar compounds.

### 3.4. Effect of the treatment conditions on the yield and the adsorption capacity of the solid products

Fig. 3 compares the yields and the adsorption capacities towards iodine of the solid residues obtained from different raw materials in presence of steam. The results show the effect of the final treatment temperature and the duration of the activation. In the selected experimental conditions, increase of the temperature from 700°C to 750°C and the duration of steam activation from 1 to 2 h result in decrease of the yield of solid

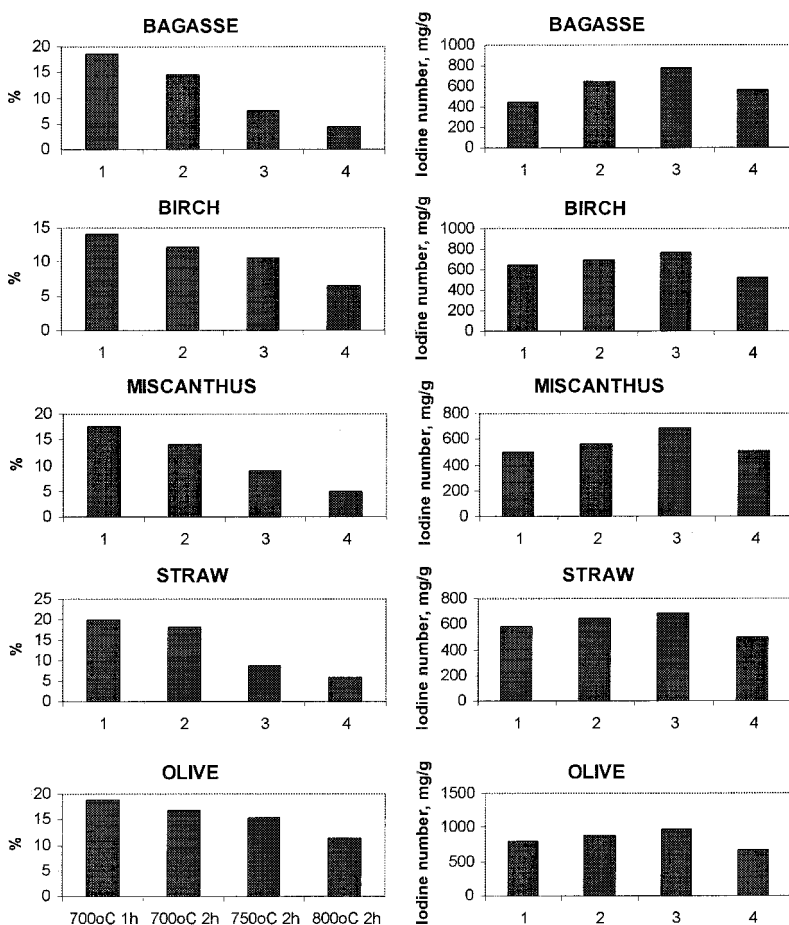


Fig. 3. Yields and adsorption capacities of solid residues from investigated raw materials depending on the final treatment temperature and the time of treatment at this temperature: (1) 700°C, 1 h; (2) 700°C, 2 h; (3) 750°C, 2 h; (4) 800°C, 2 h.

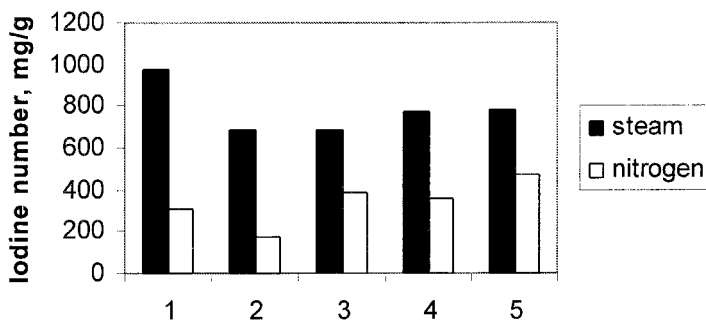


Fig. 4. Adsorption capacities towards iodine of solid residues obtained in pyrolysis in a flow of steam or nitrogen of biomass samples: (1) olive wastes, (2) straw, (3) miscanthus, (4) birch, (5) bagasse.

residues and improvement of the adsorption capacities. Further increase of the temperature decreases the yield of solid product without any improvement in the adsorption capacity. It seems that at 800°C the gasification reactions are intensified and the solid residues loose both weight and active surface. For all samples treated at 800°C, 2 h, the adsorption characteristics are worse compared to those obtained at lower temperature. The samples activated 2 h at 750°C have the best adsorption characteristics among those presented in Fig. 3. These conditions for activation are used to compare the adsorption capacities of samples obtained by pyrolysis in presence of steam and nitrogen. The results in Fig. 4 confirm the positive effect of steam during the pyrolysis on the adsorption characteristics of the solid products obtained after activation. The adsorption capacities of all samples pyrolysed in a flow of steam are much higher compared to the samples pyrolysed in inert atmosphere.

### 3.5. Oxygen-containing functional groups on the surface of the solid product

Table 3 compares the acid–base neutralisation capacities of the solid products obtained from different raw materials in presence of steam and nitrogen. EtONa, HCl,

Table 3

Acid–base neutralization capacity of solid residues from pyrolysis in the stream of steam and nitrogen (N<sub>2</sub>) (mg equiv g<sup>-1</sup>)

Sample	EtONa	HCl
Olive wastes (steam)	2.29	2.44
Olive wastes (N <sub>2</sub> )	1.30	1.12
Miscanthus (steam)	1.98	1.90
Miscanthus (N <sub>2</sub> )	0.98	1.58
Straw (steam)	0.99	2.50
Straw (N <sub>2</sub> )	0.54	1.76
Birch (steam)	1.05	1.88
Birch (N <sub>2</sub> )	0.59	0.60
Bagasse (steam)	2.30	2.15
Bagasse (N <sub>2</sub> )	1.90	1.34

$\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$  are used as reagents. The concentrations of oxygen-containing groups on the surface of the samples obtained in presence of steam are higher. Due to relatively high treatment temperature, the less thermally stable carboxylic and lactone groups are not identified (reactions with  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$ ). The elemental composition of the solid residue (Table 2) is in agreement with the higher content of oxygen-containing compounds in the solid residues obtained in presence of steam compared to those obtained in inert atmosphere.

#### 4. Conclusions

The study shows the effect of steam flow on the yield and the properties of the products obtained in pyrolysis/activation of selected samples of agricultural and forestry wastes. The results are compared with those obtained in inert atmosphere of nitrogen. The presence of steam has increased significantly the yield of liquid pyrolysis products at the expense of the gaseous and solid products. It is found that the liquid products consist predominantly of water-soluble polar compounds. Large part of the volatiles is found in the water phase condensed along with the tar.

The steam has contributed to the formation of solid residues with high surface area and good adsorption capacities. The raw materials have strong effect on the yield and the properties of the pyrolysis products. The higher yields of solid residues with good adsorption characteristics obtained from olive wastes, birch and bagasse make these raw materials suitable for preparation of activated carbon. The samples from straw and miscanthus seem more suitable for conversion into liquid and gaseous products.

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## **APPENDIX-VI**

### **PAPER VI**

**Pyrolysis of biomass in presence of steam for preparation of activated carbon, liquid and gaseous products,**

Zanzi, R., Bai, X., Capdevila, P. and Björnbom, E.

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## Pyrolysis of Biomass in Presence of Steam for Preparation of Activated Carbon, Liquid and Gaseous Products

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Biomass samples are carbonized and activated in a one-step treatment involving pyrolysis in a flow of steam in a fixed bed reactor. Different agricultural residues such as olive waste, sugar cane bagasse, miscanthus pellets, wheat straw in pelletized and untreated form, and wood species, such as birch and salix, are used as precursors. The steam flow was varied between 0.25 and 0.75 l/hour. The reactor was heated at constant rate (10°C/min and 25°C/min) to the selected final temperature (550°C, 650°C and 750°C) and kept at the final temperature for a period of 45, 60 or 120 minutes. At the selected experimental conditions the type of biomass as well as the temperature and activation time, have the greatest influence on the quality and the yield of the obtained activated carbons. The quality of the activated carbon was evaluated in terms of iodine number reflecting the surface area. The produced gas was analysed. Temperature influences the activation rate. The highest surface area of the activated carbons was reached at 650°C. At 550°C the obtained surface area was lower. At 750°C and 1 hour activation time almost all the biomass was gasified. The yield of liquid product increases and the gas yield decreases when the rate of the steam flow is increased. Straw has a higher reactivity in gasification compared to the other used biomasses.

### INTRODUCTION

Activated carbons are carbonaceous materials with highly developed internal surface area and porosity, sometimes described as solid sponges. The large surface area results in a high capacity for adsorbing chemicals from gases or liquids. Activated carbons are versatile adsorbents with wide range of applications. One of the largest uses of activated carbons is for water treatment. The carbons are added to remove compounds that affect taste and odour of the water. Increasing use of activated carbon is found also in industrial waste water and gas treatment due to the necessity of environmentally friendly processes and also for material recovery purposes. The food industry is also a major consumer of activated carbons where it is used to remove compounds that adversely affect colour, taste and odour. In the mineral industry, activated carbons are used to recover gold from leached liquors. Medicinal uses and the pharmaceutical industry also answer for a large part of the consumption. Catalysis is another area where the structure and features of activated carbon are favourable. In gas applications activated carbons are extensively used in air filters in industrial applications as well as in general air conditioning applications. An important industrial use of activated carbons is solvent recovery. Volatile organic compounds are used in a wide variety of applications and they create unacceptable environmental problems if vented straight to the atmosphere. In a cyclic adsorption – desorption process, activated carbons provide an effective means of recovering the solvent. Activated carbons are also used for storage of hydrogen and natural gas.

The preparation of activated carbons involves, frequently, two steps: carbonization of the raw material in absence of oxygen, and activation of the carbonised product with water vapour or carbon dioxide [1,2]. The activation can be carried out under well controlled conditions to a desired conversion. The pores thus produced in the char give the activated carbon its high surface area and

adsorptive properties. A three-step process for the production of activated carbons including carbonatization, oxidation in air following a stepwise heating program from low to high temperatures and finally a heating in an inert environment to a high temperature has also been described [3]. A simple one-step method for production of activated carbons by pyrolysis of solid fuels in the presence of steam has also been developed [4,5]. Another method for production of activated carbons is through chemical activation. In this method, the precursor material is impregnated with a dehydrating and stabilising chemical reactant in order to enhance the development of porous structure upon heat treatment [6].

Preparation method, type of used reactor, employed conditions and selected precursor material influence the properties of the obtained activated carbons [1,2,3,5,6,7]. Coal, coconut shell and wood have been the most frequently used precursors to manufacture activated carbon. Coconut shell has a higher volatile content, which produces granulated carbon with even and large pore volume [2]. In the last years, special emphasis on the preparation of activated carbons from several agricultural by-products has been given due to the growing interest in low cost activated carbons from renewable, copious supplies, especially for applications concerning treatment of drinking water and wastewater.

Physical activation with CO<sub>2</sub> has resulted in carbons with a pore structure consisting mainly of narrow micropores and wide macropores [8]. Introduction of potassium phosphate as a catalyst for the physical activation led to a decrease in macropore volume and diameter, and an increase in micropore diameter. Chemical activation with phosphoric acid produced a carbon with wider micropores and a significant mesoporosity [6].

In the present work the biomass samples are carbonised and activated in a one-step treatment involving pyrolysis in a flow of steam. The almost simultaneous pyrolysis and gasification of the fuel favour the high reactivity of the solid material and its conversion at milder treatment conditions into activated carbon with well developed porous structure and good adsorption capacity [9]. One-step steam pyrolysis is a promising alternative to the conventional processes for production of activated carbons and liquid and gaseous fuels [10]. Several simultaneous processes occur in steam pyrolysis: thermal decomposition, multi-component steam distillation, fast escape and stabilization of the volatiles, mild oxidation, activation of the solid residues and formation of activated carbons. The multi - component distillation, which accompanies the pyrolysis in a stream of water vapour, guarantees a 'mild' process and efficient escape of the volatiles from the solid material. The quick removal of the volatiles and stabilization of the radicals in the presence of steam results in increased yields of volatiles and formation of solid products with a highly developed active surface free from organic compounds.

Different agricultural residues and wood are used as precursors. The aim of this work is to study the effect of the temperature, the heating rate and residence time on the yield and the properties of the products obtained in pyrolysis of the selected precursors in the presence of steam.

## **EXPERIMENTAL**

Wood species of Swedish wood, birch (*Betula Pubescens*) and salix (*Salix Viminalis*), a fast growing willow, and different agricultural residues were selected as raw materials. The used agricultural residues were olive waste from oil production, sugar cane bagasse, miscanthus pellets and wheat straw in untreated and in pelletised form. Olive waste was composed of a crushed mixture of kernel and pulp. It is an inexpensive material, which is available in large quantities and can be used for preparation of activated carbon [11,12]. Sugar cane bagasse, the waste material obtained in sugar factories after extraction of the sugar juice has also been reported as a suitable resource for preparation of activated carbon [6,13]. Miscanthus is a perennial grass. It is used for production of cellulose for paper or building material such as pressed boards. Another potential use of miscanthus

is in combustion and gasification as energy crop. Straw is a crop residue, being chiefly the stalk of cereal crops left after the main crop has been harvested.

Table 1: Chemical composition of the precursors

Raw materials	Composition, wt% maf				Ash	Moisture
	C	H	N	O diff.	wt%mf	wt%
Birch	48.4	5.6	0.2	45.8	0.18	4.4
Salix	48.8	6.2	1.0	43.4	0.75	7.3
Sugar cane bagasse	47.3	6.2	0.3	46.2	0.90	6.2
Olive waste	49.5	6.3	0.5	43.7	2.02	5.0
Miscanthus	48.9	4.6	0.4	46.7	2.69	6.6
Untreated wheat straw	46.5	6.3	0.9	46.3	3.23	3.3
Pelletised wheat straw	47.0	6.1	0.5	46.4	6.34	6.9

maf: moisture and ash free

mf: moisture free

Chemical composition of the raw materials is shown in Table 1.

Biomass samples were milled, sieved and separated in fractions. A fraction of particle size 1-3.2 mm was selected for the experiments except when untreated straw and sugarcane bagasse were used as precursors. Particles of straw with a size between 0.5-0.9 mm were used. In the experiments with sugar cane bagasse a fraction of particle diameter 1.0-1.3 mm was also used in order to study the influence of the particle size.

The equipment used in the experiments included a steam generator, a cylindrical pyrolysis reactor and equipment for removal of the liquid products (water-cooled condenser, ice traps and a column with cotton and phosphorus pentoxide as drying agent) and gas meter. The reactor tube (with a length of 0.5 m and an inner diameter of 0.04 m) is heated by an electric heater. The reactor consists of two cylinders. The sample is placed in the removable inner cylinder with a net in the bottom. The outer cylinder is cone shaped at the bottom and connected to a metal tube with a screw holder, that makes it easier to clean from tar. The water is pumped to the steam generator by a peristaltic pump. The steam temperature is around 105°C. The volatiles are cooled down in a water-cooled condenser. The gas is led through a column with cotton and phosphorus pentoxide as drying agent, a gas meter and then collected in a bag. The gas composition is analyzed by a gas chromatograph for CO<sub>2</sub>, H<sub>2</sub>, CO, N<sub>2</sub>, CH<sub>4</sub>, and hydrocarbons up to C<sub>7</sub>. The gas chromatograph is equipped with three columns. A Porapak Q, 80/100 (3mm in diameter and 2 m in length) produces a good separation for carbon dioxide and hydrocarbons such as ethylene, ethane and acetylene. A molecular sieve column (MS5 60/80) (also 3mm in diameter and 2 m in length) is used for separation of hydrogen, oxygen, nitrogen, methane and carbon monoxide. Both columns use helium as carrier gas and are connected to a thermal conductivity detector. A Megabore column (bonded phase: DB-1) (0.9 mm in diameter and 16 m in length) is used for the separation of hydrocarbons such as benzene and toluene. The column uses nitrogen as carrier gas and is connected to a flame-ionization detector.

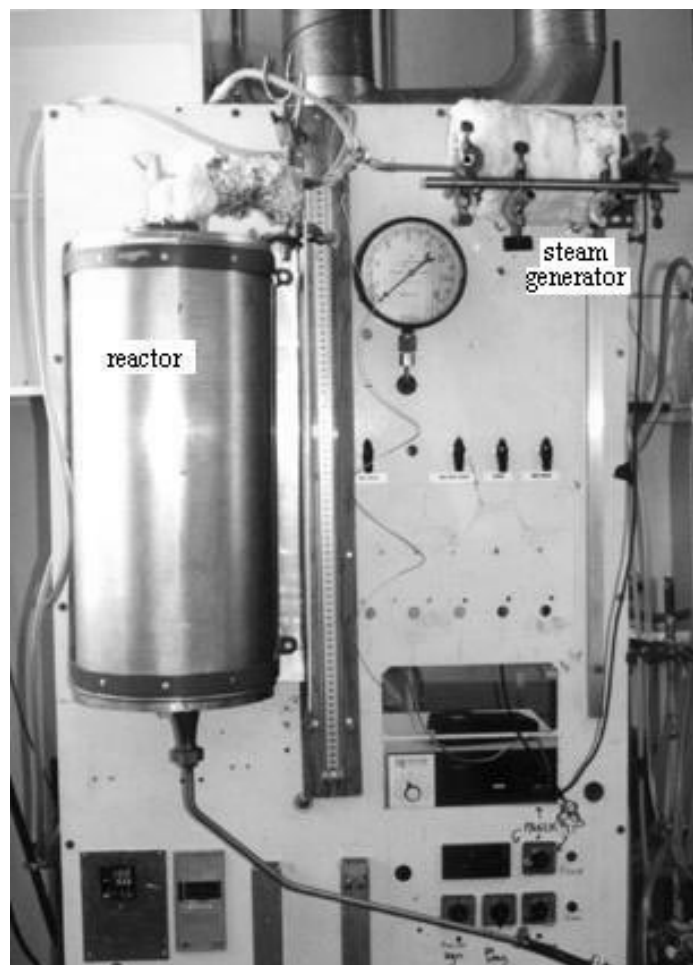


Figure 1: Equipment for preparation of activated carbon

In each experiment 65 g of biomass were subjected to pyrolysis in presence of steam at atmospheric pressure. The steam flow was varied among 0.25, 0.5 and 0.75 litre/hour. The steam was introduced into the reactor when the temperature in the reactor was 150°C. The reactor was heated at constant rate (10°C/min and 25°C/min) to the selected final temperature (550°C, 650°C and 750°C). The sample was kept at the final temperature for one hour and then the electrical heater was switched off. After the treatment the samples are left to cool down and the steam flow is interrupted at temperature 250-300°C. Before each experiment 12 litres of nitrogen was led through the system to empty it from air. After each experiment 3 litres of nitrogen was led through the system to rinse it from volatile products.

The collected char was measured and characterized. Surface area and ash and moisture contents of the obtained activated carbons are shown in table 2. The surface area is calculated by nitrogen adsorption and desorption isotherms with a Micromeritics Flowsorb II 2300 which uses dynamic flowing technique providing BET and Langmuir surface area. Surface area was also determined by the adsorption capacity towards iodine [14].

## RESULTS AND CONCLUSIONS

Table 2 shows the product distribution as well as some properties of the activated carbon obtained in the experiments. The temperature markedly affects the product distribution. At higher temperatures the yield of activated carbon decreases and the gas yield increases. The increase of the temperature

from 550°C to 650°C results in a larger surface area of the activated carbon. The experiments at 750°C result in a low yield of activated carbon due to intensified gasification.

Table 2: Product distribution in steam pyrolysis of biomass and properties of the produced activated carbons

Biomass	Selected conditions				Product distribution			Carbon properties			
	T	HR	Time	Steam Flow	Carbon yield	Gas yield	Tar, Water, losses	Surface area (N <sub>2</sub> )	Surface area I <sub>2</sub> number	Ash content	Mois- ture content
	°C	°C/ min	min	ml/h	wt% maf	wt% maf	wt% maf	m <sup>2</sup> /g	m <sup>2</sup> /g	wt% mf	wt%
Bagasse	650	25	60	500	16	39	45	nd	547	13.3	1.7
Bagasse	750	25	45	500	6	71	23	nd	775	34.8	1.3
Miscanthus	550	25	60	500	24	10	66	nd	200	11.8	7.5
Miscanthus	650	25	60	500	15	43	42	nd	515	17.3	1.3
Miscanthus	750	25	60	500	2	56	42	nd	288	67.0	1.8
Olive waste	550	25	60	500	25	12	63	nd	225	7.6	3.2
Olive waste	650	25	60	500	18	35	47	nd	405	10.2	4.1
Olive waste	750	25	60	500	1	53	46	nd	250	nd	nd
Straw pellet	550	25	60	500	25	12	63	nd	265	24.8	2.5
Straw pellet	650	25	60	500	5	39	56	nd	454	31.6	3.8
Straw pellet	750	25	60	500	3	58	39	nd	442	72.0	2.6
Straw	650	25	60	500	4	89	7	nd	550	56.3	4.4
Salix	650	25	60	500	12	49	39	nd	592	8.6	2.1
Birch	550	10	60	500	18	25	57	405	400	1.6	1.0
Birch	550	25	60	500	19	26	55	450	390	1.0	2.8
Birch	650	10	60	500	13	39	48	700	730	1.6	1.1
Birch	650	25	60	500	14	33	53	630	nd	1.6	1.4
Birch	750	10	5	500	5	59	36	780	nd	4.6	7.8
Birch	650	25	60	100	9	65	26	nd	660	2.4	7.1
Birch	650	25	60	250	11	69	20	600	nd	1.0	2.8
Birch	650	25	60	750	11	34	55	670	670	2.3	0.9
Birch	650	10	120	500	7	47	46	nd	940	2.9	2.8

T: final temperature; HR: heating rate;

time: activation time, duration of the treatment at the final temperature

maf: moisture and ash free; mf: moisture free; nd: not determined

The temperature and the activation time play an important role for the properties of the activated carbon. With an activation time of 1 hour, the highest surface area was obtained in carbons treated at 650°C. At 550°C the activation rate is lower resulting in higher yield of activated carbon with a low surface area. At 750°C the steam has reacted to a great extent with the biomass destructing the small pores. Thus the surface area of the carbons produced at 750°C was in general low.

At 750°C, only in the experiments with sugar cane bagasse the activated carbon had a relatively high surface area. In this experiment the activation time at high temperature (750°C) was reduced from 60 to 45 minutes. The increased surface area was at expense of a lower yield of activated carbon. High surface area was obtained also using birch as a precursor when the duration of the treatment at the final temperature 750°C was only 5 minutes. The highest surface area was obtained in activated carbons produced from birch at 650°C with an activation time of 2 hours. The prolonged activation time increased the porosity of the solid product resulting in high surface area.

In the experiments with sugar cane bagasse, straw pellet and birch the increase of the temperature from 550°C to 650°C results in higher yields of gaseous products and lower yields of tar and tar water due the increased cracking

In the experiments at 650°C the yields of activated carbon from birch, sugar cane bagasse, miscanthus, salix and olive residues was similar. The surface area of the obtained activated carbon was also similar. When untreated straw and straw pellets were used a low yield of activated carbon has been obtained indicating that this temperature was too high to produce a significant amount of activated carbon. Straw has a higher reactivity in the gasification in comparison with the other used biomasses. The high ash content in straw pellets increases the reactivity of the biomass in the activation stage. Ash may have a catalytic effect in gasification [15,16]. Untreated straw has a higher porosity than the other used biomasses [17]. Because of the high porosity the volatiles are removed faster from the particles.

Table 3: Composition of the gaseous products in steam pyrolysis of biomass (in vol% nitrogen free basis).

Biomass	T	HR	Time	Steam Flow	H <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub>	CO	CO <sub>2</sub>	benzene
	°C	°C/min	min	ml/h	vol %	vol %	vol %	vol %	vol %	vol %
Bagasse	650	25	60	500	27.9	13.1	1.1	30.8	27.1	0.001
Bagasse	750	25	45	500	53.7	2.9	0.3	16.0	27.1	nd
Miscanthus	550	25	60	500	10.0	7.6	1.6	27.9	52.9	nd
Miscanthus	650	25	60	500	49.7	4.4	0.5	15.5	29.9	nd
Miscanthus	750	25	60	500	46.1	4.6	0.6	18.2	30.5	nd
Olive waste	550	25	60	500	8.7	9.8	3.1	36.0	42.4	nd
Olive waste	650	25	60	500	43.5	5.3	0.8	12.9	37.5	nd
Olive waste	750	25	60	500	47.9	5.5	0.8	13.5	32.3	nd
Straw pellet	550	25	60	500	10.0	10.9	1.8	21.9	55.4	nd
Straw pellet	650	25	60	500	47.3	5.4	0.8	15.7	30.8	nd
Straw pellet	750	25	60	500	42.3	5.2	1.0	20.1	31.4	nd
Straw	650	25	60	500	48.2	2.7	0.4	11.7	37.0	nd
Salix	650	25	60	500	43.1	4.7	0.6	33.1	18.5	nd
Birch	550	10	60	500	11.9	11.0	1.1	33.3	42.7	0.001
Birch	550	25	60	500	9.7	10.0	1.1	35.1	44.1	0.001
Birch	650	10	60	500	50.5	6.6	0.8	15.5	26.6	0.002
Birch	650	25	60	500	47.0	7.5	0.6	18.5	26.4	0.002
Birch	750	10	5	500	48.9	4.3	0.4	12.8	33.7	0.023
Birch	650	25	60	100	51.5	4.9	0.3	12.7	30.6	0.001
Birch	650	25	60	250	43.1	6.7	0.5	15.6	34.1	0.006
Birch	650	25	60	750	48.4	6.5	0.5	17.3	27.3	0.001
Birch	650	10	120	500	28.5	9.8	1.5	21.8	38.4	0.003

T: final temperature; HR: heating rate; time: activation time, duration of the treatment at the final temperature

The ash contents of the solid products depend on the chemical composition of the raw materials and the degree of carbonization. Materials, which have undergone deep carbonization, accompanied by removal of large amounts of volatile organic compounds, are converted into solid residues with low contents of organic material and high content of ash.

The composition of the gaseous product is shown in table 3. Increase of the temperature from 550°C to 650°C favours cracking of the hydrocarbons in the gaseous products and thus increases the yield of hydrogen. It has also decreased the content of CO<sub>2</sub> and CO in the gases. Aromatic hydrocarbons (benzene) are products of secondary reactions at higher temperatures. Further increase of the temperature from 650 °C to 750 °C has

not affected significantly the composition of the produced gas with exception of the experiments with bagasse. In the experiments with sugar cane bagasse the hydrogen yield increased while the hydrocarbon yield in the gases decreased when the temperature was increased from 650 °C to 750 °C.

The steam flow influences the product distribution. In the experiments with birch the yield of liquid products was reduced from 50 wt% to 25 wt% and the gas yield was increased from 33 wt% to 69 wt% when the steam flow was reduced from 500 ml/h to 250 ml/h. In previous studies, higher liquid yields were observed when biomass was treated in a flow of steam in comparison with a treatment in inert atmosphere [18].

Influence of the heating rate on the product distribution, activated carbon surface area and gas composition, when the heating rate was increased from 10 °C/min to 25 °C/min, was not significant. The heating rate plays much less role when the pyrolysis is performed in a steam atmosphere compared with inert gas pyrolysis [2].

## CONCLUDING REMARKS

The type of biomass as well as the activation conditions, mainly temperature and activation time, determine the properties and the yield of activated carbon obtained by steam pyrolysis in a fixed bed reactor. Using straw in untreated or pelletized form as precursor results in a lower yield of activated carbon compared to using bagasse, birch, salix, miscanthus and olive waste. A high ash content in pelletised straw has increased the activation rate, because of the catalytic effect of the ash in gasification.

In the selected conditions a high surface area and a relatively high yield of activated carbon has been obtained at 650 °C with an activation time of 1 hour. Higher temperature increases the gas yield at the expense of the yield of activated carbon. In the case of straw lower temperature and shorter residence may be used due to the high reactivity of this biomass. In general agricultural residues are more reactive in gasification because of the higher ash content in comparison with wood.

The rate of steam flow influences the products distribution. The yield of liquid products increases while the yield of gas decreased when the steam flow was increased.

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