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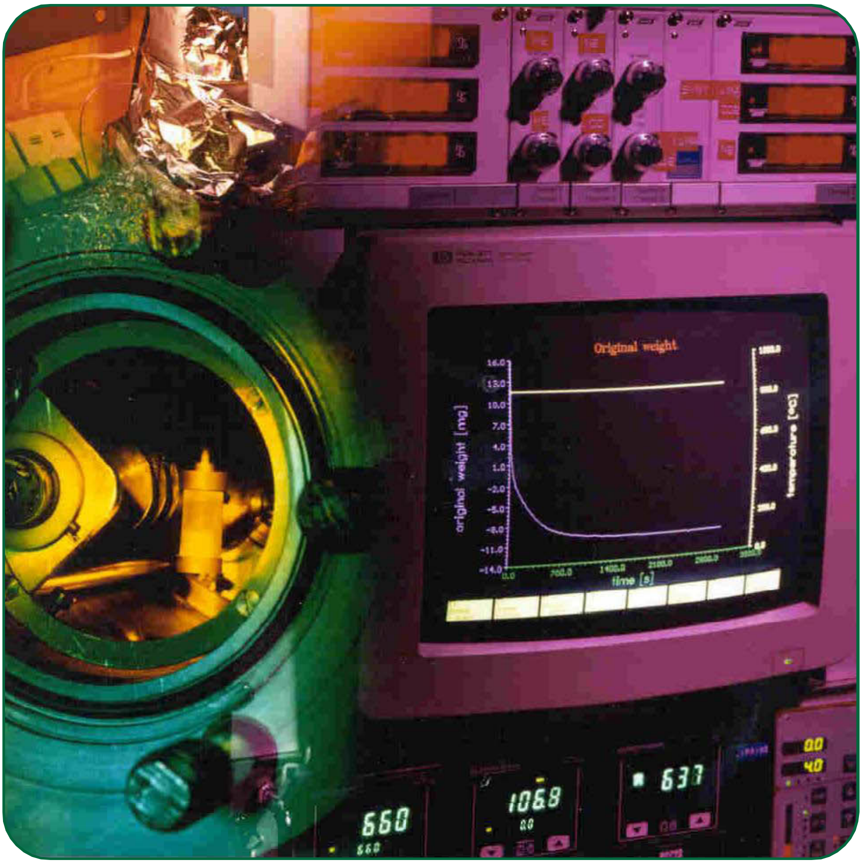

Antero Moilanen

Thermogravimetric characterisations of biomass and waste for gasification processes

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Abstract

Gasification, among the several thermochemical conversion processes, possesses great potential in the advanced utilisation of biomass and wastes as a source for energy and material production. This work deals with the characterisation of reactivity and ash sintering in the gasification of biomass and wastes using thermogravimetry (TG) as a tool.

The gasification reactivity of biomass fuels depends on many factors; in particular the catalytic factors play a large role, and the behaviour is not easy to predict. On the basis of results obtained experimentally and information available in the literature, a method was developed for the characterisation of reactivity and ash sintering of fuels to be used in fluidised bed gasification processes, both atmospheric and pressurised. The purpose was to take into account the complexity of the phenomena rather than to find systematic correlations between the various fuel properties and reactivity and ash sintering, or to determine kinetic parameters. The observed complexity was the spur to develop a method, one that would be as simple as possible, to characterise biomass and solid recovered fuels or wastes intended as feedstocks for use in gasification while taking into account the conditions of the process. Thus, the temperature and pressure ranges, heating rates and gaseous environment for the thermobalance were selected so as to be relevant for the conditions existing in fluidised bed gasifiers, including pressurised conditions. The temperature maximum was thus 1000 °C, and the heating rate of the fuel sample was adjusted to that when feedstock enters the reactor. The gaseous environment was selected so that it would sufficiently describe that existing in a gasifier.

Solid recovered fuels were selected to represent waste-based fuels rather than waste as a whole. The gasification reactivity of solid recovered fuels was found

to be similar to that of paper and higher than that of wood. Test results showed broad scattering before the samples were extracted by sample division.

The method also provides information about ash sintering. The ash is the residue remaining in the thermobalance after the gasification reactions, which thus represents the conditions of gasification, even pressurised gasification. A separate ash does not need to be prepared in the laboratory. The ash residue can be classified into three categories: non-sintered ash, partly sintered ash and totally sintered or fused ash. For some of the biomasses, ash sintering was much stronger under pressurised conditions than at atmospheric pressure. The laboratory findings for ash sintering appeared in various ways in real scale since several factors affect the ash depositing in the reactor. Each time sintering (even weak) was detected in the ash residue of the TG tests, agglomerates or deposits were found in the reactor.

The results of thermobalance tests on different fuels were in good correspondence with the behaviour of the fuels in fluidised bed gasifiers.

Preface

This thesis is based on the fuel characterisation work carried out in the gasification research group at VTT, begun in the late 1980s with peat, continued with biomass, and recently including waste-based fuels. The work was carried out in co-operation with the research group by Professor Mikko Hupa at the Åbo Akademi Process Chemistry Centre. I warmly express my gratitude to Professor Hupa, for the long-term contribution and co-operation and numerous, always captivating discussions. Special thanks are due to Professor Kai Sipilä for his sustained support and to Satu Helynen, Research Manager of Energy Production Research Field, for her encouraging attitude. Esa Kurkela, the leader of the Gasification Research Team is thanked for his involvement, from the beginning, in this part of the gasification process development.

I am most grateful to my co-authors for their contributions, as detailed at the end of the introduction. I am indebted to Kari Saviharju, Jaana Laatikainen-Luntama, Tiina Harju, Jessica Vepsäläinen, Tom E. Gustafsson, Dr. Heinz-Jürgen Mühlen, Professor Adriaan van Heiningen, Dr. Lasse Holst Sørensen and Dr. Jukka Konttinen for an inspiring and fruitful co-operation. The recent passing of Dr. Lasse Holst Sørensen is sadly noted. Lasse was a valued colleague and will be much missed.

Special thanks are expressed to Jaana Korhonen for her professional execution of the thermobalance tests. Further thanks are due to all colleagues, who have influenced this work in numerous ways, and also to all members of the technical and analytical groups for their good work. I am grateful to Maija Korhonen and Marika Johansson for revising the language of the separate publications and to Kathleen Ahonen for helping with the summary part of this thesis.

As acknowledged in the individual papers, many companies assisted in the work. Fortum Foundation kindly provided financial support during the time I was writing this thesis.

Finally, my family and friends: warmest thanks for your support and patience during those many months when I was preoccupied with writing and unable to participate in our activities.

Espoo, July 2006

Antero Moilanen

In the shade of smouldering fire

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Appendices

Papers I–VIII

1. Introduction

Gasification, among the several thermochemical conversion processes, possesses great potential in the advanced utilisation of biomass and wastes as a source for energy and material production (Kurkela et al. 2004, Maniatis 2001, 2004). In gasification, biomass and solid waste are transformed into gas, which can be burned directly as fuel or used as a raw material for synthesis gas or hydrogen production. Considerable environmental importance rests upon the development of highly efficient power cycles and on the production of liquid biofuels and hydrogen from these renewable energy sources. Even though gasification technologies have recently been successfully demonstrated, they continue to be expensive relative to energy production based on fossil fuels. Strong drivers to develop and commercialise biomass and waste gasification exist, however, in face of the urgent need to increase the rates of biomass use and waste recycling and to improve the efficiency of their use in electricity production.

As well as atmospheric pressure, gasification can also be achieved under high pressure in integrated combined cycle (IGCC) applications. The need to compress the fuel gas prior to its use in a gas turbine is then avoided. A small overpressure is also possible when the product gas is used in engines (Patel & Salo 2004). Pressurised gasification systems also have promising prospects in the large-scale production of liquid fuels from biomass based on the gasification and Fischer-Tropsch synthesis process (Kurkela et al. 2004, Maniatis 2004).

Since waste is often included with biomass in the concept of bioenergy, e.g. in European Union statistics (EC 2005a), it was considered relevant to include it in this work. However, solid recovered fuels (SRF) were selected to represent waste-based fuels rather than waste as a whole. The biomass and waste-based fuels are composed of numerous chemical compounds, which are difficult if not impossible to analyse accurately. Instead, selected characteristics of the fuels are determined in the laboratory, usually by standardised methods, to describe their behaviour. Fuels are characterised for marketing purposes, for prediction of their behaviour in thermochemical processes, and for evaluating their impact on the environment.

For the most part these characteristics are related to combustion and little attention has been paid to other processes like gasification. The present work fills a gap by developing and testing a characterisation method that provides specific information about biomass and waste-based fuels intended for use as feedstock in atmospheric and pressurised gasification processes. The method, which is based on thermogravimetry, produces information about the gasification reactivity related to the achievable conversion of carbon in the process and about the ash sintering and deposition that may hamper the process operation. Attention needs to be paid to the pre-treatment of the sample, particularly heating rate and stabilisation conditions. Importantly, it was established that pressure should be included as a parameter in the method.

The thesis comprises, in addition to the present summary, the following publications, which are attached as eight appendices. The first six papers deal with gasification reactivity, and the last two papers with ash sintering:

I Moilanen, A., Saviharju, K. & Harju, T. 1994. Steam gasification reactivities of various fuel chars. In: Bridgwater, A. V. (ed.). Advances in Thermochemical Biomass Conversion, Vol. 1. London: Blackie Academic & Professional. Pp. 131–141.

II Moilanen, A. & Kurkela, E. 1995. Gasification reactivities of solid biomass fuels. Preprints of Papers Presented at the 210th ACS National Meeting, Chicago. Vol. 40, No. 3, pp. 688–693.

III Moilanen, A. & Mühlen, H.-J. 1996. Characterisation of gasification reactivity of peat char in pressurised conditions. Effect of product gas inhibition and inorganic material. Fuel, Vol. 75, No. 11, pp. 1279–1285.

IV Moilanen, A. & Saviharju, K. 1997. Gasification reactivities of biomass fuels in pressurised conditions and product gas mixtures. In: Bridgwater, A. V. & Boocock, D. G. B. (eds.). Developments in Thermochemical Biomass Conversion, Vol. 2. London: Blackie Academic and Professional. Pp. 828–837.

V Saviharju, K., Moilanen, A. & van Heiningen, A. R. P. 1998. New high-pressure gasification rate data for fast pyrolysis of black liquor char. Journal of Pulp and Paper Science, Vol. 24, No. 7, pp. 231–236.

VI Moilanen, A., Vepsäläinen, J., Kurkela, E. & Konttinen, J. 2006. Gasification reactivity of large biomass pieces. In: Bridgwater, A. V. & Boocock, D. G. B. (eds.). Science in Thermal and Chemical Biomass Conversion. Vol. 1. Newbury: CPL Press. Pp. 509–518.

VII Moilanen, A., Kurkela, E. & Laatikainen-Luntama, J. 1999. Ash behaviour in biomass fluidised-bed gasification. In: Gupta, R. P., Wall, T. F. & Baxter, L. (eds.). Impact of Mineral Impurities in Solid Fuel Combustion. New York: Kluwer Academic/Plenum Publishers. Pp. 555–567.

VIII Moilanen, A., Sørensen, L. H., Gustafsson, T. E., Laatikainen-Luntama, J. & Kurkela, E. 2001. Characterisation method of biomass ash for gasification. In: Bridgwater, A. V. (ed.). Progress in Thermochemical Biomass Conversion. Vol. 1. Oxford: Blackwell Science Ltd. Pp. 122–136.

AUTHOR'S CONTRIBUTION

Paper I

The author contributed to the planning of the thermobalance tests in close co-operation with Kari Saviharju. Mr. Saviharju developed the kinetic model and the mathematical expression. The author contributed to the computer fitting by least squares method. Tiina Harju carried out the black liquor study. The microscopy study of the char structure was done by the author. The author wrote the paper in close co-operation with the co-authors.

Paper II

The author performed the thermobalance study and wrote the paper. Mr. Esa Kurkela performed the fluidised bed gasification study.

Paper III

In this work, the thermobalance method developed by Dr. Mühlen for the study of coals was applied to peat. The experiments and the thermobalance tests were designed by Dr. Mühlen. The author carried out the tests during his visit to Dr. Mühlen's laboratory in DMT Germany. The results as a whole were evaluated and the paper was written by the author in co-operation with Dr. Mühlen. The author searched the literature for the role of iron in catalysing gasification.

Paper IV

The experimental part was planned by the author, i.e. pyrolysis of the sample in a thermobalance *in situ* without preparation of the char in a separate reactor. The results as a whole were evaluated in co-operation with Mr. Saviharju, and the results related to ash by the author. The author wrote and finalised the paper.

Paper V

The study, which focused on black liquor, was designed by the co-authors. The thermobalance tests were designed by the author. The author participated with the co-authors in the evaluation of the results and was closely involved in writing of the paper.

Paper VI

This work was part of Jessica Vepsäläinen's master thesis, which was supervised by the author. The tests were designed by the author and performed by Ms. Vepsäläinen. The results were evaluated in co-operation with the author. The outline of the paper was drawn up her. Dr. Konttinen evaluated the results related to the modelling and Esa Kurkela to the fluidised bed gasifier. The author wrote the paper.

Paper VII

The thermobalance experiments were planned and the results were evaluated by the author. The sintering test method was designed and developed by the author. The co-authors Esa Kurkela and Jaana Laatikainen-Luntama, planned the fluidised bed gasification test runs, which were performed by Ms. Laatikainen-Luntama. The results of these test runs were evaluated in close co-operation with the co-authors. The author wrote the paper.

Paper VIII

The thermobalance experiments were planned and the results were evaluated by the author. Dr. Sørensen joined in the work with the Danish biomass feedstocks, and the evaluation of results was carried out in close co-operation with him. Esa Kurkela and Jaana Laatikainen-Luntama planned and evaluated the fluidised bed reactor test runs, which were performed by Ms. Laatikainen-Luntama. Tom Gustafsson performed the electron microscopy (SEM) needed in this work, and he developed the appropriate method for analysing the particles in SEM. The author wrote the paper in close co-operation with the co-authors.

2. Literature review

The literature reviewed in this work deals with the characteristics, reactivity, and ash sintering related to the gasification of biomasses and wastes. The focus is on biomass and the use of thermogravimetry as a method. The abundant information available on biomass and waste combustion (or incineration) and on coal gasification is mainly excluded. In addition, literature dealing with the determination of kinetic parameters for biomass gasification is not reviewed since the gasification reactivity of biomass varies widely (as observed in this work) and general conclusions cannot be drawn from tests carried out on a single biomass fuel. More detailed studies are needed to understand the factors affecting the gasification reactivity of biomass chars. Furthermore, in the literature describing the kinetics of biomass gasification, little attention has been paid to the reactivity behaviour, *i.e.* the gasification rate *vs.* conversion, which is the subject of interest here.

2.1 Gasification and gasification processes

When fuel is fed to a gasifier, water and volatile matter are released fast and a char residue is left to react further. The char gasification is what mainly controls the conversion achieved in the process. From solid carbon, product gas is formed according to the following main reactions:

$$C + H_2O \rightarrow CO + H_2 \quad (1)$$
$$C + CO_2 \rightarrow 2CO \quad (2)$$
$$C + 2H_2 \rightarrow CH_4. \quad (3)$$

In addition to the reactions of solid carbon, the most important reaction is the water-gas shift reaction, which takes place in the gas phase:

$$CO + H_2O \leftrightarrow H_2 + CO_2. \quad (4)$$

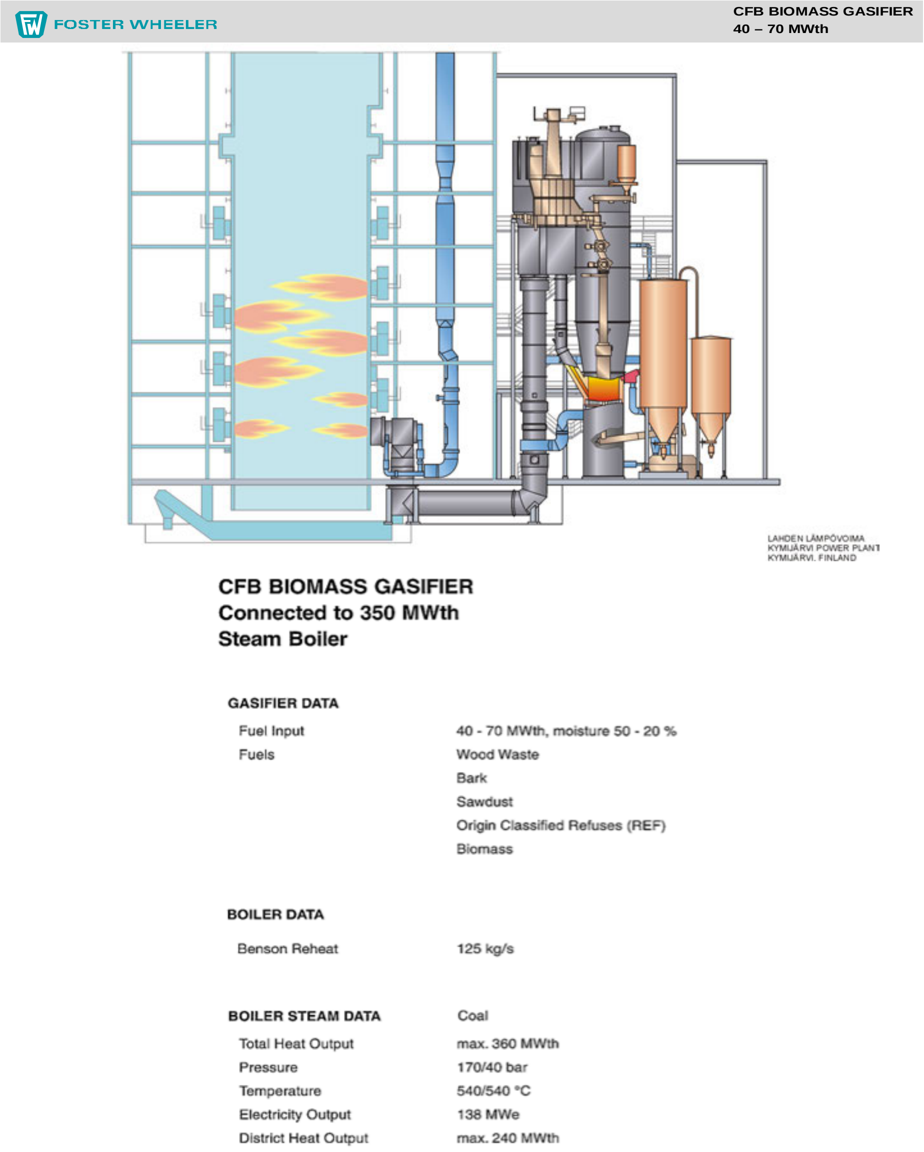
The product gas generally contains large amounts of hydrogen and carbon monoxide and a small amount of methane, as well as carbon dioxide and steam, and in air gasification nitrogen. In addition, a significant amount of other organic components in the gas, known as tar, is formed. Tar formation is a well-known phenomenon in coal (Aristoff et al. 1981, McNeil 1981) and biomass gasification (Milne et al. 1998, Simell 1997, Simell et al. 2000, CEN BT/TF 143 2004).

Since the reactions (1) – (3) are endothermic, heat is needed. The simplest way to produce the heat is to burn a part of the fuel in air. Pure oxygen can be applied to avoid the dilution of the valuable product gas components with air nitrogen. Typical lower heating values (LHV) of wet product gas from different fuels have been reported by Kurkela & Ståhlberg (1992) as 3.5–5 MJ/m^{3}n (normal cubic metre). According to Babu (2006), the higher heating value (HHV) of product gas from biomass gasification processes could exceed 17 MJ/m^{3}n.

There are three main types of gasifier – fixed bed, fluidised bed, and entrained flow – which together represent the most promising methods to gasify biomass and waste. Gasification processes based on these methods and with commercial potential in the modern utilisation of biomass and wastes were considered in a recent review by Kurkela et al. (2004).

Fixed bed gasifiers are suitable for small-scale processes, i.e., less than 10 MW. Feedstock flows by gravity, while the gas flow can be either updraft or downdraft. Ideally, the feedstock should be piece-like and fairly homogeneous to flow smoothly in the reactor. In practice, however, it contains fines and fibrous material, which cause problems in the fuel flow leading to operational problems. The flow problems can be avoided by applying a new type of technology ("Novel" fixed bed gasifier), in which the flow is forced (Kurkela et al. 2000, Kurkela et al. 2004).

Fluidised bed reactors could solve the problems related to nonhomogeneity of the feedstock, but they are too expensive in small scale. In fluidised bed technology, the feedstock must be crushed to millimetre size before it is gasified in either bubbling or circulating mode. These gasifiers are suitable for scales up to hundreds of megawatts. Recently, fluidised bed technology was applied for wastes where the product gas is combusted in a pulverised coal-fired boiler (Figure 1, Palonen et al. 1998, Kurkela et al. 2003). The same method has been used to recover aluminium from the reject produced in liquid packaging board (LPB) recycling (Palonen et al. 2000). The circulating fluidised bed has been demonstrated to be particularly suited for fuels containing high contents of alkali metals, where ash sintering problems can be avoided by using limestone and special arrangements with the feeds (Pat. WO0011115 2000).



CFB BIOMASS GASIFIER
Connected to 350 MWth
Steam Boiler

GASIFIER DATA	
Fuel Input	40 - 70 MWth, moisture 50 - 20 %
Fuels	Wood Waste Bark Sawdust Origin Classified Refuses (REF) Biomass
BOILER DATA	
Benson Reheat	125 kg/s
BOILER STEAM DATA	Coal
Total Heat Output	max. 360 MWth
Pressure	170/40 bar
Temperature	540/540 °C
Electricity Output	138 MWe
District Heat Output	max. 240 MWth

Figure 1. The fluidised bed gasifier connected to the pulverised coal-fired boiler in Lahti and the major data (Foster Wheeler Energia Oy 1998).

In the third type of gasifier, the entrained flow gasifier, pulverised fuel is gasified at high temperature. This is regarded as one of the optional processes for liquid fuel manufacture from biomass and wastes (Kurkela et al. 2004). High pressure gasification based on the entrained flow process can be applied to improve the energy recovery from black liquor (Maniatis 2004, Chemrec 2005).

2.2 Biomass and waste as fuel

Biomass-based fuels are non-fossil and renewable and are regarded as CO_2 neutral since biomass assimilates carbon dioxide from the atmosphere during growth. In the 25 member states of the European Union (EU), the share of biomass and wastes in the gross consumption of energy (Gross Inland Consumption) represented 69 millions tonnes of oil equivalent in 2003, which was 4% of the total. The amount used in the EU is expected to increase substantially (EC 2005b, EC 2006).

Vegetative biomass can be classified into the categories woody, herbaceous, agricultural by-products, energy crops, and black liquor. Black liquor is a by-product of the forest industry, consisting of organic matter dissolved in the alkali solution used to separate the fibres during chemical pulping (Grace et al. 1989). Because of the high concentration of alkali, black liquor deviates significantly from other biomass.

Chemically, biomasses consist of organic components such as cellulose, lignin, hemicelluloses, lipids, proteins, starches and sugars. They also contain water, alkaline and earth-alkaline metals, chlorine, nitrogen, phosphorus, sulphur, silicon and some trace elements and heavy metals.

The waste fuel considered in this work is solid recovered fuel (SRF). It is a relatively new concept, applied in Finland and the Netherlands and a few other European countries (de Vries et al. 2000) but not included in many studies. In Finland, 300 000 t/a of dry solid recovery fuel was co-fired in industrial and municipal boilers in 2004 (Wilén et al. 2004). If wastes are incinerated as such, heat and electricity will be produced with poor efficiency (Ludwig et al. 2003). For effective use, they need to be refined into various fuel products, such as solid recovered fuels, which are mainly processed from source-separated wastes, and refuse derived fuels (RDF), which are manufactured directly with no source separation. Source separation takes place at the site where the waste is formed, with different types of material, such as bio-organic material (food, garden waste), paper, metal, glass and LPB, being placed in separate collection bins. The remaining part, consisting mainly of plastics, paper-plastic mixtures, cartons and wood, is suitable for raw material in SRF processing. Source separation practices differ from one community to the next, and, according to the main waste streams, SRF can be categorised as originating from household waste, industrial and company waste and construction wood waste. SRFs are prepared at special processing plants, where the incoming waste material is first treated for the removal of large objects and then processed in various crushing and screening operations. Metals are removed by magnetic and eddy current separators. (Wilén et al. 2004, de Vries et al. 2000, Tekes 2003, Wilén et al. 2003, SFS 5875 2000, CEN/TC 343 2006).

Recovered fuels are less homogeneous than other solid fuels because they are mixtures of various man-made materials, and wide variation in the properties (specific gravity, chemical composition etc.) from particle to particle is probable. The quality determined for an SRF is significantly affected by the sampling. Sampling tests carried out on different SRF streams have shown wide variation in the properties at short intervals (Ajanko et al. 2005a, Moilanen et al. 2005).

The Finnish SRF standard ranks the quality on the basis of impurities rather than energy content (SFS 5875 2000). Moreover, the EU waste incineration directive lists a number of trace elements and heavy metals, the emissions of which must be limited when wastes and waste-derived fuels are used as fuel (EC 2000). In addition, the high amounts of chlorine and heavy metals like zinc, copper and lead can cause both sintering and corrosion in the combustion of waste-based fuels (Bryers 1996).

2.3 General fuel properties

The most important characteristic of fuel is the calorific value, which is the amount of energy (mega joules, MJ) in a unit of mass (kg) or volume (m^3) of a fuel. Water and ash in the fuel will lower the calorific value. Several other characteristics are determined to describe the technical and environmental aspects of the fuels, as noted below. These characteristics are usually determined by standardised methods, and they have recently been presented in the technical specifications developed by CEN (European Committee for Standardisation) for biomass fuels (CEN/TC 335 2006) and SRFs (CEN/TC 343 2006). Table 1 presents selected biomass fuel characteristics determined according to the standardised methods (Wilén et al. 1996). Biomass and waste fuel characteristics are also collected in the publications of Phyllis (2000) and Alakangas (2000).

The moisture content is the amount of water evaporated by drying, and the ash content is the residue remaining after the sample is burned. Volatile matter describes the amount of gases when a material is heated in an oxygen-free environment. The heating value is the energy content, and it is determined by burning a sample totally in a calorimeter. It can be expressed as gross calorific value or higher heating value (HHV) and as net calorific value or lower heating value (LHV) (CEN/TS 14588:fi 2003). Since the results are dependent on the measuring conditions, all determinations are carried out under controlled conditions according to the standardised methods.

The analysis of the elemental composition of biomass and waste-based fuels mainly focuses on carbon, hydrogen, oxygen, nitrogen, sulphur and chlorine. Usually, these elements are determined by instrumental methods. C, H, and S are measured by infrared absorption, while N is determined by thermal conductivity after the fuel sample has been burned completely (using Leco instruments, for example). Chlorine can be determined according to the oxygen bomb method (ASTM D 4208-88 2002) followed, for example, by a capillary electrophoresis technique.

The ash chemical composition of solid fuels is described in terms of the elements Si, Al, Fe, Ca, Mg, K, Na, Ti, S and P. These are the elements normally determined in the ash. Ash forming constituents are constituents in the fuel from which ash is formed. In biomass they are salts, organically bound compounds and extraneous material such as soil and sand. Their amounts can be determined by chemical fractionation tests (Zevenhoven-Onderwater 2001). In SRF, ash forming material is often of man-made origin – fillers in paper and plastics, pigments, metal pieces etc. The high content of alkaline metal in biomass fuels constitutes the main difference between these and fossil fuels. Alkaline metals cause ash sintering and corrosion but also catalyse oxidation reactions of char.

Table 1. Fuel characteristics for selected biomasses: A) dry basis, B) dry ash-free basis (modified from Wilén et al. 1996). HHV=higher heating value, LHV=lower heating value, O(diff) = oxygen content obtained by difference.

A) dry basis

	Moisture	Ash	Volatile matter	Fixed carbon	HHV	LHV	C	H	N	O (diff.)	S	Na	K	Cl
	%$^{*)}$	%	%	%	MJ/kg	MJ/kg	%	%	%	%	%	mg/kg	mg/kg	mg/kg
Northern Woody Biomasses														
Wood chips	3.9	0.6	80.0	19.4	20.89	19.56	51.8	6.1	0.3	41.2	0.01	42	983	42
Forest residue chips (Finland)	6.3	1.3	79.3	19.4	20.67	19.34	51.3	6.1	0.4	40.9	0.02	76	1377	76
Forest residue chips (Sweden)	6.3	4.1	74.1	21.9	20.54	19.27	51.0	5.8	0.9	38.2	0.04	640	2604	< 50
Sawdust (pine)	15.3	0.08	83.1	16.8	-	19.03	51.0	6.0	0.08	42.8	0	20	480	< 50
Spruce bark	5.3	2.3	75.2	22.5	19.83	18.54	49.9	5.9	0.4	41.4	0.03	89	3003	279
Pine bark	4.7	1.7	73.0	25.3	20.95	19.70	52.5	5.7	0.4	39.7	0.03	29	2133	85
Salix	2.4	1.2	79.9	18.9	19.75	18.42	49.7	6.1	0.4	42.6	0.03	37	4058	37
Agricultural Biomasses														
Wheat straw (Denmark)	10.3	4.7	77.7	17.6	18.94	17.65	47.3	5.9	0.6	41.5	0.07	140	5480	1710
Barley straw (Finland)	11.5	5.9	76.1	18.0	18.68	17.43	46.2	5.7	0.6	41.5	0.08	333	12188	2737
Rapeseed	8.4	2.9	79.2	17.9	19.33	18.04	48.1	5.9	0.8	42.1	0.21	166	5768	965
Flax (whole straw)	8.4	2.9	78.8	18.3	20.04	18.71	49.1	6.1	1.3	40.5	0.12	133	5147	588
Flax (shive)	6.6	1.8	78.6	19.6	20.19	18.86	50.3	6.1	0.6	41.1	0.07	87	3362	381
Reed canary grass	7.7	8.9	73.5	17.7	18.37	17.13	45.0	5.7	1.4	38.9	0.14	154	3479	639
European Biomasses														
Sweet sorghum (Italy)	7.0	4.7	77.2	18.1	18.91	17.65	47.3	5.8	0.4	41.7	0.09	678	4614	2996

Kenaf (Italy)	7.5	3.6	79.4	17.0	18.58	17.32	46.6	5.8	1.0	42.8	0.14	517	7254	1748
Miscanthus (Italy)	5.7	3.3	78.5	18.2	19.03	17.72	47.9	6.0	0.6	41.6	0.55	259	9702	3266
Cane (Italy)	5.8	3.7	77.9	18.4	18.06	16.75	47.7	6.0	0.5	41.9	0.16	183	9706	2922
Miscanthus (Germany)	8.6	2.3	79.3	18.4	19.43	18.13	48.6	6.0	0.3	42.7	0.08	27	3027	1405
Minimum	2.4	0.08	73.0	16.8	18.06	16.75	45.0	5.7	0.08	38.2	0	20	480	37
Maximum	15.3	8.9	83.1	25.3	20.95	19.70	52.5	6.1	1.4	42.8	0.55	678	12188	3266
Average	7.3	3.1	77.8	19.1	19.54	18.29	49.0	5.9	0.6	41.3	0.10	201	4687	1242

*) as received

B) dry ash-free basis

	C	H	N	S	Volatile matter	Fixed carbon	HHV	LHV
	%	%	%	%	%	%	MJ/kg	MJ/kg
Northern Woody Biomasses								
Wood chips	52.1	6.1	0.3	0.01	80.5	19.5	21.0	19.7
Forest residue chips (Finland)	52.0	6.2	0.4	0.02	80.4	19.6	20.9	19.6
Forest residue chips (Sweden)	53.2	6.0	0.9	0.04	77.2	22.8	21.4	20.1
Sawdust (pine)	51.0	6.0	0.1	0.00	83.2	16.8		19.0
Spruce bark	51.1	6.0	0.4	0.03	77.0	23.0	20.3	19.0
Pine bark	53.4	5.8	0.4	0.03	74.3	25.7	21.3	20.0
Salix	50.3	6.2	0.4	0.03	80.9	19.1	20.0	18.6
Agricultural Biomasses								
Wheat straw (Denmark)	49.6	6.2	0.6	0.07	81.5	18.5	19.9	18.5
Barley straw (Finland)	49.1	6.1	0.6	0.08	80.9	19.1	19.8	18.5
Rapeseed	49.5	6.1	0.8	0.22	81.5	18.5	19.9	18.6
Flax (whole straw)	50.6	6.3	1.3	0.12	81.2	18.8	20.6	19.3
Flax (shive)	51.2	6.2	0.6	0.07	80.0	20.0	20.6	19.2
Reed canary grass	49.4	6.3	1.5	0.15	80.6	19.4	20.2	18.8
European Biomasses								
Sweet sorghum (Italy)	49.7	6.1	0.4	0.09	81.0	19.0	19.9	18.5
Kenaf (Italy)	48.4	6.0	1.0	0.15	82.4	17.6	19.3	18.0
Miscanthus (Italy)	49.5	6.2	0.6	0.57	81.2	18.8	19.7	18.3
Cane (Italy)	49.5	6.2	0.5	0.17	80.9	19.1	18.8	17.4
Miscanthus (Germany)	49.7	6.1	0.3	0.08	81.2	18.8	19.9	18.6
Minimum	48.4	5.8	0.1	0.00	74.3	16.8	18.8	17.4
Maximum	53.4	6.3	1.5	0.57	83.2	25.7	21.4	20.1
Average	50.5	6.1	0.6	0.11	80.3	19.7	20.2	18.9

Determination of the heavy metal and trace element content is usually done by dissolving the fuel sample totally and determining the elements in the solution. SRFs containing plastics may be difficult to dissolve. The contents of heavy metals and trace elements tend to be low in biomass, but will probably be higher in biomass originating from polluted areas (Phyllis 2000). Woody biomass like heartwood (or timber) contains almost none of these elements. A summary of the trace element and heavy metal contents in timber and whole wood is presented in Table 2. In SRF, in contrast, these elements can be abundant (Ajanko et al. 2005a, 2005b, Moilanen et al. 2005) originating from a variety of materials, including pieces of metal, additives, pigments and wood impregnating agents.

Table 2. Trace element and heavy metal contents (mg/kg dry matter) of timber (heartwood) collected from various parts of Finland, compared with the contents in whole wood.

Element	Timber				Wood (Phyllis 2000)		
	City of						
	Iisalmi	Riihimäki	Tornio	Harjavalta	Min	Max	Average
Cl	20	10	10	20	10	11890	590
Hg	< 0.1	< 0.1	< 0.1	< 0.1	0	2	0,1
Cd	<0.05	0.07	0.17	0.12	0	3	0.7
Sb	< 2	< 2	< 2	< 2	0	4	0.8
As	< 1	< 1	< 1	< 1	0	6.8	1.4
Co	< 4	< 4	< 4	< 3	0.1	6	1.9
Cr	< 4	< 4	< 4	< 3	0.4	130	24
Cu	< 4	< 4	< 4	< 3	0.3	400	22
Pb	< 1	< 1	< 1	< 1	0.2	340	30
Mn	102	54	97	55	7.9	840	181
Ni	< 4	< 4	< 4	< 3	0.4	540	29
Zn	8,9	7.0	11	9.6	2.2	130	50
Tl	< 2	< 2	< 2	< 1	-	-	-
Sn	< 2	< 2	< 2	< 1	0.3	10	1.7
V	< 4	< 4	< 4	< 3	0.2	23	4.3
Fe	66	9	270	437	6	3600	227

In both fossil and biomass fuels, aluminium is present in the form of aluminium oxide, as in clays, but in SRF it can also be in metal form. Metallic aluminium is highly reactive and can cause problems in high temperature processes. It can also be harmful in the ash, since hydrogen gas may form, if the ash becomes wet during storage (Chandler et al. 1997). Thus, it is important to know the content of aluminium in SRF. One way to measure aluminium is to measure the hydrogen gas formed in its reaction with base (Muhola & Moilanen 2001).

Table 1 also summarises the characteristics of biomass fuels of different origin (Wilén et al. 1996). The selected properties, like heating value, carbon content and hydrogen content of the organic matter (i.e., the ash-free material), varied within a reasonably narrow range. The HHV varied between about 19 and 21 MJ/kg of dry ash-free material. Likewise, Ayhan (2004) observed in studies on the combustion characteristics of different biomass fuels that properties of the biomass samples such as hydrogen content, sulphur content and ignition temperatures varied within a narrow interval.

The greatest variation is in the ash content and in ash chemical composition, as shown also by Osman (1982). The ash content was lowest (0.08%) for sawdust and greatest (8.9%) for reed canary grass while potassium, silicon and calcium contents showed the greatest variability in the ash chemical composition.

In the case of SRF, the characteristics of greatest interest have been contents of halogens, heavy metals and trace elements (Ajanko et al. 2005a, 2005b and Moilanen et al. 2005). High levels of impurities, unevenly distributed were found to be typical of SRF. The uneven distribution was particularly evident in the variation in chlorine content in sampling tests. This variation in chlorine content for SRFs of different type measured from the samples taken every 20 minutes in SRF processing plants a, b, c, d and e, is shown in Table 3 and in Figure 2. The plant d was an exception, since there the sampling was carried out twice a day. In the plants the wastes were from different origin: plant a) combustible household waste; plant b) 50% combustible household waste and 50% combustible wastes from the waste mixture from industry and construction wood; plant c) combustible waste from industry; plant d) construction wood waste and plant e) SRF pellet. According to the results, the largest variation in Cl content from 0.3% to 2.3% was observed especially in the waste mixture containing wastes both from households and from industry (plant b). The elemental composition of selected SRFs is presented in Table 4 along with the fuel characteristics.

When the contents of wastes were examined by manual sorting of waste fractions to be used as fuel, it was found that the main sources of impurities were leather, plastics and rubber (Ajanko et al. 2005b). These contained much larger amounts of Hg and Cd than the rest of the waste. Materials and compounds containing the impurity elements were detected by SEM-EDS (Moilanen et al. 2002, Ollila et al. 2006). The SEM-EDS results showed that impregnated wood, metals such as aluminium, brass and copper and PVC are the most common impurities.

Table 3. Chlorine contents in SRF (% in dry matter, see text for the legend of the processing plants).

SRF processing plant	Min	Max	Average
a	0.22	0.85	0.46
b	0.16	2.3	0.59
c	0.02	0.91	0.21
d	0.02	0.05	0.14
e	0.15	1.0	0.53

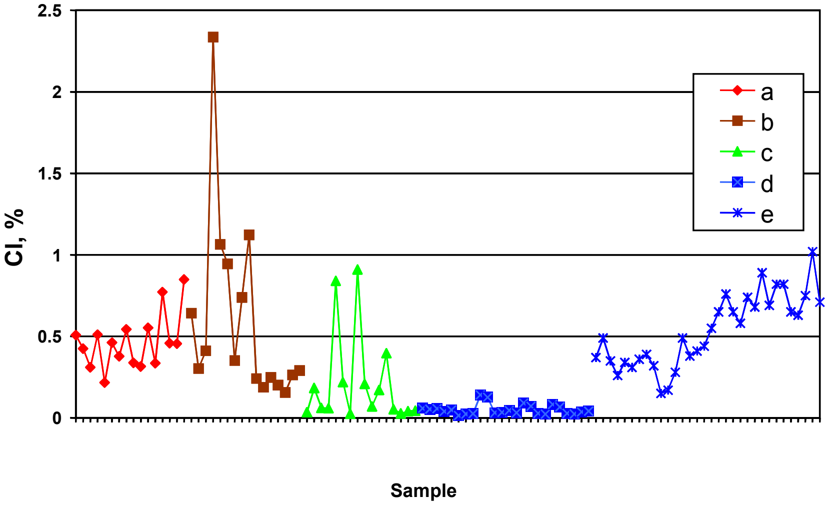


Figure 2. Chlorine content of various SRF qualities and SRF production processes, indicated with letters a, b, c, d and e (Ajanko et al. 2005a, Moilanen et al. 2005).

Table 4. Elemental analysis and fuel characteristics of SRFs produced in plants ET, F and Ew from source separated wastes from the cities of Jyväskylä, Pietarsaari and Lahti. Dry and energy wastes are included for comparison (Ajanko et al. 2005b , Moilanen et al. 2005, LHV = Lower heating value, % = weight %, d = dry matter, ar = as received).

SRF/Waste	Cl	S	N	Na + K*	Metallic Al	Hg	Cd	Sb	As	Co	Cr	Cu	Pb	Mn	Ni	Zn	Tl	Sn	V	P	Fe	Moisture	Ash	LHV	C	H
	%, d					mg/kg, d																%, ar	%, d	MJ/kg, ar	%, d	
ET/Jyväskylä	0.63	0.16	0.7	0.43	0.18	0.23	2.5	54	29	370	77	1400	530	210	260	250	<5	140	18	880	11500	26.2	43.4	9.47	29.5	3.8
ET/Pietarsaari	1.04	0.12	0.9	0.47	0.58	0.11	5.0	18	4.0	20	65	650	220	120	82	440	<5	110	<6	940	2400	35.2	14.5	13.15	51.1	7.1
ET/Lahti	0.49	0.10	0.5	0.16	0.19	0.15	2.3	13	8.1	77	35	210	50	60	250	230	<5	12	<70	430	1400	15.7	8.6	18.73	54.0	7.4
F/Jyväskylä	0.76	0.10	0.5	0.38	0.63	0.6	1.3	19	5.6	2.0	120	192	80	103	21	937	<1	96	4	437	2227	23.0	9.7	16.68	52.3	7.2
F/Pietarsaari	0.82	0.08	0.6	0.37	0.87	0.29	0.43	25	3.7	1.6	67	451	287	71	5.0	180	<1	183	4	453	857	24.2	9.4	16.44	52.2	7.3
F/Lahti	0.34	0.06	0.4	0.17	0.16	0	0.33	19	3.0	1.1	16	153	250	27	4.0	88	<1	247	<4	187	873	11.8	7.3	19.92	53.7	7.4
Ew/Jyväskylä	1.04	0.24	0.5	0.40	0.84	0.31	9.4	48	5.9	3.9	96	987	150	113	14	377	<1	32	6	633	2900	2.2	12.8	21.49	51.6	7.1
Ew/Pietarsaari	0.96	0.13	0.5	0.35	0.83	0	1.6	16	5.5	4.2	70	753	62	88	20	683	<1	13	5	620	1363	2.7	9.4	22.45	53.8	7.6
Ew/Lahti	0.85	0.08	0.3	7.5	0.18	0.3	2.1	19	3.6	2.0	50	163	34	59	15	127	<1	12	5	280	2270	1.7	8.6	22.64	54.0	7.5
Waste from stores	1.04	0.06	0.3	0.21	0.07	<0.09	3.0	3.4	<4	0.8	48	60	18	15	<7	110	<1	43	<4	180	550	18.1	2.6	26.39	71.8	10.2
Dry waste from Jyväskylä	1.03	0.18	1.5	0.65	0.48	0.5	5.2	16	<4	3.0	340	32	54	37	5.7	240	<2	15	<6	460	840	31.5	7.6	15.24	56.7	7.4
Dry waste from Pietarsaari	1.04	0.12	0.9	0.47	0.58	0.11	5.0	na.	na.	na.	na.	na.	na.	na.	na.	na.	na.	na.	na.	na.	na.	35.2	14.5	13.15	51.1	7.1
Energy waste from Lahti	0.65	0.06	0.7	0.19	0.23	<0.1	5.3	<10	<10	5	20	30	20	25	<10	95	<1	10	<4	220	685	33.9	6.6	15.11	56.2	7.8

*Total content of water-soluble and ion-exchangeable proportion for dry matter

2.4 Characterisation of biomass and waste fuels for gasification

This section presents a review of methods for characterisation of biomass and waste fuels published in the literature, especially where gasification is intended. First, the general fuel characterisation is described, and then the reactivity and ash sintering aspects are discussed. Previous studies on the reactivity of fuels in small-scale reactors and the thermobalance are noted. In the case of the thermobalance, these are mostly studies on coal rather than biomass. Various parameters affecting the results of thermogravimetric measurements, together with some special applications, are described. Since the gasification studies of solid fuels in a thermobalance are often at the same time studies on char gasification, the literature on char reactivity and related properties is also reviewed. Brief note is made of the kinetic parameters of biomass gasification since gasification studies of biomass often involve investigation of the kinetics. The thermogravimetric characterisation of waste in a thermobalance is described in a separate section. Finally, previous work on the characterisation of ash sintering with the main focus on gasification is summarised.

2.4.1 General fuel characterisation

Characterisation of biomass for gasification and other thermochemical processes is often based solely on determination of the general fuel characteristics (e.g. proximate and ultimate analysis, heating values, ash fusion temperatures etc.), the chemical composition and physical properties relevant for gasification. By way of example, Graboski & Bain (1979), Rossi (1984) and Mattsson (1998) identified moisture content, heating value, ash content, ash fusion temperature and alkali content as important parameters of feedstock quality for thermochemical conversion technologies. Also included in the list were particle shape, particle size and size distribution, flowability and bulk density. Characterisation is also often reported for a single biomass or a selection of biomasses existing locally. Coovattanachai (1986) was interested in the gasification characteristics of the main agricultural residues in Thailand and determined the natural size, bulk density, ash content, ash melting point and moisture content for gasification. Faaij et al. (1997b) investigated 18 different biomasses in the Netherlands for gasification. These originated from agriculture, organic waste, wood and sludges. Their study also examined the suitability for gasification in terms of the general fuel properties, such as moisture and ash contents and nitrogen and chlorine contents. Faaij et al. (1997a) completed the characterisation with a determination of the fuel-gas composition by laboratory-scale fuel reactivity tests and subsequent model calculations for gasification of clean wood, verge grass, organic domestic waste, demolition wood and a wood-sludge mixture.

Waste-based fuels are characterised in the same way as the conventional fuels. Schönberger et al. (1978) compared the fuel characteristics of refuse derived fuel (RDF) from two Pennsylvania communities. In both cases, the heating value of RDF correlated with moisture and ash content, and a great statistical significance was calculated for ash. Glaub and Trezek (1987) regarded mixed paper waste as an attractive energy source since it is relatively homogeneous and mostly free of putrescibles, metals and other non-combustibles. They concluded that minimal processing is required to convert it to fuel for gasification. When processed into densified fuel, the heating value is close to that of wood.

2.4.2 Reactivity characterisation in small-scale reactors

The behaviour of a fuel in a process is a combination of many factors including, in addition to the fuel characteristics, the physical properties of the feedstock, the process parameters, fragmentation of the fuel, fuel char and type of reactor. Thus, the fuel is often studied in *small-scale reactors*, which describe the fuel behaviour in the process as a whole. Rensfelt et al. (1978) studied pyrolysis and gasification in laboratory-scale reactors designed for experiments with biomass and peat for fluidised bed gasification. Sipilä (1988) used an atmospheric bench-scale fluidised bed reactor to study the reactivity of wood, peat and lignite chars, monitoring the reactivity and variation of char properties as a function of conversion. The tests indicated the essential effect of the pore structure of 2–4 mm particles on the reaction rate at 820°C; the reaction was significantly affected by pore diffusion at this temperature. Meister (2002) gasified almond shell, walnut pruning, rice straw, whole tree wood chips, sludge, and non-recyclable waste paper in a bench-scale atmospheric fluidised bed reactor. Only a general fuel characterisation was included. The laboratory results for proximate, ultimate, bulk density and particle size distribution analyses done during the gasification tests were compared with predictions obtained with a bubbling fluidised bed model. Furthermore, for fixed bed gasification, Di Blasi et al. (1999) used a laboratory-scale fixed bed gasifier to produce data for process modelling and to compare the air gasification characteristics of beech wood, nutshells, olive husks and grape residues. Williams and Goss (1979) assessed the gasification characteristics of selected agricultural and forest industry residues using a laboratory-scale downdraft gasifier.

2.4.3 Reactivity characterisation in the thermobalance

Combustion and gasification are frequently studied in the laboratory with a thermobalance. A defined set of parameters, such as temperature, pressure and gas composition, is selected for the reactor, and the weight of a sample is monitored as a function of time. Wide-scale characterisation has been carried out on gasification reactivity of fossil fuels like coals and lignites: one of the best known studies was that done by Johnson (1974) who used extensively a pressurised thermobalance to develop kinetic models of coal gasification. A thermobalance has been used to study the kinetics of coal gasification under different conditions by Walker et al. (1953), Pilcher et al. (1955), Jenkins et al. (1973), Hippo & Walker (1975), Tomita et al. (1977), Mahajan et al. (1978), Schmal et al. (1982) and Saffer (1983). Thermogravimetric method has been described as a tool for the study of heterogeneous kinetics of char gasification by Laurendau (1978), and also by Graboski (1979) for biomass. Steam gasification reactivity of peat was studied by Sipilä et al. (1980) in a thermobalance. Stenseng et al. (2001) investigated different stages in combustion and gasification processes (pyrolysis, char reactivity, ash melting behaviour) using the differential scanning calorimeter and thermogravimetric analysis configuration. They found that this type of thermal analysis could be used to describe the pyrolysis behaviour as well as to estimate the heat of the reaction, and to determine the ash-melting properties of the combustion ashes of straws. Schenk et al. (1997) investigated a wide variety of biomasses with a package of tools developed to determine gasification characteristics and evaluate gasification concepts. These tools consisted of models, laboratory equipment and pilot-scale installations. The models required a series of empirical input parameters, which were derived from standardised laboratory tests. Standardised experimental procedures to determine these parameters were developed, relying, for example, on a laboratory-scale fluidised bed reactor and a thermogravimetric analyser.

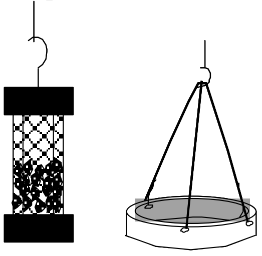
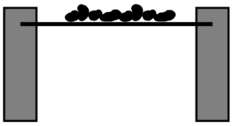
Pressure was including in some of the thermogravimetric measurements. In addition to the above-mentioned work by Johnson (1974), also other groups have used a pressurised thermobalance. Sears et al. (1982) designed for coal gasification studies a pressurised thermobalance operable at high temperatures (< 1700°C). Mühlen (1983); Mühlen and Sulimma (1987), van Heek and Mühlen (1991), Sowa (1991) and Löwenthal (1993) studied coal and lignite gasification, including pressure, using a thermobalance for reaction kinetic measurements with the aim of modelling a large-scale gasification reactor. Gardner et al. (1980) as well as Richard & Rouan (1989) constructed a new apparatus to measure the reaction rates of wood and coal char in a high-pressure environment. In this apparatus the entire reactor, the gas lines and the attached thermocouples are weighed during the test. Richard & Rouan (1989) performed gasification tests with different mixtures of oxygen and nitrogen on a wood and coal char. Sørensen (1996) used a pressurised thermobalance in his studies of air gasification reactivities of various chars including biomass char. Espenäs (1994) measured steam gasification reactivities for biomass chars of wood, straw and peat in a pressurised thermobalance. Reaction rates ranged widely, for straw fuels, example, by a factor of about 25, which corresponds to a temperature difference of 130°C. He also concluded that high reactivity of the char is favoured by process conditions in which the volatiles are rapidly removed from the char.

In the use of a thermobalance, there are *instrument-specific parameters and sample treatment* factors that have to be considered when the results are to be applied for process prediction. The instrument-specific parameters are related to the heating rate of the fuel and the diffusion of the gas in the sample layer. Usually, the thermobalance is used in a non-isothermal mode, i.e. the reactor is heated slowly, a few degrees per minute, up to a certain final temperature. The sample heats up at the same heating rate. This slow heating rate may be irrelevant where fuel is fed to a hot reactor. When a feedstock enters the reactor, it heats up fairly rapidly, and thus is pyrolysed fast. The conditions during pyrolysis have an effect on the char gasification reactivity, the important factors being heating rate, residence time and the final temperature. Sipilä et al. (1980) and Espenäs (1994) have reported the effects for peat. According to their findings, char after slow heating rate is of lower reactivity than char after fast heating rate (see also section 2.4.4).

Since the course and product yields of pyrolysis and gasification are influenced by final temperature, residence time, rate of heating, gas atmosphere and pressure, and since the thermobalance alone does not reflect the fuel behaviour in a process, Mühlen et al. (1989) established *a number of methods* for the characterisation of fuels for pyrolysis and gasification. Different instruments are required for the characterisation, as shown in Table 5.

Table 5. Classification of heating rates in coal conversion, and laboratory equipment for pyrolysis and gasification, pressure range 0.1–10 MPa (modified from Mühlen et al. 1989).

	Heating rate, K/s	**Heating time to 1000°C, d_p 100 µm**	**Technical reactor type**
Slow	<< 1	>>20 min	Coke oven Fixed bed gasifier
Medium	5–100	10 s – 4 min	Lurgi/Ruhrgas – type carbonisation
Fast	500–100 000	10 ms – 2 s	Fluidised bed Entrained phase
Flash	$>10^5$	< 1 ms	Plasma reactor

Apparatus	Thermobalance sample holder  Cylindrical wire mesh Cup	Wire-mesh reactor 	Curie-point or pyroprobe technique 
Sample size, mg	1000	10	5
Heating rate, K/s	0.05	200–1500	1000–10 000
Final temperature, °C	1000	1000	Adjustable
Results	Kinetics	Kinetics, swelling, high speed camera	Kinetics, products

Some researchers have modified *the thermobalance to simulate more directly the real-scale process.* Stoltze et al. (1995) used a thermogravimetric analyser (TGA) designed for sample size of 10 g to simulate and model a large-scale unit for gasification of straw. In their large-sample TGA, data can be produced in which heat and mass transport and diffusion phenomena are included, and reactivity can be measured under the conditions that exist in a real gasifier. The results will therefore be directly applicable in the modelling and dimensioning of gasifiers. A large-sample TGA is also useful when measuring the gasification rates of large pieces. Straw, wood chips, municipal solid waste, corncobs etc. can be analysed without damaging the structure of the material. Olgun et al. (2001) studied biomass and waste fuels for fixed bed gasification using a laboratory-scale large-sample thermogravimetric analyser, with the objective of understanding the decomposition behaviour of a range of biomass and waste feedstocks during gasification in a downdraft gasifier. The conditions chosen simulated the behaviour in a gasifier for diverse biomass fuels and wastes, namely hazelnut, pistachio and peanut shells, wood chips and sewage sludge pellets.

When a thermobalance is used for fuel characterisation, and especially for study of kinetics, attention needs to be paid to the *diffusion effects* caused by the measurement arrangements – the thickness of the sample layer, the form of the sample holder and the location of the sample in the holder. These effects are especially significant when reaction rates are high. Ollero et al. (2002) studied the diffusion effects in gasification experiments carried out in a thermobalance for kinetic determination in CO_2 and CO partial pressures, paying attention to the effect of the geometry of the sample holder on the kinetics. They observed that the internal diffusion resistance in a 3-mm-deep sample char bed was significant because of the inhibiting effect of CO and its accumulation inside the sample layer.

2.4.4 Characterisation of char reactivity

Characterisation of the gasification reactivity is usually focused on the reactivity of the char residue, since the volatile matter is rapidly released from the fuel and transferred to the gaseous environment. Several factors affect the char properties, and thus the reactivity, as well. Zanzi et al. (1994), Chen et al. (1997)

and Chen (1998) studied the *effect of heating rate* during pyrolysis on wood char reactivity. The pyrolysis was carried out both in a free-fall tubular reactor and in a thermobalance. The char obtained was further gasified with carbon dioxide and steam in the thermobalance. The reaction rates of the char were observed to be strongly affected by the time-temperature history of the char formation because of the influence of this on the structure of the char particles. The char reactivity decreased with the increase in the residence time during pyrolysis. Prolonged contact time between tar and char reduced the reactivity of the char in the reaction with steam. A rapid heating rate of the raw material in the free-fall reactor gave a char of higher reactivity in reaction both with carbon dioxide and with steam than did a slow heating rate in the thermobalance. Fushimi et al. (2003) used a thermobalance to measure the effect of heating rates of 1, 10 and 100 Ks^{-1} on the steam gasification of lignin. They found that a higher heating rate substantially increased the reaction rate of lignin char in steam gasification because porous char was produced during devolatilisation due to the rapid evolution of volatiles. In a study of the influence of pyrolysis conditions on the gasification reactivity of biomass chars, Cetin et al. (2004) observed char reactivity to increase with pyrolysis heating rate and furthermore with decreasing pyrolysis pressure. As an explanation for the greater effect of heating rate on the reactivity in calcium catalysed gasification, Cazorla-Amorós et al. (1993) proposed that the heating rate affects the calcium dispersion and thereby the reactivity: the higher the heating rate, the higher the calcium dispersion and the reactivity.

Devi & Kannan (2000) studied the effect of *heat treatment temperature* (HTT) on air gasification of biomass materials (coir, wheat straw and potato pulp). They observed that the effect was not straightforward: the gasification rate of the chars decreased with increasing HTT up to a certain value of HTT (500, 550, and 750 °C), but above this value it increased dramatically. This result was in contrast to the observation of monotonic decrease in reactivity reported for coal chars. The authors suggested that this effect was due to a change in the chemical state of the indigenous potassium species catalysing the gasification at the HTT inflection temperature. Kumar & Gupta (1994) found for wood (various Acacia and Eucalyptus species) chars that the CO_2 reactivity was reduced when carbonisation temperature increased from 800°C to 1200°C when the carbonisation (char preparation) heating rate was slow (4°C/min). When the heating rate was faster (30°C/min) the reactivity did not depend on the final temperature.

2.4.5 Reactivity and fuel characteristics

The dependence between the reactivity and fuel characteristics has been studied by several researchers, especially the relationship between gasification reactivity and inorganic material in biomass. In measurements of the reactivity, Mühlen (1990) observed for brown coal that the gasification reaction rate as a function of conversion and pressure followed unpredictable patterns and varied from one brown coal grade to another. This was in accordance with Miura et al. (1989 and 1990) who, in studies on the gasification reactivity of coals, observed that gasification reactivity correlated well with carbon content above 80% on dry ash-free basis, while the correlation was much poorer for lower carbonised coals (younger coals). In a comparison of the reactivity of coal chars derived from lignites and sub-bituminous coals with that of chars derived from a range of biomass fuels, Clemens et al. (2002) found that samples of coal chars derived from lignites and sub-bituminous coals were significantly more reactive than those derived from biomass. They explained that organically bound calcium in the coals is a good catalyst of the gasification reaction. When calcium was added to the biomass samples, char reactivity increased dramatically.

Henriksen et al. (1997) found reactivity in gasification of straw to depend on the content of *water-soluble compounds*. Washing reduced the reactivity significantly, and the original high reactivity was restored by readsorption of the water-soluble compounds back into the sample. Water soluble compounds were observed to have the same effect on the reactivity during the gasification, while their presence during pyrolysis had no measurable effect on the gasification reactivity. A linear correlation was found between the gasification reactivity and the concentration of the water solubles.

Kannan & Richards (1990) concluded from their CO_2 reactivity measurements that, owing to the *catalytic effect of ash*, the gasification reactivities of chars from any type of biomass with low Si content can be predicted with reasonable certainty from knowledge of the indigenous metal content. In the case of high silicon content, the silicon reacts with potassium to form silicate, blocking the catalytic effect of potassium. They also concluded that the chemical and physical properties of biomass chars are remarkably similar, despite the wide range of plant species and morphologies from which they are derived.

2.4.6 Kinetic parameters

Although, study of the kinetic parameters of gasification reactions was not an objective of this work, an overview of kinetic parameters is given in the following. Reactivity studies published in the literature have largely focused on determination of the kinetic parameters of gasification reactions for modelling. Pfab (2001) carried out kinetic studies on char reactions with carbon dioxide in a thermogravimetric apparatus for modelling of the biomass fluidised bed gasification. The char samples were prepared by fast pyrolysis in a separate reactor. Ollero et al. (2003) studied the CO_2 gasification kinetics of olive residue using a thermobalance. Struis et al. (2001) and Risnes et al. (2001) studied gasification reactivity of biomass chars in various ways to understand the reaction mechanism under different conditions. Hansen et al. (1997) studied the H_2O gasification char kinetics of wheat straw, barley straw, willow and giganteus at 1–10 bar total pressure, 0.15–1.5 bar H_2O and 0–1.0 bar H_2 and 750–925 °C in a pressurised thermogravimetric analyser and observed a distribution in the reactivity values of about one order of magnitude from lowest (wheat and giganteus) to highest (barley). The difference was probably due to different contents of catalytic elements. Rathmann & Illerup (1995) investigated the combustion and CO_2 gasification reactivities of pulverised wheat straw char up to 40 bar pressure by isothermal pressurised thermogravimetric analysis, and compared their findings with those obtained with a typical sub-bituminous coal. The effects of temperature and partial pressure of the reactants O_2 and CO_2 were seen, and also the inhibiting effect of CO. A distinct total pressure effect was not observed. Barrio (2002) investigated the gasification kinetics of woody biomass for fixed-bed gasifiers using thermogravimetry.

2.4.7 Thermogravimetric characterisation of waste

There is little information in the literature on the thermogravimetric characterisation specifically of waste and waste-based fuels for gasification. The thermobalance has been used by a few groups to characterise the gasification of RDF and of wastes and individual components of the waste. For gasification the pyrolysis stage is regarded as essential. Thus Kawaguchi et al. (2002) stressed that it is important to investigate the pyrolysis processes of municipal solid waste (MSW) in the same way as for any mixture containing multiple substances. Using thermal analysis, they measured mass changes during pyrolysis for the typical components of MSW and found mass changes at about 350°C. According to their results, the mass change of a mixture in pyrolysis can be predicted by using a weighted sum of the individual components. The model turned out to be useful in experiments with RDF, and furthermore, the weight yield (pyrolysis gas, tars, solid residues) of the mixture could be calculated by adding together the mass balances of the separate components. Lin et al. (1999) studied RDF by thermogravimetric analysis to obtain data on thermal degradation kinetics. They detected at least two distinct weight loss stages relevant to the gasification. Shoji et al. (2001) applied thermogravimetric analysis to waste treated in an entrained-flow gasifier, using a constant heating rate of 2 K/min. They found that common plastics were rapidly decomposed (temperatures were reported in Kelvin scale) at 600–750 K, while PVC and rubber were decomposed at 500–800 K. Sawdust and cellulose were pyrolysed at 550–800 K, and waste plastics and municipal solid waste at 500–800 K. The char gasification with CO_2 and/or H_2O was observed to depend on the char components. They also observed that TG curves of the waste plastic and municipal waste were well simulated by summing the reaction ratios of individual components. Likewise Heikkinen et al. (2004) used thermogravimetric analysis to investigate the pyrolysis of individual waste components and waste mixtures to be able to determine the composition of an unknown waste mixture. They concluded that the weighted sum of the individual components can provide an indication of the total composition. Biagini et al. (2004) characterised the devolatilisation of secondary fuels, in view of the fact that devolatilisation is the basic step in all thermal treatments of materials. They obtained the kinetics of devolatilisation as a function of the heating rate under a wide range of conditions using, among others, TG, a wire mesh reactor, and an electrodynamic balance on laboratory scale.

A few researchers have used a thermobalance to study the gasification of char from waste. Meza-Renken (1998) examined chars and catalytic gasification from the pyrolysis of waste materials. Copper and iron were found to have a catalytic effect on gasification when doped to pure carbon such as carbon black or graphite. But the increased gasification rate was not as high as the rate obtained with the char derived from waste. Cozzani (2000) used a thermobalance to study the gasification reactivity of RDF chars in oxygen and carbon dioxide. The chars were produced in a fixed-bed pyrolysis reactor at low heating rates (60 ºC/min) and at temperatures between 500 and 800 ºC. The chars were found to be fairly similar in reactivity to chars obtained from municipal solid wastes and wood. The kinetics for gasification reaction of RDF was estimated by Ryu et al. (2003) and on that basis the optimal gasifier–reactor size using thermogravimetry. Henrich et al. (1999) studied the combustion and gasification kinetics of pyrolysis chars from municipal waste, electronic scrap, wood and straw. They measured reaction rates with oxygen and carbon dioxide using a thermobalance, a differential flow reactor and a fluidised bed of sand. The chars from waste and biomass, they conclude, are among the most reactive carbon materials. The conclusion may, however, be an oversimplification, since, according to Onischak et al. (1988) who analysed an RDF feedstock for pressurised fluidised bed gasification in a thermobalance, RDF char carbon was not completely converted under such conditions.

Waste fractions have been studied by Antonetti et al. (2004), who presented experimental results relevant to the recovery of copper in scrap composite materials from the electronic pcb (printed circuit board) industry. The process involved thermal treatment of the scrap in a fluidised bed whose particles fix the harmful gases emitted by gasification of the organic glue. A series of experiments were carried out with small samples in a thermobalance coupled to an FTIR spectrometer and GC/MS. Experiments made in a a laboratory-scale fluidised bed coupled to FTIR and MS, at 350° confirmed the results obtained with the thermobalance.

Small-scale reactors, as described above for biomass, have also been used in some degree to study the gasification of waste-based fuels for characterisation purposes. Hamel & Krumm (1998) investigated the combustion and gasification characteristics (CO_2 gasification) of domestic waste, waste plastics, wood, sewage sludge and Rhenish brown coal in a laboratory-scale bubbling atmospheric fluidised bed. Wu & Wen (1997) investigated the gasification of char from RDF (from Shanghai municipal solid waste) and the influence of feedstock properties in a batch, fixed bed gasifying reactor. Their results showed that the properties and components of RDF affect the gasification process.

2.4.8 Characterisation of ash sintering

One of the essential aspects in utilising biomass fuels is the ash sintering behaviour. Ash deposit formation is a well-known problem in biomass combustion, but it is also a significant problem in gasification. Osman (1982) reported about slag-problems in biomass gasification and Rosen et al. (1999) observed this problem in a comparison of the gasification characteristics of olive waste and wood. The low melting temperature of the ash from olive waste caused depositional problems. As well, increased pressure influenced the ash behaviour negatively.

It had been observed in earlier work that ash behaviour in the process, particularly deposit formation and agglomeration, cannot always be predicted by standardised ash fusion tests. Moilanen (1993) noted this for peat gasification and Skrifvars (1994) for biomass combustion. Osman (1982) studied the relationship between ash fusion temperature and ash chemical composition and slag formation in biomass gasification. He found that the ash fusion temperature is not an indicator whether the fuel slags or not.

The ash deposition and bed agglomeration are affected by a combination of the chemical properties of the ash forming constituents in the fuel and the process conditions. Bitowft & Bjerle (1988) studied the sintering properties of wood char during steam gasification in a laboratory-scale fluidised bed reactor at atmospheric pressure. The reactor was designed to promote clinker formation. They found that clinker was formed at average bed temperatures as low as 640 ºC, but consistent behaviour based on the average bed temperature was hard to achieve. Hallgren (1996) and Nordin (1993) based their characterisation of biomass fuels for gasification and combustion on the use of fluidised bed reactors. Their work was mainly focused on ash sintering characterisation.

Van der Drift & Olsen (1999) developed a methodology to predict ash/bed agglomeration and sintering problems and to identify solutions for different types of biomass. The fuels, including verge grass, Danish wheat straw (both stored dry and partly leached due to rainfall), sewage sludge, cacao shells and willow, were investigated by different methods to determine the agglomeration temperature. The methods were chemical analysis of fuel and ashes, determination of standard ash melting temperatures, compression strength measurements of the ash, differential thermal and thermogravimetric analysis (DTA/TG) of the ash, scanning electron microscopy (SEM) and combustion in two different lab-scale bubbling fluidised bed facilities – a lab-scale bubbling fluidised bed gasifier and a circulating fluidised bed gasifier. The lab-scale facilities were used to test additives and bed materials that might reduce the problem of agglomeration. According to the results, chemical analysis of the fuel can give a first indication of an agglomeration problem during thermal conversion. In general, high potassium content means an increased risk for agglomeration. However, the potassium content alone is a poor indicator; chlorine is important as well. Among the several methods, the laboratory fluidised bed agglomeration experiments tended to give the most reliable information about conditions and temperatures where agglomeration takes place. The authors concluded that, in contrast to laboratory methods such as DTA and measurement of compression strength and ash melting temperatures, in fluidised bed experiments all processes affect the agglomeration (fuel – bed material interactions, volatilisation and condensation, shear forces, temperature homogeneity and accumulation). They also concluded that the design of fluidised beds is of significance for agglomeration. Thus, in their view, the results from lab-scale facilities can be used to compare fuels and suggest possible solutions, but they should be used with care in attempting to draw conclusions relevant for full-scale plants.

The ash sintering properties can be determined with special laboratory methods. Skrifvars (1994) and Skrifvars et al. (1996) used the following methods to study sintering with 10 different types of biomass: combined DTA-TGA for ash thermal behaviour, compression strength sintering testing method for ash sintering tendency, chemical analysis of the ashes and sintering tested samples, standard fuel characterisation analyses, and reactivity analyses for the selected biomasses. The results showed clear differences in the thermal behaviour of the ashes: the sintering tendencies varied significantly. The chemical analyses showed that, under both oxidising and reducing conditions, ashes rich in silicon started to sinter at 800–900 ºC, while ashes with low silicon content did not. When CO_2 was present in the gas atmosphere, the ashes with low silicon content showed an increase in sintering at approximately 700 ºC and a decrease above 700 ºC. Furthermore, if the gasification rate decreased as a function of the conversion, ash sintering was hindered (see below and also section 5.2).

Arvelakis et al. (2002) studied the effect of leaching on the ash behaviour of olive residue during fluidised bed gasification. All gasification tests performed with the non-leached olive residue material as feedstock resulted in a rapid agglomeration of the reactor bed material and a rapid end of the gasification tests. In contrast, the gasification tests with the leached olive residue material were concluded with no agglomeration or deposition problems.

Koukios et al. (1999) and Arvelakis et al. (1999a) characterised the ash behaviour by simple sintering tests performed in a laboratory muffle furnace and by electron microscopy. Arvelakis et al. (1999b) applied a non-isothermal thermoanalytical method for the examination of low-temperature ash melts and the losses caused by the volatilisation of alkali material in biomass combustion and gasification. They concluded that, in combination with ash elemental analyses of the materials, the applied techniques offer valuable information for prediction of the ash behaviour in fluidised bed reactors.

Zevenhoven-Onderwater et al. (2001) studied the ash chemistry in fluidised bed gasification of biomass fuels and the correlation between the ash behaviour modelling and the results of bench-scale agglomeration tests. The agglomeration was allowed to occur without any corrective changes in the process operation. Small-scale experiments showed clear de-fluidisation in five out of 13 cases, while some degree of bed disturbance or agglomeration occurred in seven cases. In nine cases, agglomerates were also found in the samples analysed by SEM. In six out of 13 cases, the thermodynamic multi-phase multi-component equilibrium calculations, i.e. the prediction of agglomerates, were in agreement with the SEM analysis, while in two cases, none or only small amounts of agglomerates were predicted and no agglomeration was found in SEM analysis. In two cases out of 13, the modelling predicted some degree of agglomeration and no agglomerates were detected in SEM analysis. However, agglomerates were found in the pilot-scale experiments.

Operational problems caused by ash deposits have also been reported in large-scale fluidised bed gasification processes. In pressurised steam – oxygen gasification of peat, ash deposits have been formed in the upper part of the gasifier and in the cyclones (Moilanen 1993). Furthermore, straw ash has been found to cause both bed sintering and deposit formation in air-blown gasification (Kurkela et al. 1996). In this last case, the gasification temperature had to be reduced below 800–850 °C, which resulted in poor carbon conversion and high tar concentrations. On the other hand, co-gasification of coal and straw (up to 50 wt-% straw) was carried out with no sign of ash problems even at high operating temperatures of 950–980 °C. One factor that was relevant to the behaviour of ash in the gasification process was carbon conversion. (Kurkela et al. 1996, Skrifvars et al. 1996). The completeness of fuel carbon conversion is dependent on the reactivity of residual char and the operating conditions. If the reactivity is high, ash is formed rapidly and, consequently, deposits are also formed rapidly. When the carbon conversion in char was not complete, it was assumed that it prevented the ash from sintering.

The sintering/melting temperatures determined for ash indicate the limit temperature above which difficulties can be expected to occur. Kurkela et al. in Pat. WO0011115 (2000) nevertheless demonstrated a process for operating a gasifier at higher temperature than the sintering point or melting point of ash. In their process straw was gasified in a circulating fluidised bed containing porous and brittle material (limestone and dolomite). Evidently, the fragments formed by bed attrition remove the harmful potassium from the reactor.

3. Focus of the work

This work deals with the characterisation of reactivity and ash sintering in the gasification of biomass and waste. Waste was included in the study for the reason that it is often classed with biomass in the concept of bioenergy in the EU (EC 2005a). The waste investigated was not miscellaneous waste but in the form of SRF. On the basis of results obtained experimentally and information available in the literature, a method was developed for the characterisation of reactivity and ash sintering of fuels to be used in fluidised bed gasification processes, both atmospheric and pressurised. Thermogravimetry and microscopy are the sole tools.

The method is based on that described by Mühlen (1983), Mühlen & Sulimma (1986 and 1987) and Mühlen et al. (1989) for coal and lignite and extended for pressurised gasification by van Heek & Mühlen (1991) and Sowa (1991). In this earlier work, the kinetic parameters of the gasification reactions were measured in a thermobalance, first in the pure gases of CO_2 and H_2O, then in the binary gas mixtures of $CO_2 - CO$ and $H_2O - H_2$, and finally in the gas mixture containing all the components, $H_2O - CO_2 - H_2 - CO$.

These earlier studies were carried out for bituminous coal, and the findings were in agreement with those reviewed by Miura et al. (1989), who concluded that the reactivity measured in steam or CO_2 correlates well with the carbon content of the fuel when this is above the value of 80% on dry ash-free basis. Below this limit value no correlation appears, and Mühlen (1990) concluded that the reactivity of brown coals as a function of pressure and gas composition does not follow any regular pattern but varies from coal to coal.

When the method developed for coal was applied to peat (Paper III), a relatively strong inhibition was observed, which was assumed to be due to high iron content. In the measurements on wood (Paper IV) the reactivity measured in binary gas mixtures of steam and hydrogen was observed to deviate from that measured in the binary gas mixture of CO_2-CO.

Wide scattering was also obtained in testing of the SRF samples for reactivity, but this was reduced when the samples were extracted by cone and quartering sample division from the large sample amount (Moilanen & Konttinen 2006).

These findings led to the conclusion that in younger fuels like biomass the reactivity depends on many factors; in particular the catalytic factors play a large role, and the behaviour is not easy to predict. The importance of catalytic components was identified by Meijer et al. (1994) in their study on alkali catalysed gasification of carbon. They used acid-washed steam-activated char impregnated with catalysts comprising of different alkali-carbonates and they concluded that, for a complete description of the gasification rate of coal char, at least two factors need to be considered. These are catalyst redispersion and concentration effects, and loss of potassium by evaporation and by reaction with mineral matter. Their study was carried out with pure compounds, while biomass contains a wide spectrum of various forms of inorganic compounds. More research is needed to understand the behaviour of these inorganic compounds during sample heating, pyrolysis and char gasification. Thus, in the present work an effort was made to discover the measurement conditions in which all these reactions take place simultaneously, so that the result would correspond to the reality as closely as possibly.

In evaluating the behaviour of biomass in fluidised bed gasification, the conditions to be taken into account are those existing in the bed and in the freeboard of the reactor. The product gas components are important for the freeboard, since these have been found to reduce the gasification rate of coal and peat char significantly (Mühlen et al. 1985, van Heek & Mühlen 1991, Hüttinger & Merdes 1992, Paper III). As an explanation of the inhibition, Meijer et al. (1994), for example, suggested that hydrogen reduces potassium leading to loss of active potassium. Another explanation is that hydrogen blocks the active carbon sites. CO, in turn, inhibits reaction through the formation of chemisorbed carbon dioxide with the result that fewer sites are available in H_2O gasification. Furthermore, the chemisorption of CO on the carbon surface reduces the number of active sites for gasification.

The purpose of the research, as reported in the publications attached to this thesis as appendices, was to take into account the complexity of the phenomena rather than to find systematic correlations between the various fuel properties and reactivity and ash sintering, or to determine kinetic parameters. The observed complexity was the spur to develop a method, one that would be as simple as possible, to characterise biomass and solid recovered fuels or wastes intended as feedstocks for use in gasification while taking into account the conditions of the process.

For purposes of characterisation, the temperature and pressure ranges, heating rates and gaseous environment for the thermobalance were selected so as to be relevant for the conditions existing in fluidised bed gasifiers, including pressurised conditions. The temperature maximum was thus 1000 °C, and the heating rate of the fuel sample was adjusted to that when feedstock enters the reactor. The pressure range extended from 1 bar to 30 bars. The gaseous environment was selected so that it would sufficiently describe that existing in a gasifier. The characterisation was carried out with the same fuel samples as used in conventional fuel analysis.

The method described also provides information about ash sintering. The ash is the residue remaining in the thermobalance after the gasification reactions, which thus represents the conditions of gasification, even pressurised gasification. A separate ash does not need to be prepared in the laboratory.

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4. Experimental

The reactivity was determined by measuring the weight of the sample as a function of time in a pressurised thermobalance (PTG). The thermobalance set-up, as generally employed in the study is shown in Figure 3; it can be used at atmospheric pressure or pressurised up to 100 bars. Another type of thermobalance set-up, as described by Moilanen & Saviharju (1994), was used in the study presented in Paper I. This thermobalance operated only under atmospheric conditions.

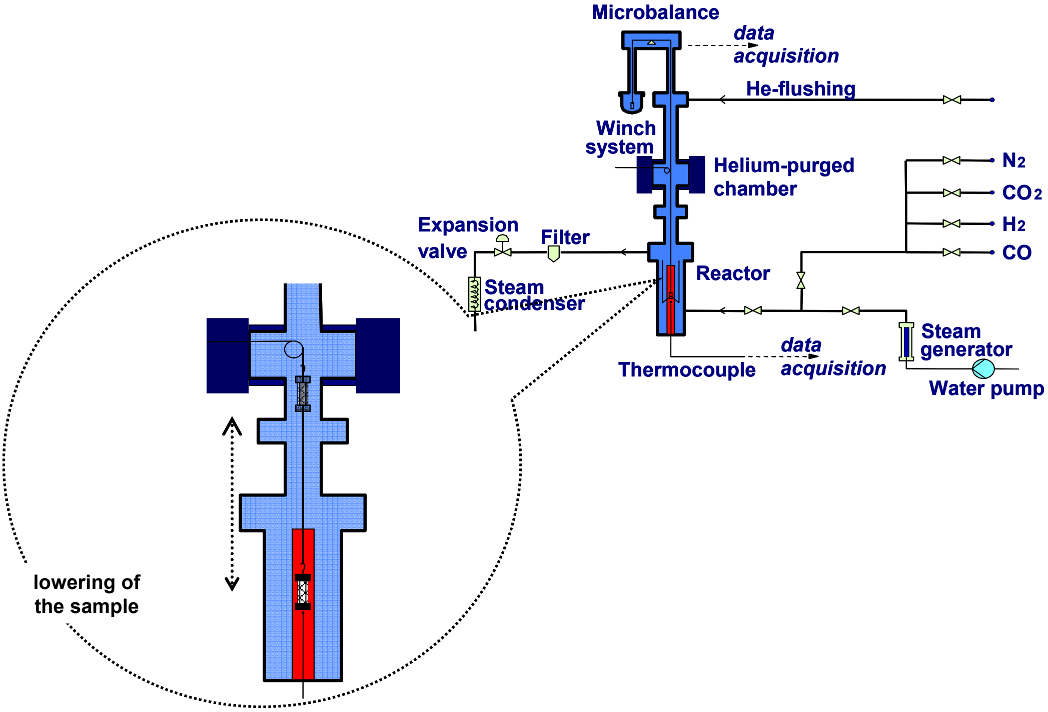

Figure 3. Thermobalance set-up, where the enlargement shows how the sample is lowered into the reactor to achieve a fast heating rate.

Sample holder

The sample holder in PTG was cylindrical in form, as shown in Figure 4. Typically the sample weight of a biomass fuel was in the range of 50 to 150 mg. The thermocouple of type K was located under the bottom of the sample holder at a distance of 5 mm measured at room temperature. At the measuring temperatures, this distance decreased due to thermal expansion of the thermocouple and the hanging wire, so that the thermocouple was as close as possible to the sample without touching it. Thus, both the tip of the thermocouple and the sample holder were in the constant temperature zone of the reactor tube. The pulverised sample was placed in the annular space around the shaft, as illustrated in Figure 4. For a fuller description, see Mühlen (1983) and Papers III and VII. A holder of this form enables good gas – solid interaction, which is less dependent on the diffusion effects than when a cup-form sample holder is used. However, in the thermogravimetric measurements of black liquor, a cup-form sample holder made of alumina was used, because of the high alkalinity and strong corrosivity of the liquor (Paper V).

Gasification agents

The gasification agents were 100% steam and 100% carbon dioxide at 1 bar or at higher pressure (e.g. 30 bar). To test the effect of the product gas on reactivity, hydrogen was added to steam and carbon monoxide to carbon dioxide. Due to the water-gas shift reaction (formula 4), CO was not added to steam.

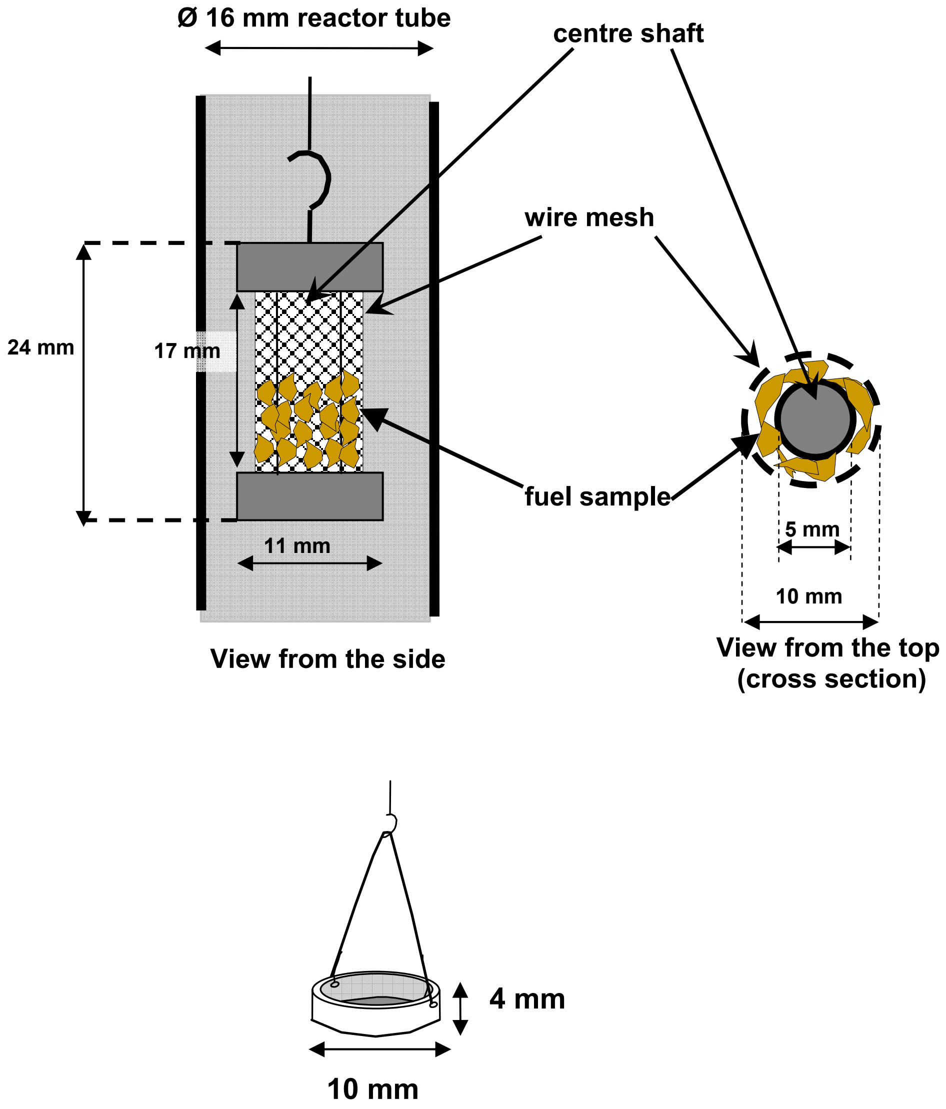

Figure 4. Structure of the sample holder showing the fuel sample in the annular space formed by the wire mesh around the centre shaft. The sample holder shown below is the one used in the black liquor tests (Paper V).

Measurement procedure

Measurements were carried out at constant temperature (isothermal measurement) under fast heating to resemble the heating occurring when the fuel is fed to a reactor. The heating took place *in situ*. The sample, located in the sample holder, was weighed with an accuracy of 0.1 mg and placed in the helium-purged chamber. After the reaction conditions in the reactor (gasification agent, temperature, pressure) had been adjusted and stabilised, the sample holder was lowered down to the reaction tube with an electrically driven winch system (Figure 3). The main part of the weight loss caused by the pyrolysis took place during this lowering period, which took from 7 to 10 seconds. Recording of the weight started when the sample holder was at its lowest position. During the first 30 to 60 seconds, the weight signal was considered to be stabilising. Also during this time, the heating and the pyrolysis were completed. This first part of the monitored result was removed from the data evaluation (Figure 1 in Paper IV and Figure 5). The heating rate of the sample was estimated to be approximately 20 ºC/s when the reactor was at 850 ºC.

The weight was usually monitored as a function of time to the complete burn-off when no more weight change was observed and the rest of the mass was ash. Measurements were taken at intervals ranging from 2 to over 60 seconds depending on the weight loss rate; if it was fast the time interval was short. If the reaction was so slow that the test run was not completed, the residual unreacted mass was estimated on the basis of the ash content measured for the fuel. The weight-time curve was plotted so that the weight of ash was presented as zero in the resulting graph.

Data evaluation

The rate of mass change was given as an instantaneous rate of reaction designated r” (%/min), i.e. it was calculated by dividing the rate of mass change of the sample by the residual ash-free mass. The conversion, expressed as per cent, was the reacted part of the total ash-free sample. The rate r” (%/min) was calculated from the measured data points (Figure 5) using a spreadsheet calculation according to the formula (5):

$$r'' = 100 \times \frac{m_i - m_{i+1}}{(t_{i+1} - t_i) \times (m_{i+1} - m_{ash})} \tag{5}$$

where

m_i is the mass at time t_i
m_{i+1} is the mass at time t_{i+1}
m_{ash} is the mass of ash

$i =$ 1, 2, 3, 4 etc.

Fuel conversion X (%) was calculated according to the formula

$$X = 100 \times \frac{m_o - m}{m_o - m_{ash}} \tag{6}$$

where

m_o is the original sample mass
m is the instantaneous mass [in this work the same as m_{i+1} in formula (5)]
m_{ash} is the mass of ash.

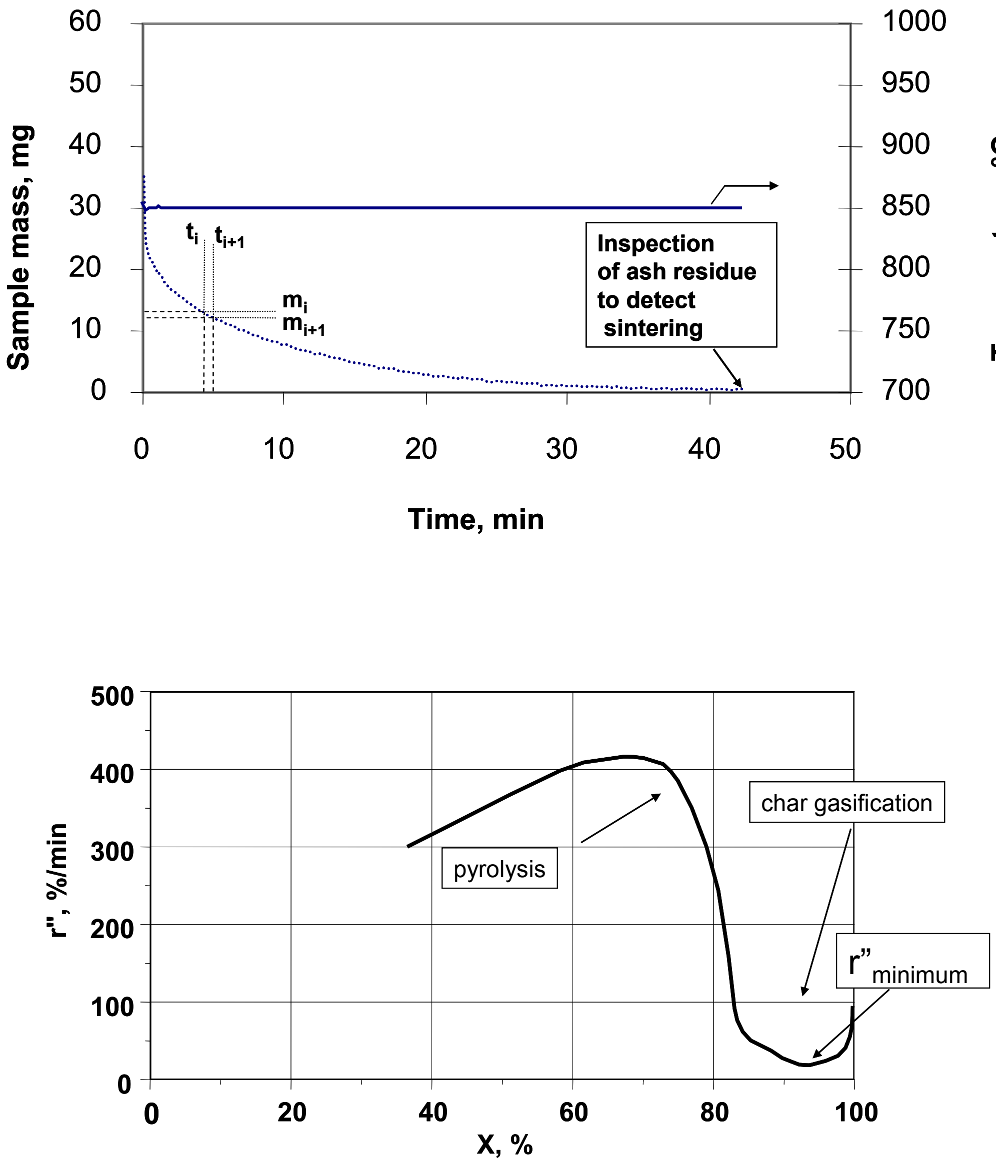

Figure 5. A typical mass versus *time curve obtained from the thermobalance, and the instantaneous reaction rate (r", %/min)* versus *conversion (X, %) (lower graph).*

Ash sintering

After the reactivity measurement in the thermobalance, the residual ash was inspected under a microscope (an ordinary stereomicroscope) to detect any sintering of ash particles or molten phases. A molten phase is detected as distinct spherical particles of shiny or glassy appearance. The spherical particles are also of larger size than the powdery ash particles. The following classification criteria were used (Figure 6, Paper VII):

- Non-sintered ash residue: ash structure resembles the original fuel particles, easily crumbles when touched; no asterisk: designated o.
- Partly sintered ash (different degrees in this group): particles contain clearly fused ash; designated with 1 or 2 asterisks: *, **
- Totally sintered ash: the residue is totally fused to larger blocks; designated with 3 asterisks: ***.

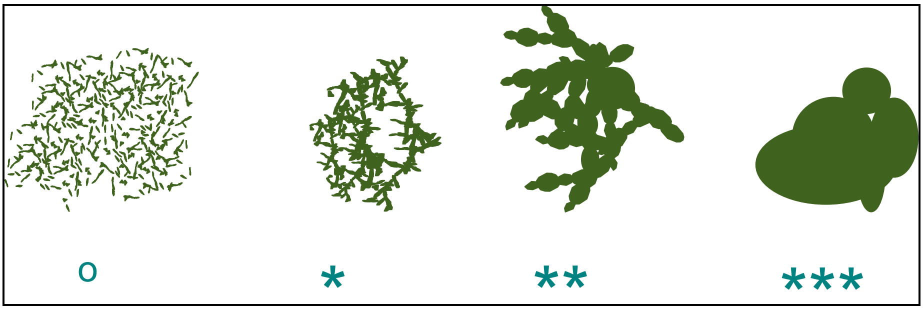

Figure 6. The degrees of sintering as seen under a microscope (from Paper VII).

Fluidised bed reactors

The pressurised fluidised bed gasification test rig described in Figure 1 of Paper II, in Kurkela & Ståhlberg (1992) and in Kurkela (1996), was used for comparison of the carbon conversion in a fluidised bed gasifier. The gasification test conditions are described in Table 4 of Paper II. In these tests, air and a small amount of steam were used as gasification agents at 5 bar total pressure.

The behaviour of ash in a fluidised bed gasifier was studied in VTT's bench-scale atmospheric fluidised-bed reactor (AFB, fuel feed rate 0.5 kg/h, bed diameter 5 cm, freeboard diameter 10 cm, electrically heated jackets, Figure 2 in Paper VII). In this reactor, the ash agglomeration and deposit formation could be monitored in both bed and freeboard by collecting samples from the reactor after the tests.

5. Results

5.1 Reactivity of biomass and waste

This section presents the results of the thermobalance tests measuring the reactivity of the biomass fuels and SRF. Study of the numerous factors (i.e. fuel properties) affecting the reactivity was outside the scope of this work and their influence on the reactivity is merely suggested in the form of calculated linear correlations between the gasification rate and fuel properties.

5.1.1 Reactivity of biomass

The tests on various types of biomass feedstock were carried out as described in the following. The reactivity was first measured in 1 bar steam at 850 ºC. This value was taken as the set-point in the reactivity characterisation, against which other measurements were compared. This relatively high temperature was also selected with a view to the possible ash sintering, since it represents the typical temperature level in a fluidised bed gasifier. The test revealed whether the fuel was characterised by high or low reactivity, and whether the ash residue was sintered. Reactivity measurements were then carried out at lower or higher temperatures as required until no sintering occurred. If the reaction rate was 50 %/min or higher the fuel was considered to be of high reactivity. The effect of pressure was tested if the feedstock was to be used in pressurised gasification.

Variation in reactivities between biomass fuels

Figure 6 in Paper IV and Table 6 below show the reaction rate values measured for various biomass fuels in steam and carbon dioxide gasification at 850 ºC. Table 7 shows the results of the measurements at lower temperatures of 700 ºC and 750 ºC. A wide variation in the rates is evident. For instance, at 1 bar steam and 850 °C the minimum gasification rate for the different fuels ranged from 7 to 67%/min. Figure 6 (in Paper IV) shows that also the reaction rate as a function of conversion varied widely from one biomass to another. Tables 6 and 7 present the reactivity values as the minimum rate (r” min), the conversion at which the rate was at minimum (X at min), and the rate at the fuel conversion of

95% (r” at X = 95%). The rate value at 95% conversion was selected to obtain an idea of the development of the rate as a function of fuel conversion. By comparing to the minimum reaction rate with the corresponding fuel conversion X at min, it can be seen whether the rate is increasing or decreasing with the conversion. For instance, if the conversion is higher than 95%, when the rate is at minimum, the rate profile is decreasing.

Table 6. The minimum instantaneous gasification rates (r”, %/min) of the samples and the rates at the conversion value of 95% measured at 850 °C; X at min (%) is the fuel conversion at the minimum gasification rate (Paper II).

Sample	**1 bar CO_2**			**30 bar CO_2**			**1 bar H_2O**			**30 bar H_2O**		
	r” min. (%/min)	**X at min (%)**	**r” at X=95% (%/min)**	**r” min. (%/min)**	**X at min (%)**	**r” at X=95% (%/min)**	**r” min. (%/min)**	**X at min (%)**	**r” at X=95% (%/min)**	**r” min. (%/min)**	**X at min (%)**	**r” at X=95% (%/min)**
Pine sawdust	27	93	39	22	88	43	25	94	25	50	84	71
Pine bark	9	88	16	7	84	13	7	91	13	44	90	71
Forest residue (pine)	18	92	20	12	90	39	28	94	30	47	83	81
Salix	29	91	42	23	89	50	30	84	130	60	80	225
Wheat straw	16	98	19	25	87	42	13	97	17	46	99	58
Barley straw	19	90	22	29	80	53	12	99	23	44	83	96
Reed canary grass	3	93	3	10	84	15	15	98	19	35	96	44
Miscanthus	18	90	25	26	83	59	24	84	45	71	87	143
Sweet sorghum	20	91	23	26	86	51	29	84	62	89	88	110
Kenaf	50	80	83	55	88	103	67	91	83	155	88	290

Table 7. The minimum instantaneous gasification rates (r", %/min) of the samples and the rates at the conversion value of 95% measured at 750 °C and 700 °C; X at min (%) is the fuel conversion at the point of minimum gasification rate.

Sample	**750 °C**						**700 °C**		
	1 bar CO_2			**30 bar H_2O**			**30 bar H_2O**		
	r" min. (%/min)	X at min (%)	r" at X=95% (%/min)	r" min. (%/min)	X at min (%)	r" at X=95% (%/min)	r" min. (%/min)	X at min (%)	r" at X=95% (%/min)
Pine sawdust	2	91	3	na	na	na	3	88	3.3
Pine bark	0.5	86	na	na	na	na	1	87	na
Forest residue (pine)	0.8	90	1.2	na	na	na	na	na	na
Salix	2	91	2.6	2	99	40	12	85	25.1
Wheat straw	1.8	91	1.7	5	96	6	2.4	96	2.5
Barley straw	1	98	1.2	na	na	na	na	na	na
Reed canary grass	0.2	93	na	na	na	na	1.5	92	na
Miscanthus	2	86	3.5	na	na	na	3.3	85	5
Sweet sorghum	2	87	2.1	na	na	na	1	95	1
Kenaf	8	90	11,6	na	na	na	10	99	24

na = not analysed

Influence of pressure and product gas on reactivity

Figure 7 below presents the char gasification rates of various biomasses measured at atmospheric pressure and at 30 bar pressure, in steam and in CO_2. Gasification rates measured at atmospheric pressure were similar, but at 30 bar pressure the reactivity in steam was clearly higher than that in CO_2. For peat, as shown in Figure 8 (and Paper III), the gasification rates were observed to decrease at higher pressure in both steam and carbon dioxide, and the burn-off behaviour was different in steam and carbon dioxide.

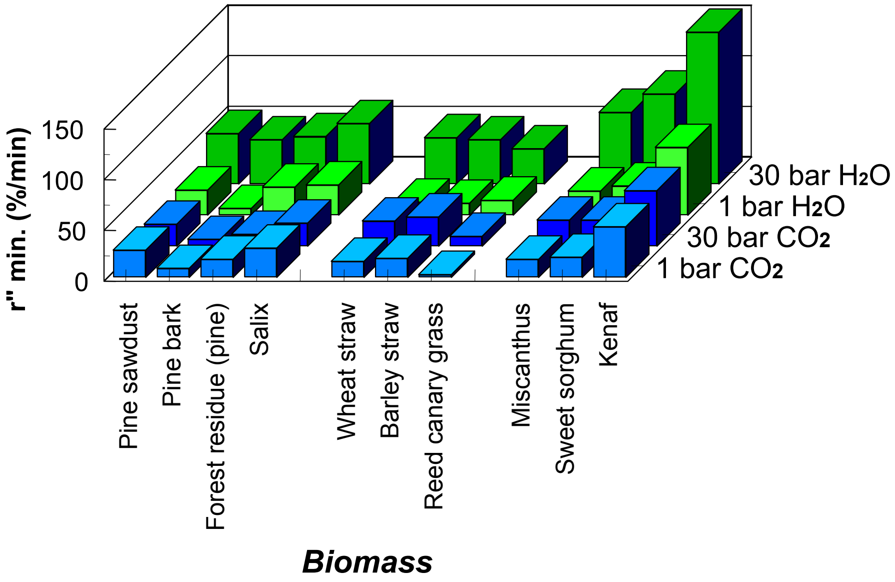

Figure 7. Comparison of the unpressurised and pressurised gasification reactivities of biomass fuels.

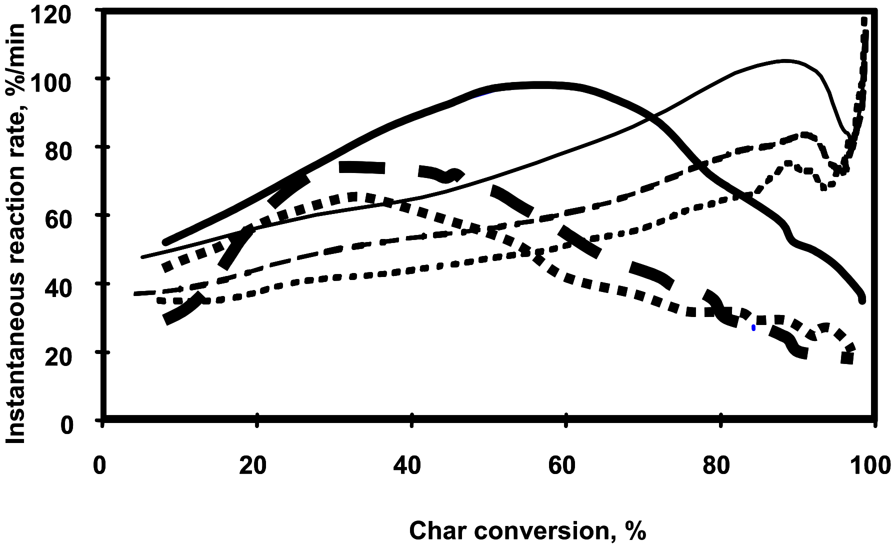

Figure 8. Comparison of steam (thick lines) and carbon dioxide gasification rates of peat char vs. *char burnoff at different pressures (measurement temperature 850°C): ——— 1 bar; — — — 5 bar; -------- 15 bar (modified from Paper III).*

As presented in Figure 9 below, the complexity of the biomass gasification (see Paper IV) was evident in the dependence of the gasification rate of wood char on pressure measured in the range of 1–15 bar CO_2 and H_2O at temperatures of 750 and 850 °C. At both temperatures the rate of CO_2 gasification decreased slightly when the pressure was raised, while the rate of H_2O gasification noticeably increased. The complexity was also seen in the effect of the product gas on the gasification reactivity. For wood char this was studied with use of binary gas mixtures CO_2 - CO and H_2O - H_2. The dependence of the reaction rate on the partial pressure of the product gas components was described with Langmuir-Hinshelwood formulas as used for coal by van Heek & Mühlen (1991). According to the Langmuir-Hinshelwood kinetic expression, the reciprocal of the reaction rate (here r”) should be linearly correlated with the ratio of the partial pressures, e.g. the ratio P_{CO}/P_{CO2}, where P_{CO} is the partial pressure of CO and P_{CO2} is the partial pressure of CO_2. The measurements indicated that the reciprocal of the reaction rate in the gasification of wood char in the CO_2 - CO system is in reasonably good linear dependence on the ratio of partial pressures, while the level of dependence is dependent on the total pressure (Figure 10). The corresponding dependencies in the H_2O - H_2 mixtures were significantly better, and the total pressure was of no great significance. Thus, in this work the inhibition mechanism for CO was detected under high pressures. Barrio et al. (2001), Barrio & Hustad (2001) and Barrio (2002) observed a different mechanism in the gasification under atmospheric pressure.

The reason for the differences observed is assumed to relate to the behaviour of ash-forming substances during gasification. The behaviour of ash-forming substances during gasification is often very complex, as indicated by Meijer et al. (1994) in their study of alkali catalysed carbon gasification. Ash-forming substances may also react with each other or with the gas phase, and new compounds, different in their catalytic effect may be formed (Meijer et al. 1991). Ash composition can be regarded as an essential factor in the wide variation of the gasification reactivity since it varies significantly from one biomass to the next (Wilén et al. 1996). However, it is not well known how these ash forming substances react during gasification.

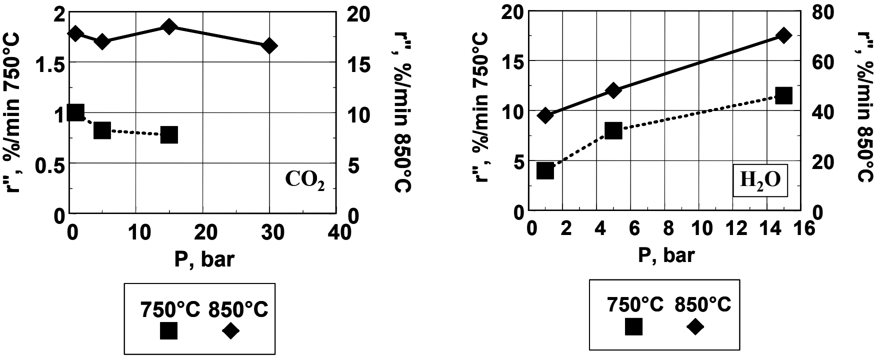

Figure 9. Dependence of the gasification rate of wood char on CO_2 and H_2O pressure at 750 and 850 °C.

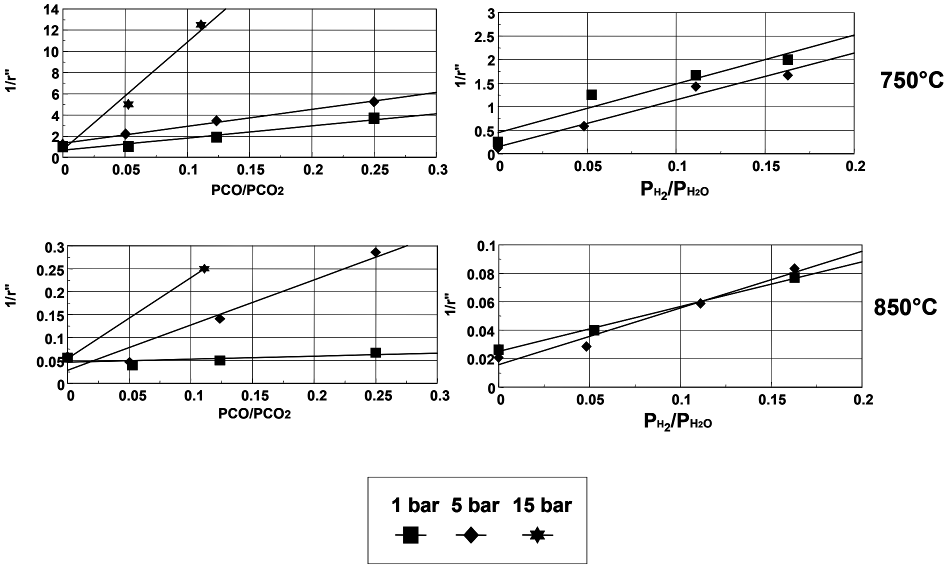

Figure 10. The effect of CO in CO_2 gasification (left) and H_2 in steam gasification (right), from Paper IV (see text).

In view of the complex behaviour of wood char, several other biomasses were tested for both hydrogen and carbon monoxide inhibition. Variable reaction behaviour was evident in the presence of hydrogen, as seen in the results for several biomasses presented in Figure 11. For willow (Salix), for instance, the product gas H_2 had almost no effect, whereas for reed canary grass it caused the rate to collapse almost to zero. The explanation of this behaviour could be the reduction of alkali metal compounds and the loss of the alkali metals (Meijer et al. 1994).

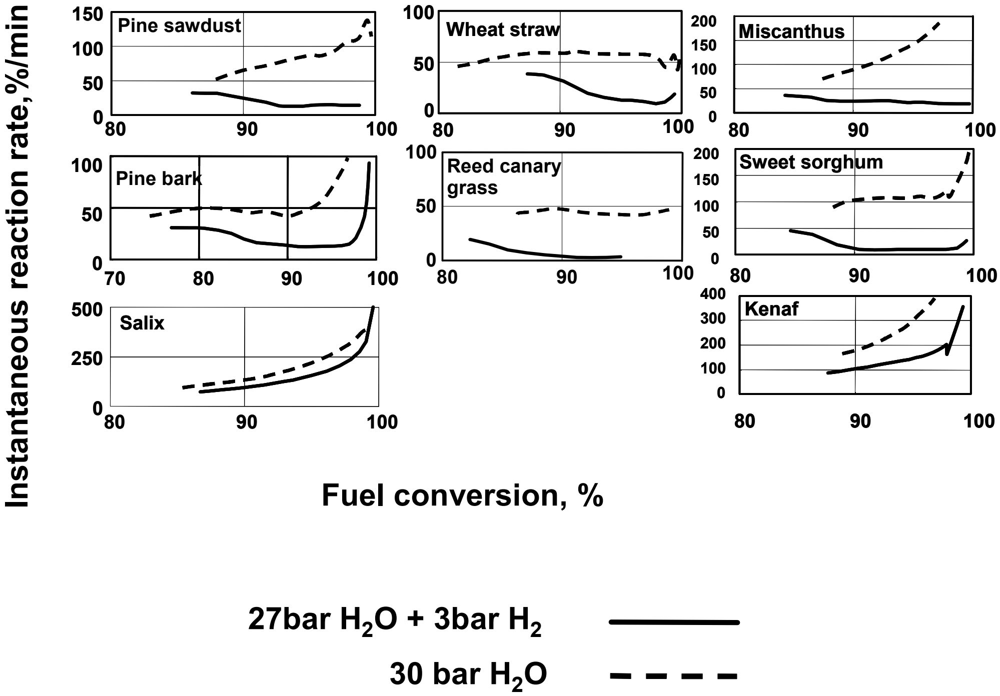

Figure 11. Effect of product gas on reactivity: hydrogen in steam (Paper IV).

Influence of fuel properties on reactivity

It is well known that the gasification rate of chars depends on the catalytically active components in biomass. Kannan & Richards (1990) reported that the CO_2 gasification rate depends on the silicon content in the fuel, and, when the silicon content is low, also on the sum of K and Ca contents. Henriksen et al. (1997) found a linear correlation between the gasification reactivity and the concentration of the water solubles in straw. Table 8 shows the basic fuel characteristics, including ash chemical composition, for the biomasses of the study. The dependence of the gasification rate on the silicon content was evident also in this work, as presented in Figure 12 (and Paper II). The dependence between the gasification rate and the concentration of the water solubles was not studied and could be a topic for a systematic research in the future.

Table 8. Fuel and ash characteristics of the biomass fuels used in the reactivity measurements (Paper II).

Sample	Volatile m., % d	Fixed C, % d.	Ash, % d	C, % d	H, % d	N, % d	Odiff, % d	S, % d	%, in ash									
									SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	SO_3	P_2O_5
Pine sawdust	83.1	16.8	0.1	51.0	6.0	0.1	42.8	-	8.3	2.0	1.8	41.8	11.8	12.3	0.3	0.12	1.9	5.2
Pine bark	73.1	25.3	1.7	52.5	5.7	0.4	39.7	0.03	1.3	5.3	0.3	40.6	4.5	7.6	0.5	0.12	2	4.8
Forest residue (pine)	79.3	19.4	1.3	51.3	5.8	0.4	40.9	0.02	38.5	4.7	3.7	15.4	4	8.3	0.4	0.5	1.6	3.2
Salix (willow)	79.9	18.9	1.2	49.7	6.1	0.4	42.6	0.03	0.4	0.3	0.2	30.8	5.1	26.5	0.3	0.02	3	11.5
Wheat straw	77.7	17.6	4.7	47.5	5.9	0.6	41.5	0.07	59.9	0.8	0.5	7.3	1.8	16.9	0.5	0.04	1.1	2.3
Barley straw	76.1	18.0	5.9	46.2	5.7	0.6	41.5	0.08	62.0	0.2	0.2	4.5	2.2	19.3	0.5	0.02	1.4	2.5
Reed canary grass	73.5	17.6	8.9	45.0	5.7	1.4	38.9	0.14	89.8	1.4	1.1	3.5	1.5	3.1	0.1	0.05	1.1	4.1
Miscanthus	78.5	18.2	3.3	47.9	6.0	0.6	41.6	0.6	42.8	0.5	0.4	7.6	4.8	25.3	0.7	0.03	2.1	5.3
Sweet sorghum	77.2	18.1	4.7	47.3	5.8	0.4	41.7	0.1	57.8	0.7	0.5	9	2.7	8.2	1.5	0.05	3	3
Kenaf	79.4	17.0	3.6	46.6	5.8	1	42.8	0.1	6.6	1.8	1.2	30.8	6	13.3	1.3	0.08	5.7	2.7

The correlations between the gasification rate and fuel characteristics were also studied by incorporating the data from a recent publication by Kurkela et al. (2006) which included a larger selection of biomass fuels (some from India). The correlations between the fuel characteristics and the instantaneous reaction rate r” measured in 1 bar steam at 850 °C were determined with the Correlation Tool of Data Analysis in Microsoft Excel 2003. The results are shown in Table 9. According to the results there was some correlation between rate and fuel characteristic – e.g. the silica content in ash (as noted earlier, correlation coefficient $r = -0.54$) and the sum of alkali metal oxides and calcium oxide in ash ($r = -0.67$). The correlations nevertheless appeared to be fairly vague indicating that there are several factors affecting the rate.

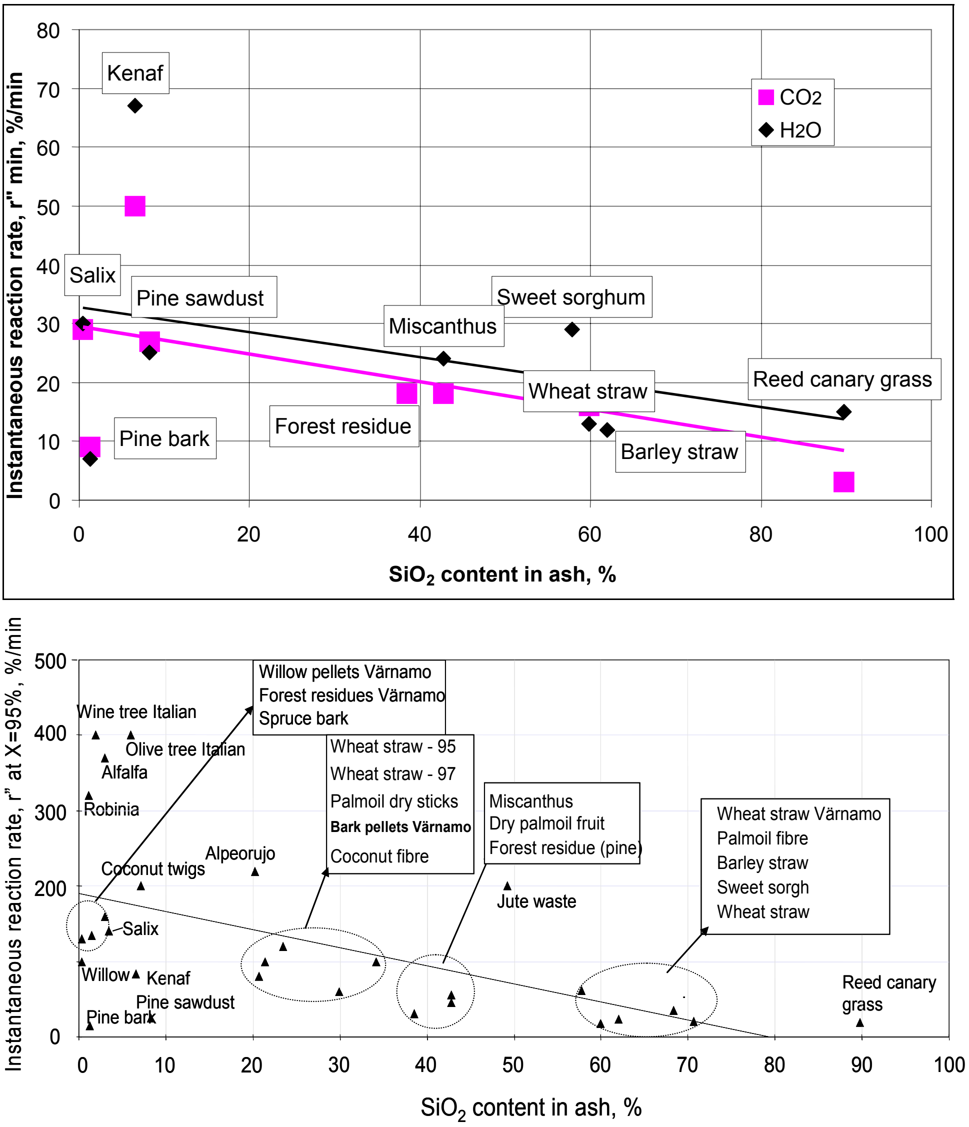

Figure 12. Dependence of gasification reaction rates (the minimum rate in the upper graph) of biomass fuels in 1 bar steam and in 1 bar CO_2 (as indicated from Table 8) on silicon content in ash. Additional biomass fuels are included (as reported by Kurkela et al. 2006 and presented in Table 9) in the lower graph (the rate at 95% fuel conversion and in 1 bar steam).

Table 9. Correlation between fuel characteristics and the instantaneous reaction rate at 95% fuel conversion and in 1 bar steam (values combined with those from Paper II and from Kurkela et al. 2006).

Biomass fuel	**r" at X = 95% (%/min)**	**Fuel characteristics**	**Correlation coefficient for r" at X=95% (%/min)**
Pine sawdust	25	Ash, % d.	-0.022
Pine bark	13	Volatile matter, % d.	0.070
Spruce bark	135	Fixed carbon, % d.	-0.065
Forest residue (pine)	30	C, % d.	-0.021
Salix	130	H, % d.	0.051
Willow	100	N, % d.	0.249
Wheat straw	17	Odiff, % d.	0.008
Wheat straw -95	100	S, % d.	-0.102
Wheat straw -97	60	Na, ppm, d.	0.084
Barley straw	23	K, ppm, d.	0.243
Reed canary grass	19	Cl, ppm, d.	-0.006
Miscanthus	45	Na+K, ppm, d.	0.251
Sweet sorghum	62	*in ash, %*	
Kenaf	83	SiO_2	-0.544
Alpeorujo (Spain)	220	Al_2O_3	-0.152
Alfalfa	370	Fe_2O_3	-0.073
Indian biomass fuels		CaO	0.514
Palm oil dry sticks	120	MgO	0.453
Coconut fibre	80	K_2O	0.430
Coconut twigs	200	Na_2O	0.185
Palm oil fibre	35	TiO_2	-0.073
Dry palm oil fruit	55	SO_3	0.346
Jute waste	200	P_2O_5	0.305
Värnamo biomass fuels		Na_2O+K_2O	0.447
Forest residues	140	Na_2O+K_2O+CaO	0.669
Bark pellets	100	$Na_2O+K_2O+CaO+MgO$	0.666
Willow pellets	160	$CaO+K_2O$	0.658
Wheat straw	20	$(Na_2O+K_2O)/SiO_2$	0.171
Italian biomass fuels		$(Na_2O+K_2O+CaO)/SiO_2$	0.187
Olive tree	400	$SiO_2+Al_2O_3$	-0.550
Wine tree	400		
Robinia	320		

d. = dry matter

The role of silicon is theorised in the following: Biomass fuels contain very variable amounts of silicon, as shown in Table 1 and also reported by Osman (1982) and Kurkela et al. (2006). Silicon occurs in plants dominantly as amorphous silica hydrate $SiO_2 \cdot nH_2O$ or as polymerised silicic acid (Mengel & Kirkby 1982), and silicon distribution is highly dependent on the plant species. Silicon flocculates in cell structures protecting and supporting the plant (like straw). Silicon may also migrate to biomass fuels from extraneous sources like clays and sand e.g. during harvesting. In fuel use, silicon may suppress the reactivity. The suppressing effect of silicon has been observed in the gasification of rice husks as a reduction in carbon conversion (Ganesh et al. 1992). Kannan & Richards (1990) discovered the reactivity-reducing effect of silicon when they added fine quartz powder to well-gasifiable biomass and the gasification reactivity collapsed. In the present work, the amount of water-soluble potassium of straw was observed to decrease above the conversion level of 50% (Figure 2 in Paper VIII). Since straws contain high content of silicon (Table 8 as well as Tables 2 and 4 in Paper VIII), we can assume that potassium reacts with silicon to potassium silicate and loses its catalytic activity. In support of this assumption, the total amount of potassium decreased slightly with the increase in conversion (Figure 2 in Paper VIII).

In fuels with low silicon content, Kannan & Richards (1990) observed a correlation between reaction rate and the K + Ca content. A similar correlation was found in the material published by Kurkela et al. (2006): the correlation coefficient r of 0.79 was calculated between the potassium content (measured directly in fuel) and the gasification rate (presented in Table 9) in biomass fuels with less than 10% silica in ash. The correlation coefficient was a little higher, 0.83, when calcium was added to potassium (calcium was not analysed directly, but calculated from the chemical composition of ash).

Influence of heat treatment on reactivity

The significance of pyrolysis *in situ* on reactivity was reported in Paper VI and shown in Figure 13. As can be seen, in gasification reactivity experiments with birch wood the heat treatment with slow heating rate and high char preparation temperature (higher than the gasification temperature) lowered the char reactivity. The SHT (slow heat treatment) char was prepared, in a similar way to that reported by Barrio et al. 2001 and Barrio 2002, by heating birch wood sawdust in an inert gas phase of nitrogen (N_2) at a heating rate of 24 °C/min to 600 °C and keeping it at this temperature for 30 minutes. Thereafter the sample was held at 200 °C for 10 min, and then heated at 24 °C/min to 1000 °C where it was kept for 30 minutes. This char was compared with a char produced by with the volatile matter (VM) method and *in situ* method. In the VM method, the sample was put in a crucible, which was used in measurement of the volatile matter content. The crucible was inserted into a furnace heated to 850°C, where it was kept for two holding times: 1–2 minutes and 3 minutes.

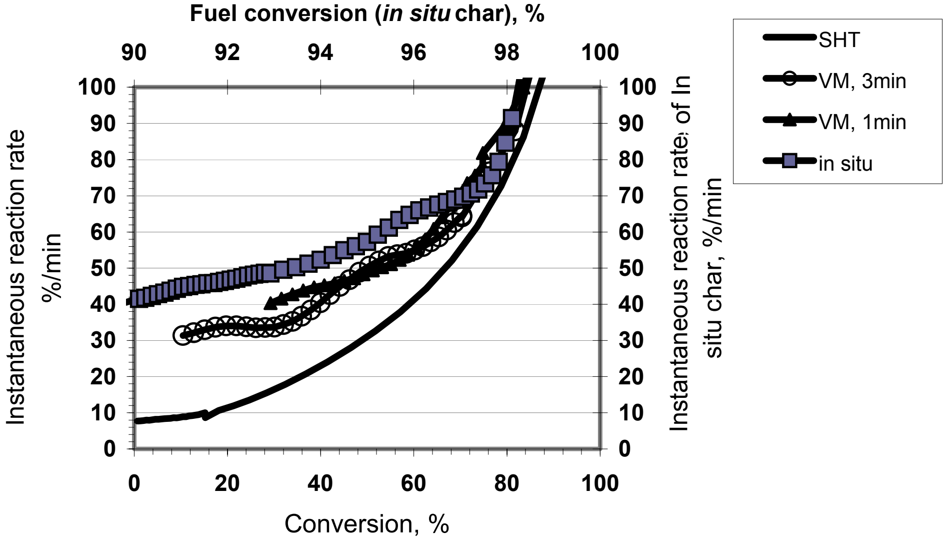

Figure 13. Effect of high char preparation temperature on char gasification reactivity. SHT = slow heat treatment, VM = volatile matter method (see text, Paper VI).

CO gas can be used to ensure oxygen-free conditions in the gas atmosphere during pyrolysis when char samples are produced for the reactivity measurement. In a test of the effect of CO gas with black liquor char (Paper V), a char prepared with CO treatment was found to be much less reactive under pressure in CO_2 gasification than a char prepared without CO treatment. However this result was not obtained in pressurised steam gasification nor in atmospheric gasification of CO_2 and steam.

Evaluation of the achievable conversion

The rate versus conversion, i.e., the rate profile, can qualitatively be used to evaluate the achievable conversion of carbon in a gasification process. If the instantaneous reaction rate does not increase with the conversion, it is more difficult to achieve 100% conversion than when the rate increases (Figure 16 below). Also, the profile was observed to be of significance in ash sintering. If the rate decreased as a function of the conversion, ash sintering was hindered. This observation was made when a wheat straw was gasified in a fluidised bed that did not have ash agglomeration problems (Skrifvars et al. 1996, Kurkela et al. 1996). The straw had a decreasing reactivity profile, as depicted in Figure 25, indicating that the residual char prevented the ash particles from fusing together.

The rate at other temperatures can be estimated on the basis of the activation energy, which was found to be mainly 190–230 kJ/mol for char gasification of various fuels (Figure 15). Literature values for the activation energy lie between 180 and 270 kJ/mol, as reported by Barrio et al. 2001 and Barrio 2002 in a summary of the results for diverse biomasses reported by several authors. The effect of mass transfer on the reactivity measurements can be seen in Figure 15 (Paper I) as a deviation from the linear relationship of the logarithm of the reaction rate and reciprocal temperature. The effect was taken into account by a mathematical expression, as presented in Paper I. For the mathematical calculations, it was necessary to give a single value for the reactivity, and the reciprocal value of the time needed to achieve 50% char ash-free conversion was selected. Thus, R in Paper I is 1/*time*, where time is in minutes.

In measurements of kinetic parameters such as activation energy, it is necessary to know when the chemical reaction is controlling the rate. The diffusion effect can be seen as a deviation from the linear Arrhenius relationship between logarithm r and 1/T (temperature in kelvins), as shown schematically in Figure 14. In the calculations of the activation energy, the diffusion effects were taken into account by using a resistance model, as described in Paper I. The model was solved by finding the best fit according to least squares method.

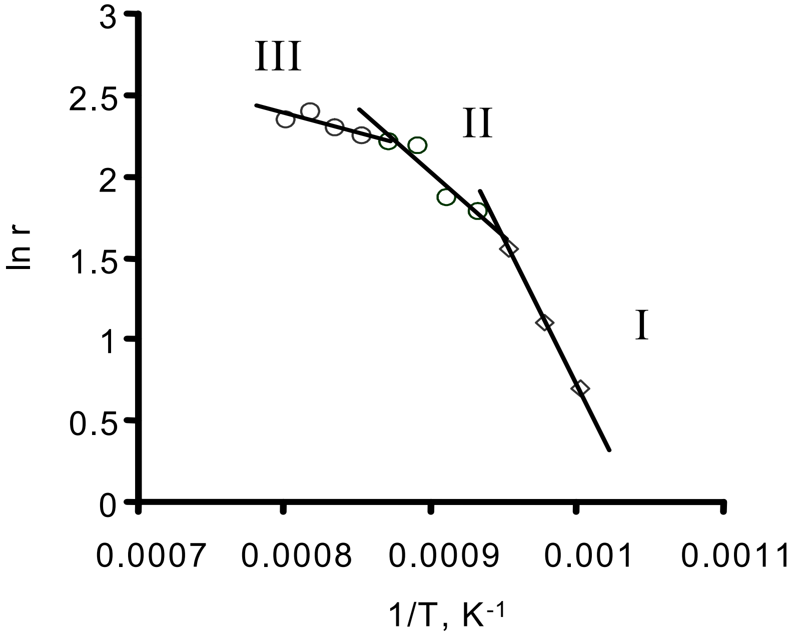

Figure 14. Control regimes in ln r vs. *1/T diagram in solid gas reaction as measured in a thermobalance (arbitrary data points). Roman numerals indicate the approximate controlling regimes expressed as linear regression lines: I = chemical reaction control, II = pore diffusion control, III = film diffusion control.*

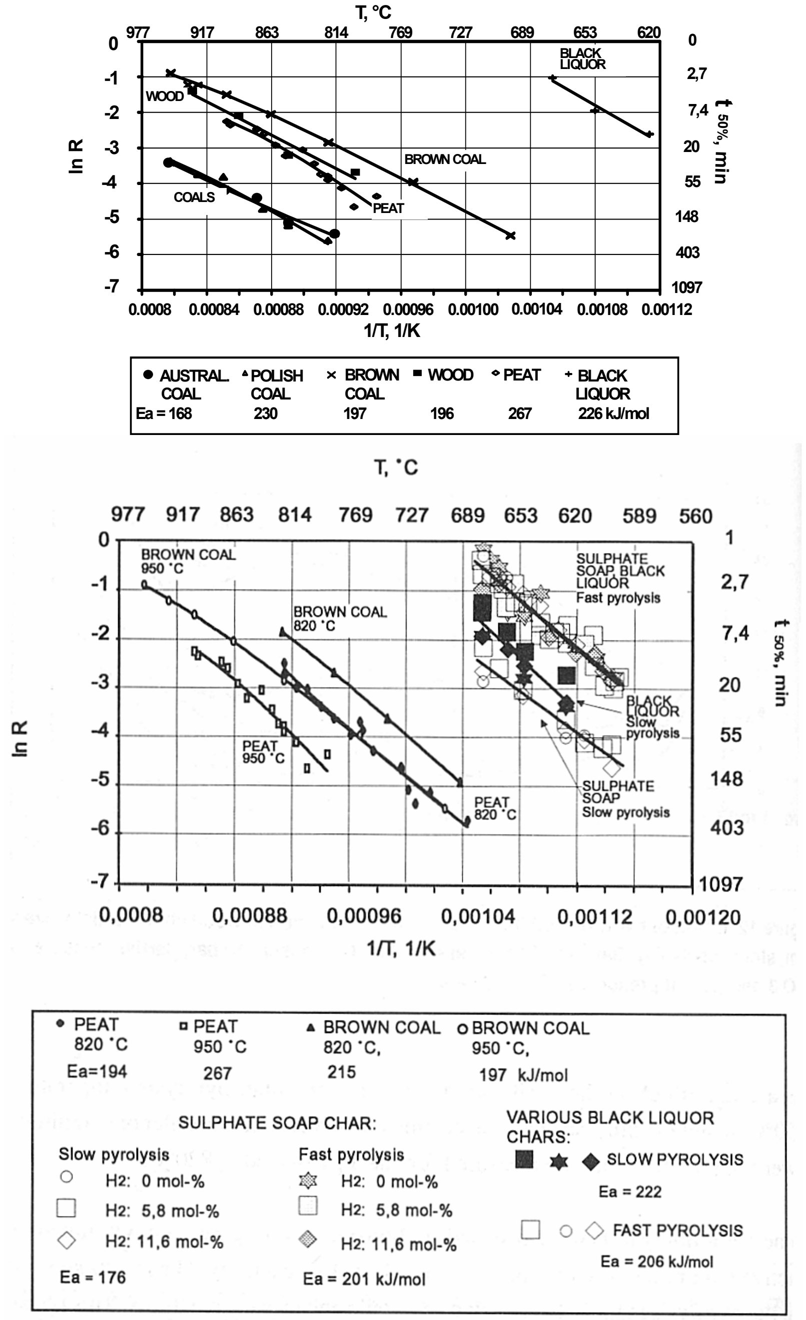

Figure 15. Comparison of gasification reactivities of the solid fuel chars (upper graph from Paper I and lower from Moilanen et al. 1993), Ea = activation energy (here, exceptionally, R = 1/time, min^{-1} instead of %/min).

According to Kurkela (1996) the conversion in a gasifier can be calculated in two ways:

- On the basis of gas evolution: i.e., mass flow rate of carbon in product gas and tars divided by the mass flow rate of carbon in fuel
- On the basis of unreacted carbon: i.e., mass flow rate of carbon in output solid products divided by the mass flow rate of carbon in fuel

Conversion can be estimated from the thermogravimetric data as follows: The instantaneous reaction rate can be expressed as

$$r'' = \frac{dX}{dt}(1-X)^{-1} \tag{7}$$

as is generally presented in the literature, e.g. by Johnson (1974), van Heek and Mühlen (1991) and Sowa (1991). This, after integration, gives the conversion as a function of time:

$$X = 1 - e^{-r''t} \tag{8}$$

Note. In the formulas (7) and (8) the terms r” and X are fractional instead of per cent; thus, r” is 1/min and X is fractional conversion; t is time.

Figure 16 shows how the conversion varies as a function of time for different instantaneous reaction rates calculated with formula (8). It can be seen that when the instantaneous reaction rate is 100 %/min expressed as an average value, total conversion is achieved in about five minutes. This is the case, when the rate is constant as a function of conversion. If the rate were to increase with conversion the time would be shorter, and if it were to decrease the time would be longer.

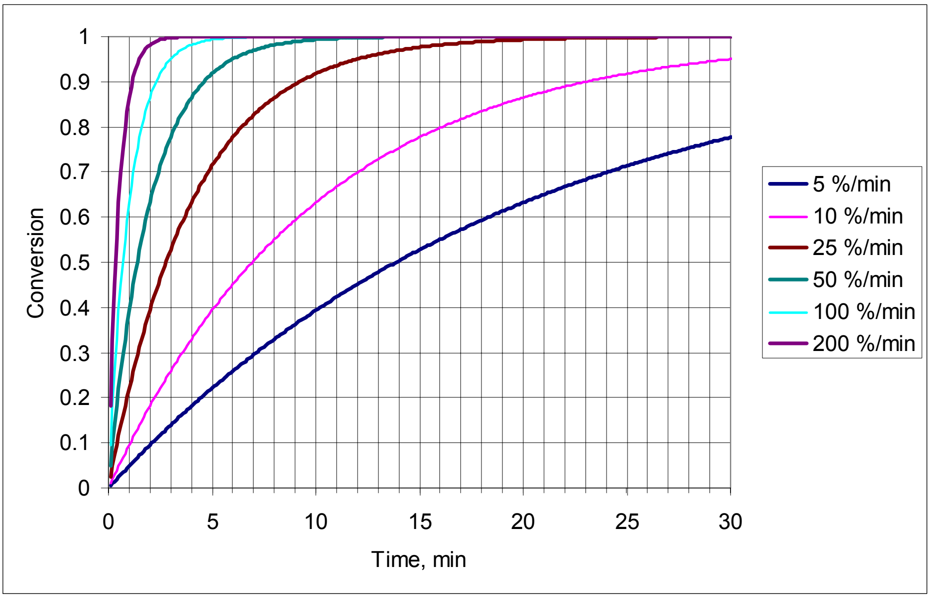

Figure 16. Conversion (fractional) vs. *time at different instantaneous reaction rates. Note: here zero conversion corresponds to the value of fuel conversion (from 80% to 90%) immediately after the pyrolysis.*

Comparison of the results of the thermobalance measurements with the results of fluidised bed gasification was based on the reaction rate measured in TG and on calculations of the carbon conversions from the material balances of the fluidised bed reactor tests (Paper II). The differences in the gasification behaviour of the various feedstocks used in the fluidised bed measurements can be seen in the data presented in Figure 17. The two bituminous coals behaved similarly, while for the other fuels there were clear correlations between carbon conversion and the temperature. The low reactivity, as for the coals, was seen in the several hours that it took for steady-state char inventory to be achieved in the bed, freeboard and recycling loop of the reactor.

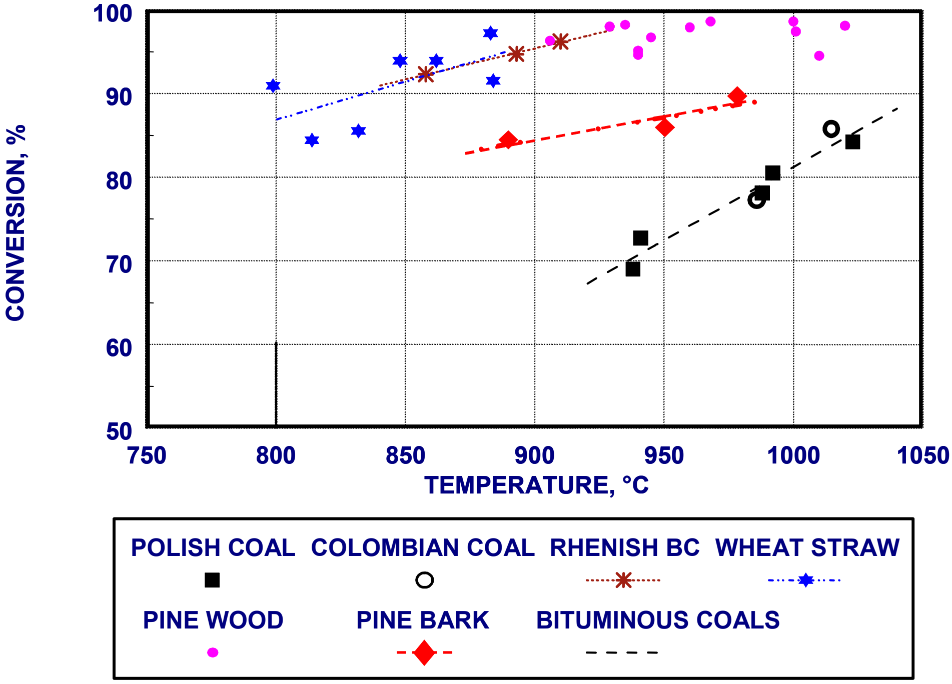

Figure 17. Carbon conversions achieved in a fluidised bed gasifier as a function of the freeboard temperature (BC = brown coal, Paper II).

Each of the biomass fuels exhibited distinct gasification behaviour. In the gasification of pine wood, high carbon conversions were achieved at relatively low temperatures. The complete gasification of bark and straw was more difficult. In the case of straw gasification, high conversion efficiencies were achieved above 850ºC, but sintering of the ash caused severe operational problems. Ash sintering was not a problem with the pine bark, but its reactivity was clearly lower than that of wood or straw. Obtaining high conversion efficiencies with pine bark thus requires high gasification temperatures and efficient recycling of elutriated fines. The brown coal is an excellent feedstock for fluidised-bed gasification; over 95% carbon conversion was reached at about 900ºC. This fuel also exhibited a high reactivity when measured in the thermobalance (Paper I and Figure 15). Table 10 shows the reactivity measured in the thermobalance compared with the achieved conversion in the fluidised bed gasification of the respective fuel.

Table 10. Comparison of the char reactivity values measured in a thermobalance (TG) and the achieved carbon conversion in the fluidised bed gasification (FB) presented in Figure 17. The reactivities are for steam at 1 bar and 850 °C.

Fuel	**TG r" min. (%/min)**	**FB %**
Pine sawdust	25	95
Pine bark	7	82
Wheat straw	13	92
Brown coal	24*	92
Bituminous coal	0.05**	55***

* calculated using Ea value of 197 kJ/mol (Figure 15) from the value of 60%/min measured in steam at 1 bar at 900°C by Mühlen (1990)

** Konttinen et al. (2006b)

*** extrapolated from the data of Figure 17

The results obtained from the thermobalance can be considered to represent the primary reactivity of a fuel, but the conversion in the gasifier is affected by many factors, including the partial pressure of the gasification agent, product gas inhibition, fragmentation and feedstock particle size distribution. Modelling is required, if all these parameters are to be included. Modelling has recently been introduced for biomass and waste-based fuels in the building of a predictor by Konttinen et al. (2003, 2006a and 2006b) and Moilanen & Konttinen (2006).

5.1.2 Reactivity of SRF

The gasification reactivity of SRFs was found to be similar to that of paper and higher than that of wood (Figure 18, Moilanen & Konttinen 2006, Cozzani 2000). Also here, as noted above for chlorine analysis (Figure 2), the test results showed broad scattering before the samples were extracted by sample division (Figure 19).

Figures 20–22 present the gasification rates in steam and CO_2. The inhibiting effects of H_2 and CO are included. As can be seen, there was a difference in the reactivity behaviour of the various SRF qualities. Also the inhibition effect was fairly strong for both H_2 and CO.

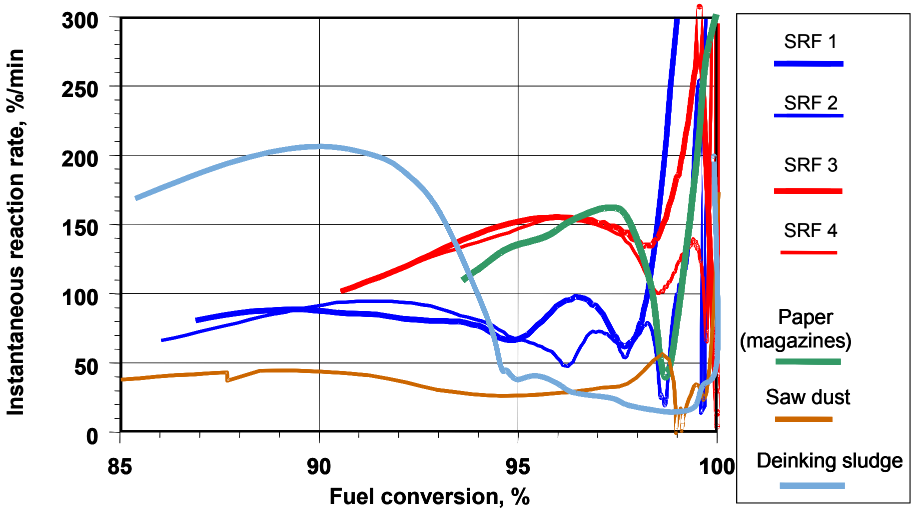

Figure 18. Comparison of gasification reactivity of SRF (various SRF samples) with that of paper, sawdust and deinking sludge.

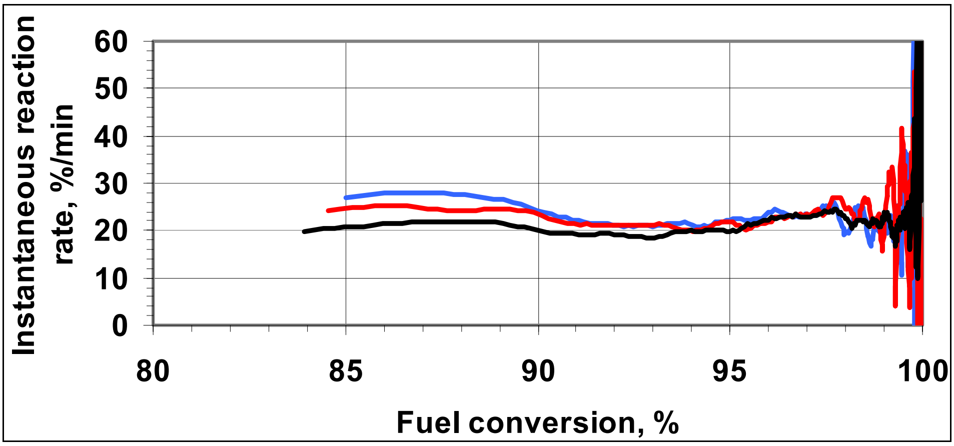

Figure 19. The gasification reactivity test results for three SRF samples taken by sample division (measured in 1 bar CO_2 at 800°C).

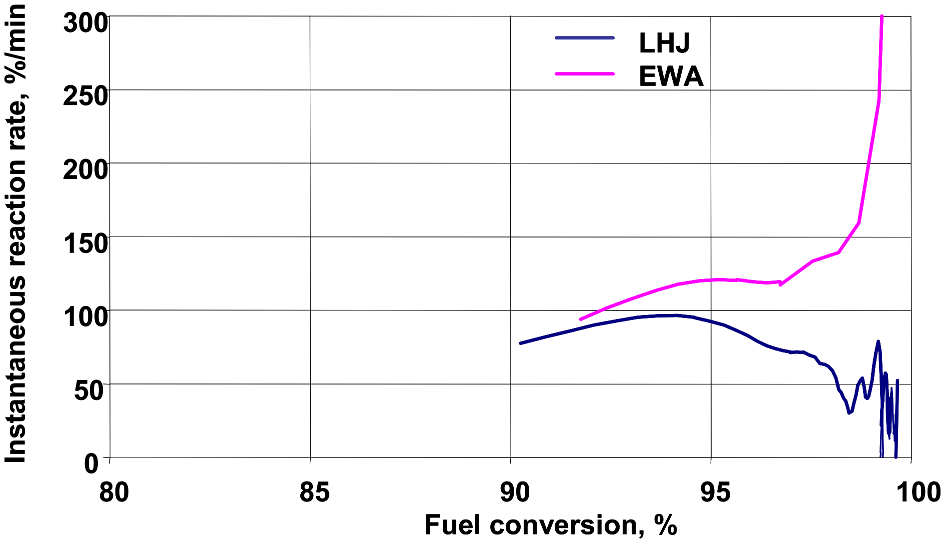

Figure 20. Steam gasification reactivity of two SRF samples (LHJ and EWA) at 850 °C.

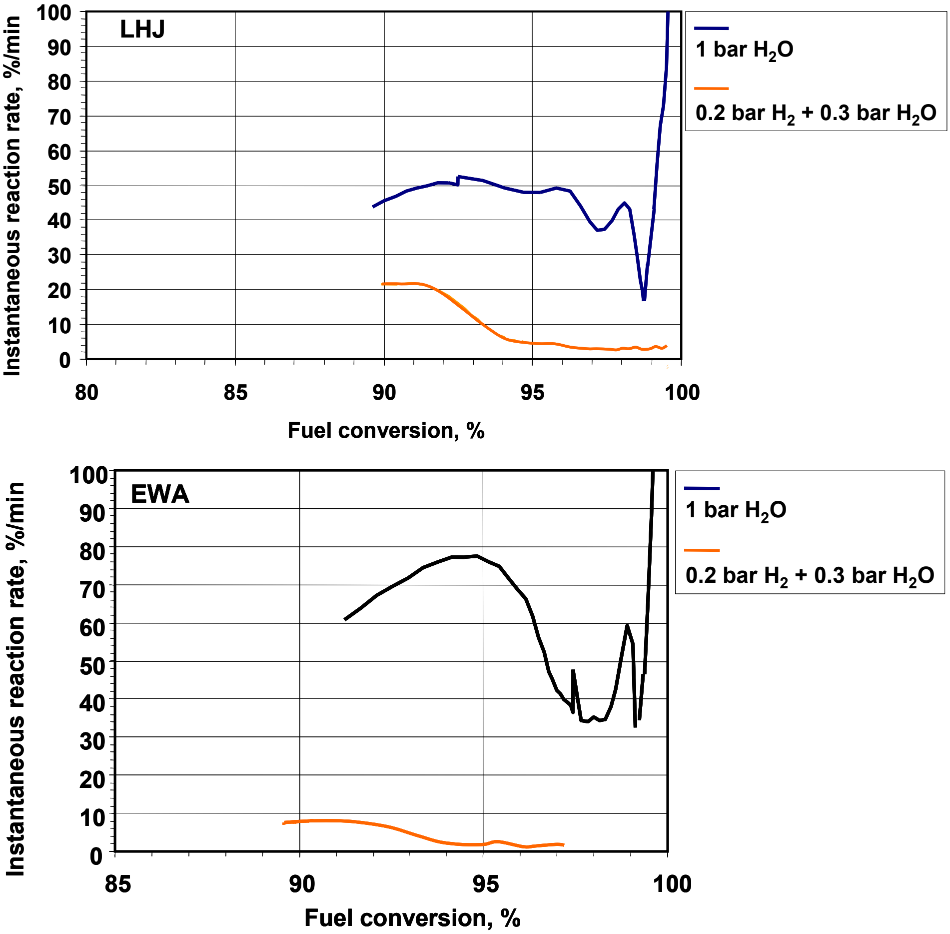

Figure 21. Steam gasification reactivity of two SRF samples (LHJ and EWA) and the inhibition effect of H_2 at 800 °C.

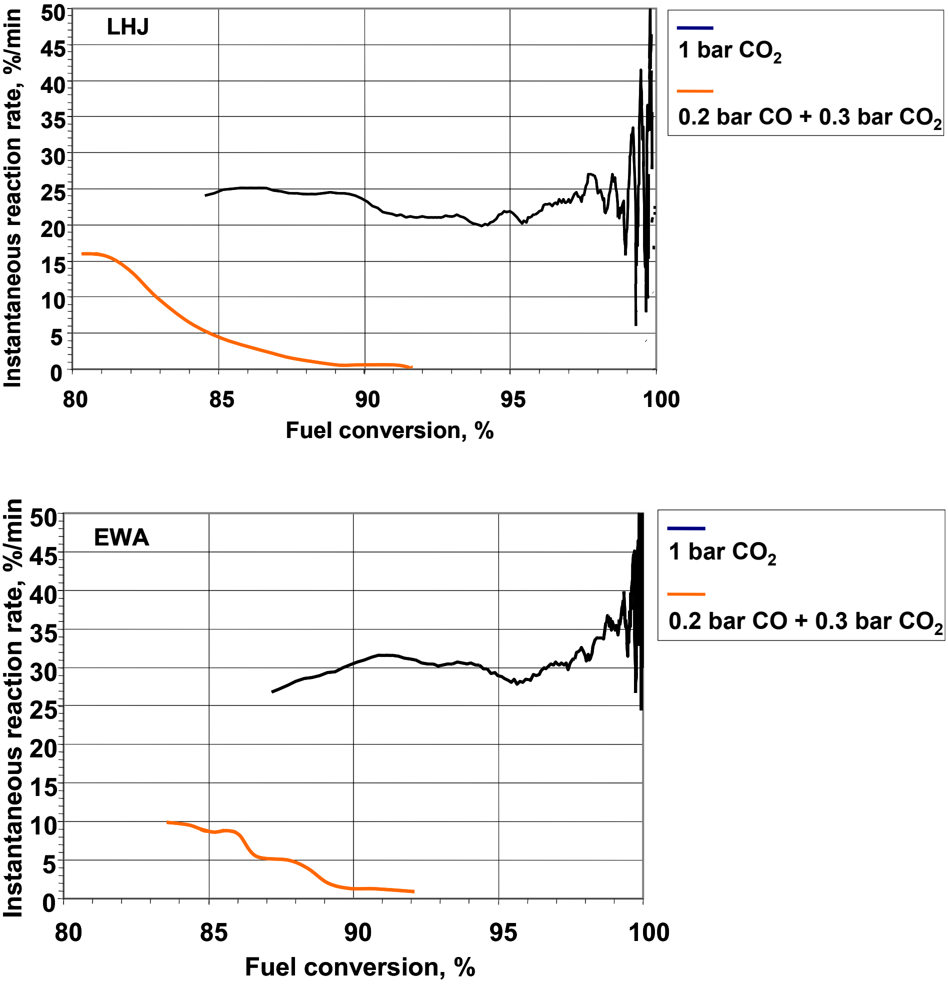

Figure 22. CO_2 gasification reactivity of two SRF samples (LHJ and EWA) and the inhibition effect of CO at 800 °C.

5.2 Ash sintering of biomass fuels

The results of the ash sintering measured for a selection of biomasses in the thermobalance are presented in Table 11.

Table 11. Conditions in the thermobalance and degree of sintering of ash residue determined by microscopy (Paper VII).

Biomass	Temperature and gasification agent				
	850 °C			750 °C	
	H_2O		CO_2	H_2O	
	1 bar	30 bar	1 bar	1 bar	30 bar
Pine bark	o	o	na.	na.	na.
Pine sawdust (ash amount small)	***	***	o	o	o
Spruce bark	o	***	*	na.	***
Forest residue B, total	o	o	na.	o	na.
Forest residue B:					
– bark	na.	***	na.	na.	***
– needles	o	*	na.	na.	o
– stem	o	o	na.	na.	na.
Finnish willow	o	***	***	o	***
Swedish willow	o	***	**	o	**
Finnish wheat straw	***	***	**	@	***
Danish wheat straw A (-93)	***	***	na.	na.	**
Danish wheat straw B (-93)	***	***	*	*	*
Danish wheat straw –95	***	***	*	**(*)	na.
Alfalfa	**	***	*	*	***

o no sintering; * slightly sintered; ** moderately sintered; *** completely sintered; @ not totally gasified; na.: not analysed

For some of the biomasses, ash sintering was much stronger under pressurised conditions than at atmospheric pressure. This effect of pressure has also been reported by Rosen et al. (1999). Willows (Finnish and Swedish), spruce bark and alfalfa all exhibited sensitivity to pressure. Under 30 bar steam the ash residues were sintered completely when willow and spruce bark samples were gasified at 850 °C, and the same result was obtained at 750°C. This was despite the standardised ash fusion tests which for willow had suggested there should be no problems. According to the tests, the melting temperatures were much above 1000 ºC and so above the operating temperature of the gasifier (Wilén et al. 1996). With alfalfa, the ash residue was completely sintered at 700 °C and lower (Figure 1 in Paper VIII). In contrast to this no sintering was detected for willow or spruce at 850 °C and atmospheric pressure and the sintering for alfalfa was clearly weaker. This intense melting behaviour under pressure could be related to the carbonates that form at high pressure. The reasons for sintering were not explored in this work.

Sintering behaviour in gasification in CO_2 was clearly different from that in steam. At 850 °C and 1 bar pressure CO_2, the ash residue of willow was strongly sintered, but the ash of spruce bark and alfalfa only slightly The reason for the only slight sintering was assumed to be the lack of silicon in these ashes, while calcium and potassium contents were relatively high. The carbonate chemistry involved in the ash under pressure may be relevant, as noted above and discussed in Paper VIII. Phase diagrams presented in the literature show that a mixture of calcium and potassium carbonates forms a eutectic at about 750 °C (Levin et al. 1985). Carbonates can form in the ash during gasification, and they decompose slowly, especially at higher CO_2 partial pressures.

As presented in Paper VIII, the behaviour of alfalfa was such as to suggest that chemical compounds other than carbonates were involved in sintering. One explanation may be in the chlorine chemistry. The chlorine content of Danish straw ashes prepared at 550 ºC in a laboratory furnace may be as high as 10% as reported in Table 4 of Paper VIII, and mixtures of compounds $CaCl_2$ and KCl, and also KCl and K_2CO_3, are possible. The former mixture has a eutectic of 595 °C and the latter a eutectic of 640 °C (Levin et al. 1985).

The ash of pine bark differed from that of spruce bark. Although pine and spruce barks are fairly similar with respect to the chemical composition of their ash, and both are low in silica (Table 2 in Paper VIII), no sintering was observed for pine bark, while strong sintering took place in spruce bark under pressure. Similar behaviour to that of pine bark was observed for willow bark, as presented in Figure 23. This observation for pine bark was consistent with the results of tests in the fluidised-bed gasifier, where it showed no ash problems. In the fluidised-bed gasification tests of the spruce-based forest residues at VTT, ash deposits were formed in the cyclone tube of the reactor. To discover the reason for this, the feedstock was separated into needles, bark and stem. The results in pressurised gasification suggested that the spruce bark was the most critical component of the forest residue feedstock. The bark ash (forest residue B in Table 11) showed strong sintering under pressure, while the ash from needles appeared to have only a weak sintering tendency, and stem ash showed no signs of sintering. Similarly, no sintering was found for willow bark or heart wood, as displayed in Figure 23.

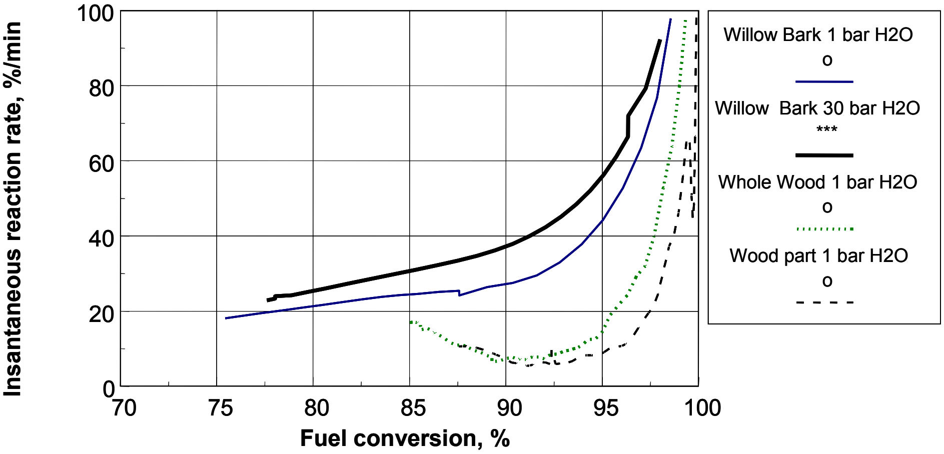

Figure 23. Steam gasification reactivity of willow bark and heartwood measured at 750°C, ash sintering indicated in the graphs.

Wheat straw ash typically showed strong agglomeration in the fluidised bed gasification tests performed earlier at VTT, but this behaviour also varied with the quality of the straw used as feedstock (Kurkela et al. 1996). The wheat straw ashes sintered strongly when gasified at 850 °C under steam at both 1 bar and 30 bar. Strong sintering was observed in certain samples even at 750 °C (Tables 2 and 4 in Paper VIII).

The relationship between the chemical composition, ash sintering and gasification reactivity of wheat straw was studied more closely in Paper VII. The reactivity showed that the gasification rate may increase or decrease as a function of conversion, depending on the quality of the straw. The difference seems to be associated with the ratio of potassium to silicon in the ash. Potassium is a strong catalyst in gasification reactions, and the formation of potassium silicate could decrease its activity (Kannan & Richards 1990). Gasification reactivity behaviour has been observed to affect the sintering of ash in such a way that slower gasification rate prolongs the achievement of the total conversion and, as a consequence, ash is formed more slowly and the carbon material prevents ash particles from agglomerating. This finding suggests that control of the carbon conversion may help to slow ash sintering in gasifiers.

Figure 24 (from Paper VII) shows that the time required to achieve ash conversion of 100% was more than four times as long for Straw A, which showed a decreasing trend in the gasification rate, than for Straw B, which displayed an upwards trend. However, when straw A was gasified completely, the resulting ash residue was totally sintered (see Table 2 of Paper VII). The effect of potassium content on the reactivity was studied by washing the straw samples with distilled water. When Straw B was washed with water, it behaved similarly to Straw A (Figure 25). The decrease in gasification reactivity through leaching of potassium from straw has also been reported by Henriksen et al. (1997).

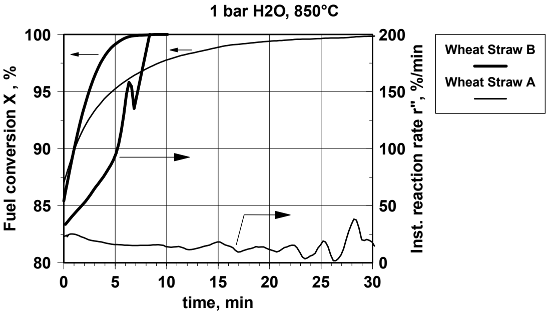

Figure 24. Development of the gasification rate of straw A and straw B and conversion as a function of time measured at 1 bar H_2O and 850 °C (Paper VII).

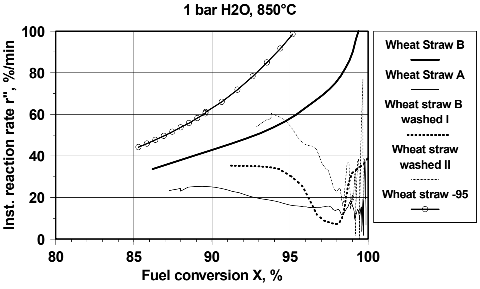

Figure 25. Gasification reactivity of unwashed and washed straws measured at 1 bar H_2O and 850 °C (Paper VII).

The behaviour of potassium with silicon during straw gasification was studied more closely in a thermobalance (Paper VIII) by measuring the relationship between water-soluble potassium and insoluble potassium (the insoluble potassium was assumed to represent potassium silicate). The gasification was stopped at certain conversion levels in the thermobalance, and the samples were leached with water to determine the water-soluble potassium and the total potassium. The results (Figure 2 in Paper VIII) showed that the amount of soluble potassium was relatively constant to the conversion level of 50%, after which it decreased to about 15% of the original value.

Biomass fuels with silica-rich ash (like wheat straw) tend to produce a viscous potassium silicate slag with a low melting point. Risnes et al. (2003) showed that abundant enrichment of the calcium of inorganic straw ash in general leads to increased formation of calcium silicates and reduced sintering tendency. The same result was obtained in our thermobalance tests.

Ash sintering in the fluidised bed reactor

The laboratory findings, i.e. the thermobalance tests investigating the ash sintering behaviour, were further explored with different straws in an atmospheric fluidised bed (Papers VII and VIII). The laboratory findings for ash sintering appeared in various ways in real scale since several factors were affecting the ash depositing in the reactor. Van der Drift & Olsen (1999) likewise observed that there are several factors affecting the ash deposit formation in the process. Each time sintering (even weak) was detected in the ash residue of the TG tests, agglomerates or deposits were found in the reactor. The strongest ash sintering was observed for wheat straw, both in the thermobalance and in the reactor. In the fluidised bed tests carried out for wheat straw, the bed agglomeration was also influenced by the bed material: against expectation, the agglomeration tended to be stronger in the alumina bed material than in the limestone or dolomite bed. Agglomeration in limestone and dolomite beds was observed to depend on the calcination of these materials. According to the phase diagrams, a partial melting could also take place in limestone and dolomite, but the surfaces of these particles were not smooth (unlike those of corundum, the alumina grade used in the tests). In addition, the surfaces eroded easily. This erosion was assumed to be the reason for the removal of alkalis from the reactor when lime bed material was used (Paper VIII and Kurkela et al. 2006). At the same time, the potassium, and also chlorine, were concentrated in the cyclone and particularly the filter dusts. One reason for the concentration in the filter dust may have been that the surfaces of the limestone particles containing potassium were fragmented by attrition and thus escaped from the bed. Use of limestone together with the advanced feeding enabled trouble-free straw gasification in the circulating fluidised bed (Pat. WO0011115 2000).

6. Summary and conclusions

The results of the studies on reactivity and ash sintering of biomass and waste-based fuels, as presented above and in the appended papers, are summarised in the following.

6.1 Reactivity

In testing the reactivity, the temperature and pressure ranges, heating rates and gaseous environment for the thermobalance should be selected so as to be relevant for the conditions existing in fluidised bed gasifiers, i.e. fast heating rate for the fuel and no heat treatment of the char. In this work, the sample was pyrolysed in the thermobalance *in situ* to ensure a fast heating rate during the pyrolysis. The pyrolysis took place while the the sample was being lowered into the thermobalance reactor. The time was approximately 7 to 10 seconds. From the weight-time curve the reactivity can be expressed as instantaneous reaction rate versus conversion; and thus the rate versus conversion, i.e., the rate profile, can be seen.

Gasification reactivity is easily limited by mass transfer in a thermobalance and the result will be misleading if only a few points are measured. In Paper I, the limiting mechanism was studied by light microscopy and by fitting curves to the experimental data, taking into account the mass transfer. Average activation energy of 230 kJ/mol was measured for several solid fuels, ranging from 196 for wood to 265 for peat char. The activation energy for black liquor, which is an extremely reactive fuel, was close to 226 kJ/mol. The activation energy for sawdust was 217 kJ/mol in steam and 229 kJ/mol in CO_2 (see also Paper IV). These results are in agreement with literature values, although much lower activation energies have also been presented. The results of this work also showed that gasification reactivity of biomasses varies widely. But comparison of results obtained in a PTG and a pressurised fluidised bed gasifier (PFB) showed that the gasification rates measured in a PTG are of the same order as the reactivities in a PFB based on achieved carbon conversion calculations (Paper II).

The complexity of gasification behaviour was demonstrated with peat (Paper III). At about 50% char conversion the steam gasification rate of peat char was slightly higher than the CO_2 gasification rate, but at higher conversion the order was reversed. Demineralisation of peat decreased the reactivity, and also eliminated the negative burn-off behaviour observed in steam gasification. The presence of product gases H_2 and CO slowed the gasification rate of peat char almost to zero. In peat, the catalytic behaviour of iron which was present in high content in the ash (54% as Fe_2O_3,), was assumed to be the reason for the result.

The most significant conclusion in regard to the reactivity of biomass fuels (Paper IV) was that the determination of characteristics that describe gasification reactivity (in particular, in gas containing product gas) of biomass fuels requires detailed knowledge of fuel structure and chemistry. The deviations found, such as reduction of reaction rate at increased pressure and differences in the gasification behaviour of CO_2 - CO and H_2O - H_2 mixtures, are due to the behaviour of ash-forming substances in gasification.

The study on black liquor (Paper V) focused on how to achieve good gasification data. Obtaining good data depends on a uniform and constant temperature of the sample, which, in turn, requires that the sample be kept in an inert atmosphere for a certain period of time, e.g. 400 s, before introduction to the gasifying atmosphere. CO can also be added to stabilise the sample. However, the addition of carbon monoxide to the "inert" atmosphere clearly retarded the pressurised CO_2 gasification rate though not the rate for steam.

Heating rate during the pyrolysis stage was studied with wood (Paper VI) by simulating the situation when feedstock enters a gasifier. High temperature (1000 °C) treatment with slow pyrolysis produced char that was significantly less reactive at low conversion than chars produced in fast pyrolysis i.e. pyrolysis *in situ*. Exceptionally, in the fast pyrolysis of large wood pieces, the char was of lower reactivity, perhaps due to a different structure of char formed from large pieces. Similarly, large pieces of char reacted more slowly than small, here perhaps due to the inhibiting effect of the product gases formed inside the pieces. In both cases there was a correlation between the reaction rate and the dimension and the outer surface area of the original wood piece.

The gasification reactivity of solid recovered fuels was found to be similar to that of paper and higher than that of wood. Test results showed broad scattering before the samples were extracted by the method of sample division. Thus, for waste-based fuels, proper sampling is essential if the results are to be reliable.

6.2 Ash sintering

After the gasification is complete, the ash residue is inspected under a microscope to detect possible molten phases and sintering. A separate ash does not need to be prepared in the laboratory. The ash residue can be classified as non-sintered ash residue, partly sintered ash and totally sintered or fused ash. Whenever sintering (even weak) is detected in the ash residue of TG tests, agglomerates or deposits will likely be found somewhere in the reactor. If the reaction rate decreases with conversion, the ash sintering will be hindered so that agglomeration takes place slower than with fuels having a rising rate profile.

As reported in Papers VII and VIII characteristic data on ash behaviour can be obtained by thermobalance tests and can be used for planning run conditions for tests with pilot or PDU (process development unit) equipment. Ash sintering was sometimes much stronger in pressurised conditions than under atmospheric pressure. This finding appears to be related to the silicon content in ash: when the silicon content is low the ash sintering is stronger in pressurised than in atmospheric conditions. However, the chemistry needs to be studied in more detail to understand the behaviour. The water-soluble constituents of straw (potassium, calcium) affect the relationship between ash sintering and reactivity.

6.3 The method in brief

A method has been described for obtaining specific information about biomass and waste-based fuels intended for use as feedstock in atmospheric and pressurised gasification. Information is produced about the gasification reactivity related to the achievable conversion of carbon in the process, as well as about the ash sintering and deposition that may hamper the process operation. Although the gasification reactivity and ash sintering of the fuels are highly complex phenomena, the method is simply based on thermogravimetry, and the reactivity and sintering behaviour are determined in a single thermobalance test. The pre-treatment steps, like heating during pyrolysis and stabilisation by hot treatment, are of significance for the result. Total pressure must be included as a parameter.

A special advantage of the method is that if a gasifier is tuned for a certain biomass feedstock and another biomass or waste-based fuel is then introduced, the reactivity and sintering behaviour of the new fuel can be estimated in relation to the reactivity and ash sintering of the first.

The following recommendations are made for the characterisation of gasification reactivity and ash sintering by the new method:

- Use a fast heating rate, i.e. pyrolysis *in situ.*
- Carry out first test at 850 ºC in 1 bar steam.
- If ash is sintered, carry out a measurement at a lower temperature, e.g. at 750 °C; if ash is not sintered and the reactivity is low, use a higher temperature (an instantaneous reaction rate greater than 50%/min (average) is suggested to represent high reactivity).
- In the case of pressurised gasification, also do a test at higher pressure.
- Note the reactivity profile and the effect of the product gas components.

With the method, the reactivity and ash sintering of biomass and waste based fuels that are candidates for a feedstock to a gasifier can be characterised. Thus it offers a basis for the selection of a feedstock. If it is desirable to model the behaviour of the selected feedstock (either a single biomass or a mixture of various biomasses) in the gasifier, the kinetic parameters needed in the modelling can be determined with careful measurements in a thermobalance taking account of the pre-treatment, diffusion effects, and all other factors affecting the results.

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PAPER I

Steam gasification reactivities of various fuel chars

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STEAM GASIFICATION REACTIVITIES OF VARIOUS FUEL CHARS

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ABSTRACT

Steam gasification rates of various fuel chars were determined to produce basic data for modelling fluid-bed gasification. The gasification rates were measured in a thermobalance, and microscopy was used to study changes due to gasification reactions in char structure. The fuels studied were wood, black liquor, cellulosic fibres, peat, brown coal and two types of bituminous coal. The gasification rates were determined in different gaseous environments under atmospheric pressure at temperatures below 1 000 °C. Reactant gases and their concentrations, pyrolysis temperature, heating rate during pyrolysis and particle sizes were also varied. The results show that gasification rates of the chars - except for peat char - showed an increasing trend as a function of char conversion. With peat char, a decreasing trend was observed, respectively. According to microscopic examination, this may be due to carbon deposition on reaction surfaces inside particles. The measured activation energies were as follows: wood based fuels: 195 kJ/mol for wood char, 230 kJ/mol for black liquor char and 265 kJ/mol for peat char; 200 kJ/mol for brown coal char and 165 - 230 kJ/mol for bituminous coal chars. These results - except for black liquor char - are given as examples of fuel samples pyrolyzed in the thermobalance at a heating rate of 20 °C/min to 950 °C. The black liquor samples were pyrolyzed, prior to thermogravimetric analysis, in a wire mesh pyrolyzer at a heating rate of 300 - 400 °C/s to 600 °C. The gasification rate was decreased at a high final pyrolysis temperature in the thermobalance, while it was increased by a higher pyrolysis rate. The microscopic structure of the partially gasified chars taken from the thermobalance was compared to corresponding chars obtained from a fluidized bed reactor.

INTRODUCTION

Fuel reactivity and the description of the flow field are the most difficult processes when modelling fluidized beds. An economic development of pressurized fluidized-bed combustion and gasification processes involves a better understanding of combustion and gasification phenomena, and correct input values for models are obtained from laboratory experiments.

In the projects going on in our laboratory, the reactivity of solid fuels is studied with a special focus on gasification reactivity, which depends mainly on 1) the amount and 2) the properties of char formed in pyrolysis, and on 3) fragmentation of char in the bed Hence, the concept of reactivity is approached via the following research stages:

1) Effect of pyrolysis on the properties of char particles
2) Attrition in fluidized bed
3) Oxidation-diffusion processes and chemical kinetics of char particles
4) Properties describing the reactivity of fuels.

Fragmentation of fuel due to attrition, essentially involved in fluidized-bed conditions, was studied in hot drum equipment developed in particular for the study [1].

The reactivity of the solid particle is controlled by steps well-known in a solid-gas reaction system: 1) film diffusion of oxidizing gas, 2) diffusion through the ash layer and the particle, 3) adsorption onto the reaction surface, 4) chemical reaction, 5) desorption of product gas from the surface, 6) diffusion of product gas through the particle and the ash layer, 7) film diffusion back into the ambient gas. Depending on temperature, particle size, etc., each stage may control the reactivity. The stages can be described by a resistance net in which individual resistances are parallel or in series (Figure 1). The size of each resistance is dependent on reaction conditions. At low temperatures the resistance due to the chemical reaction (step 4) is higher than the resistances due to mass transfer, and at high temperatures the chemical reaction proceeds fast, and the mass transfer resistance becomes significant.

This study is a continuation for studies in an actual fluidized-bed gasifier [2]. The work has been carried out in a thermobalance bearing in mind the reaction conditions typical of a fluidized-bed reactor, i.e. the maximum reaction temperatures ranged from 950 to 1 000 °C and the size of the fuel particles was a few millimeters. In reactivity measurements, the crucial point is to find the controlling mechanism for the reactivity. Therefore, an essential part of the research has been the monitoring of changes in the microscopic structure of the gasified char particle [3, 4].

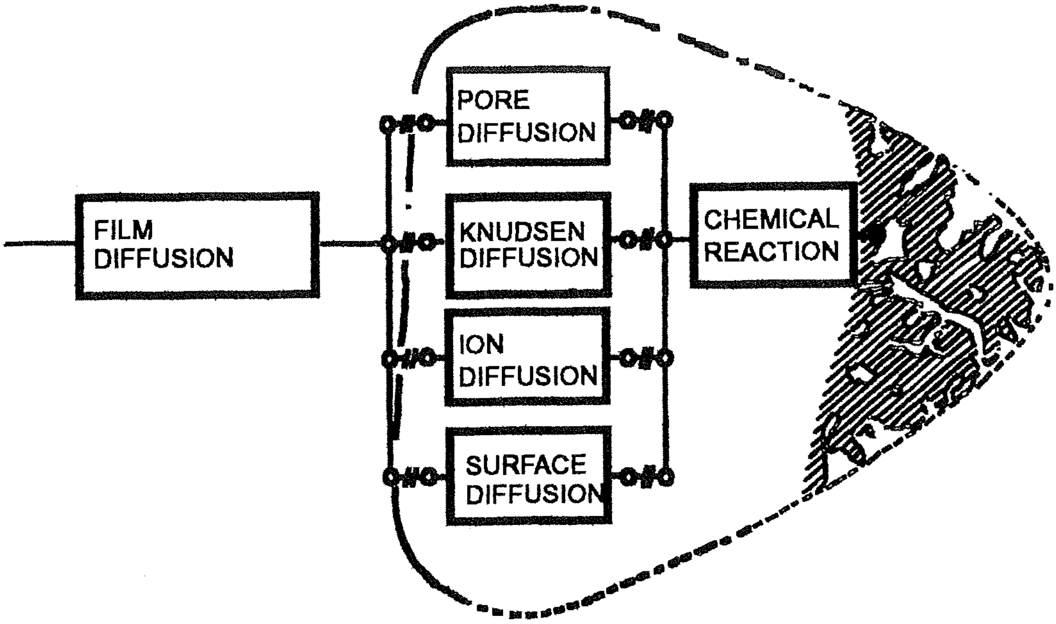


Figure 1. The resistance net describing reaction stages inside a char particle.

EXPERIMENTAL

The reactivity measurements have been made in the thermobalance; the experimental arrangements have been presented in detail in [4]. The fuel sample was introduced as a monoparticle layer on the sample holder. Through varying the particle and sample size, and the carrier gas the possible mass transfer limitation in the reactivity was checked. Finally it was subtracted from the results with curve fitting. Before isothermal gasification, the sample was pyrolyzed in the thermobalance using a heating rate of 20 °C/min. The sample was kept at the pyrolysis temperature (which was the same or higher than the gasification temperature) for 10 minutes before bringing it to the gasification temperature, where the sample was kept for 15 minutes before introducing the oxygen carrier. The gasification experiments were mainly performed in an atmosphere, which consisted of 15 % steam as an oxygen carrier in nitrogen. Steam was produced via bubbling nitrogen through water, which had the desired temperature to produce the required vapour pressure. After gasification the ash content of the residual char was determined by introducing air into the reactor.

The aim of the research work was to verify the existing data, which include great variations, and hence, fuels with different reactivities were studied. The fuels used in this research were wood, peat, brown coal, two types of bituminous coal and black liquor, all having a particle size between 2 and 4 mm. Black liquor, which is a "liquid" fuel, was pyrolysed before the experiment separately, and only char was introduced into the reactor. This was done because black liquor has a low ash melting point. The basic characteristics of the fuels are given in Table 1.

TABLE 1
Basic characteristics of the fuels used in the reactivity measurements

Dry fuel prior to pyrolysis*		Australian coal	Polish coal	Brown coal***	Peat	Black liquor char	Wood
Ash	%	15.0	21.0	5.5	7.8	**	0.2
Volatiles	%	24.9	26.8	49.8	65.9	-	83.0
C	%	70.2	66.2	64.4	55.4	39.9**	50.2
H	%	4.1	4.0	0.9	2.0	1.5	6.1
N	%	1.5	1.2	4.6	5.8	0	0.1
O	%	-	-	-	-	33.0**	-
S	%	0.80	2.0	-	-	-	0.0
Na	%	-	-	-	-	24.4**	-
K	%	-	-	-	-	0.1	-
Cl	%	-	-	-	-	0.2	-

* Except for black liquor char
** CO_3^{2-} = 34.9 %, SO_4^{2-} = 1.3 %, SO_3^{2-} = 0.7 %, Na^+ = 24.4 % in the sample
*** same as in [2]

RESULTS

Reactivities of different chars are expressed as Arrhenius plots, where 1/time (time expressed here as the time needed to achieve 50 % ash-free char conversion) is expressed as a function of 1/T, as can be seen from Figures 2 and 3.

The kinetic parameters in Arrhenius plot are calculated here with a simple model in which mass transfer and chemical kinetics are described only by two resistances, resulting in the following expression for the total reaction rate R:

$$R = -\frac{1}{W}\frac{dW}{dt} = -\frac{d\ln W}{dt} = \frac{A \cdot k_D \cdot k_C}{k_D + k_C} \qquad (1)$$

where

k_D = quantity comparable to mass transfer rate = $a \cdot T^m$
k_C = quantity comparable to chemical reaction rate = $b \cdot exp(-T_a/T)$
m = 0.5 ... 1 for diffusion

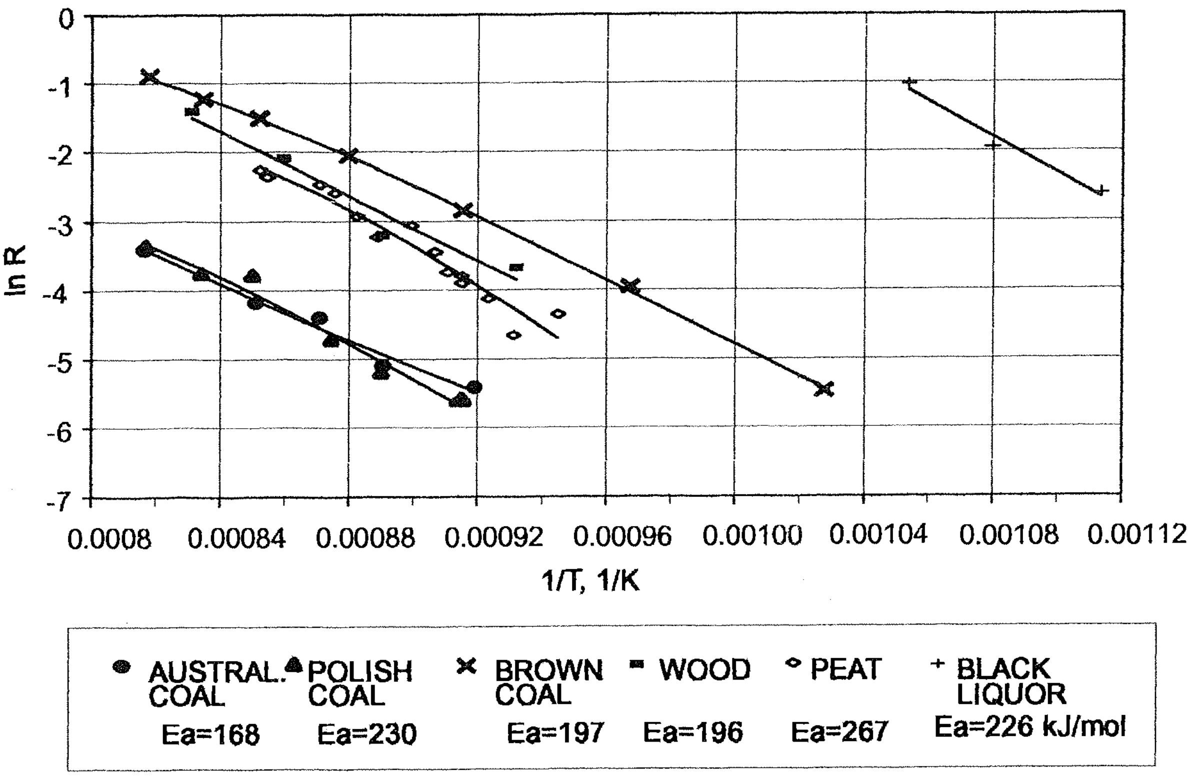


Figure 2. Comparison of steam gasification reactivities of solid fuel chars pyrolyzed at 950 °C.

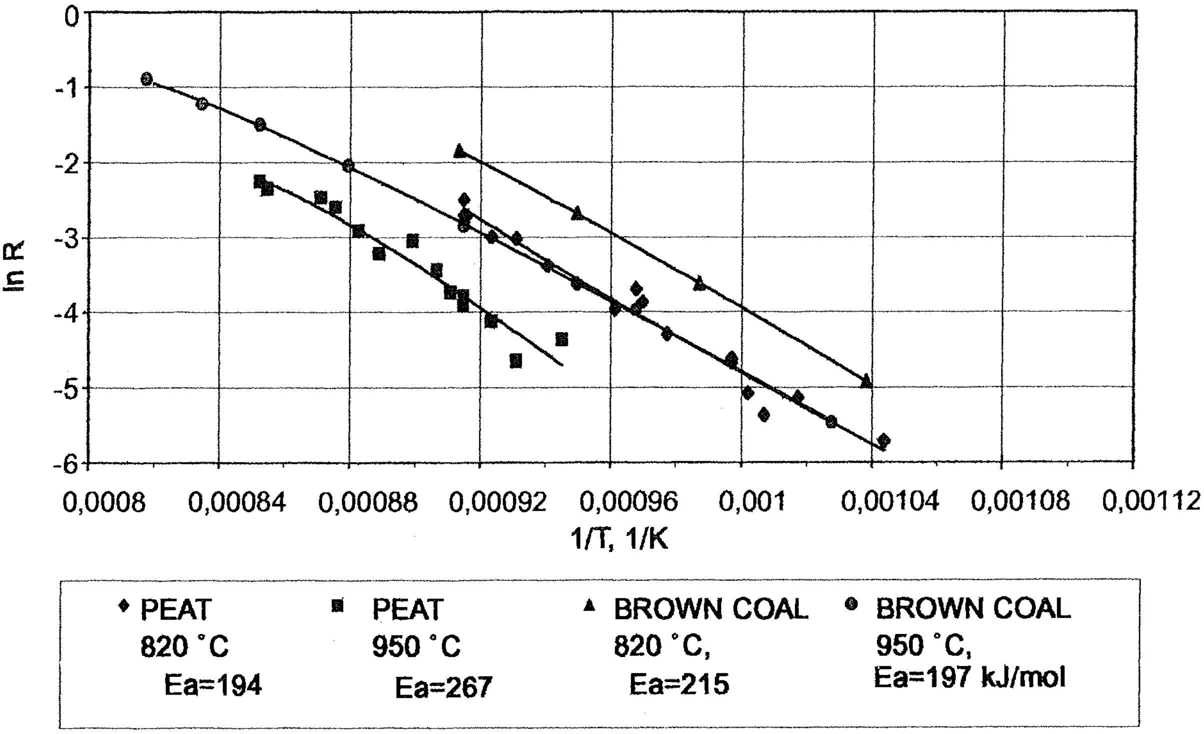


Figure 3. Comparison of the effect of pyrolysis temperature on the steam gasification reactivity of solid fuel chars.

t = time

T = reaction temperature, K

T_a = activation temperature = E_a/R, where E_a = acivation energy and R = gas constant

W = char mass (ash-free)

A, a, b = constants

For the diffusion the apparent activation energy $E_d = m \cdot T$. Now formula (1) may be rewritten to give:

$$\frac{d\,ln\,R}{d(1/T)} = -\frac{E_d \cdot k_D + E_a \cdot k_C}{k_D + k_C} \qquad (2)$$

The constants A, a, b, m and T_a have been solved from the experimental data through finding the best fit according to the least square, each constant as a variable.

In Figure 2, the reactivities of various fuel chars are compared, which had the same final temperature i.e. 950 °C in pyrolysis. The activation energy values obtained with the model for the chars are 196 kJ/mol for wood, 267 kJ/mol for peat, 197 kJ/mol for brown coal, 168 for Australian coal, 230 kJ/mol for Polish coal and 226 for black liquor. In Figure 3, the effect of the final pyrolysis temperature on the reactivity for peat and lignite is studied. The activation energies as a function of the final pyrolysis temperature are shown in Table 2.

In addition to the Arrhenius plots, the dependence of gasification rate on char conversion was determined. The momentary gasification rate R at time t (expressed as %/min) was calculated from the weight-change curve, i.e. mass vs. time, according to formula (1). The rates were plotted against char conversion, as presented in Figure 4. It shows these plots at 900 °C and 800 °C.

TABLE 2
The activation energy as a function of the pyrolysis temperature

Final pyrolysis temperature, °C	Peat, kJ/mol	Brown coal, kJ/mol
950	267	197
820	194	215
Average	231	206

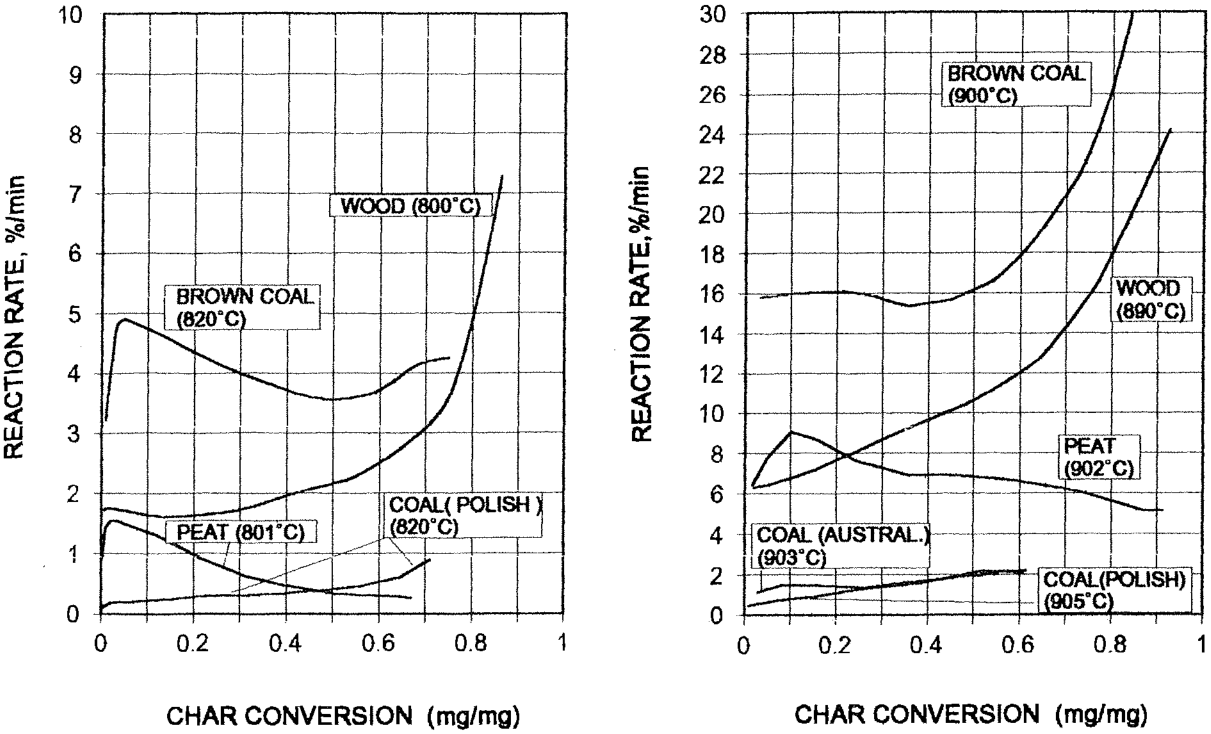


Figure 4. The reaction rate of the char as a function of char conversion at 800 °C and 900 °C.

DISCUSSION

Gasification reactivity has been studied extensively, but the "full" picture is still far from clear. Reviews concerning steam gasification are available, e.g., in [5, 6]. Most of the work has been concentrated on coal. Some data is available on biomass [7]., which are characterized by a high volatile content and often by a high moisture content.

In this work different high-volatile fuels close to wood have been gasified with steam in a thermobalance. As a reference, two different bituminous coals and cellulosic fibre have been tested. The reactivities of the chars at 700 - 800 °C and 15 % steam differ from each other by three orders of magnitude, but differences in the activation energies are only moderate except for Australian coal. In the latter case the number of measuring points and the difference between the minimum and the maximum temperature are small which may lead to error in E_a. The very high reactivity of black liquor, which is a by-product from pulping, is due to a high Na content, 20 % of dry solids, and to very strong swelling during pyrolysis (the char may have a 10 - 40-fold volume compared to that of the original fuel). Although the fuel is high in Na_2CO_3 and thus their catalytic effect should be strong the activation energy is 226 kJ/mol.

The activation energies measured in this work are given in Table 3 (see also Figure 2).

TABLE 3
The activation energy, E_a, kJ/mol for different feeds

Fuel	Australian coal	Polish coal	Brown coal	Peat	Black liquor char	Wood
Pyrolysis at						
950 °C	168	230	197	267	226*	196
820 °C			215	194	215	
Average				231		

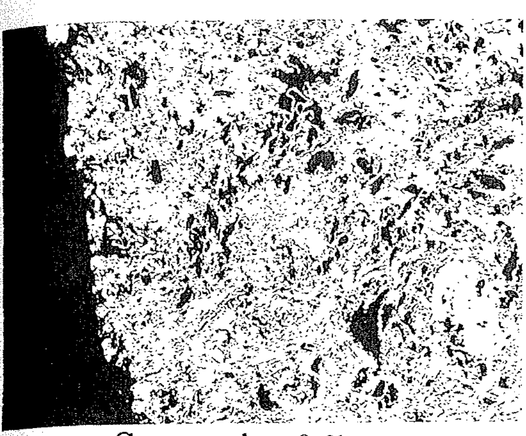
* Pyrolyzed 300 - 400 °C/s to 600 °C.

The values of activation energies are comparable with those in the literature, where lower values also exist. One explanation in these low values is that in many measurements the mass transfer limitation has influenced the results.

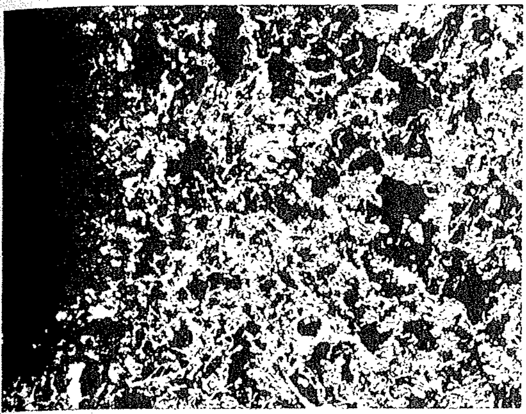
The comparison of reaction rates plotted against char conversion indicates that in general, the momentary gasification rate increases when char conversion increases which may depend on

1) the catalyst to carbon ratio is increased with conversion
2) the porosity is increasing with conversion up to the maximum and decreasing again, which results in a maximum in the rate curve
3) the amount of active sites is increasing with conversion.

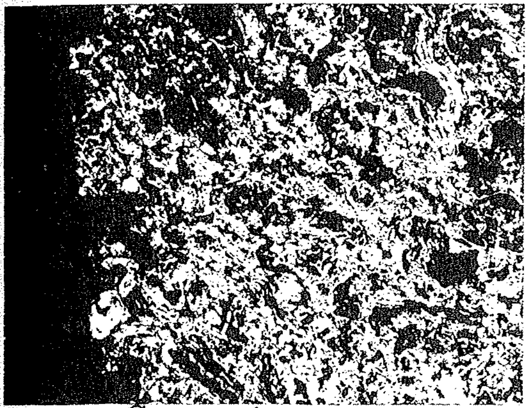
The increase in the reaction rate when the catalyst to carbon ratio is increasing with conversion is very clear with black liquor. However, in contrast to others, the gasification rate of peat char decreased while the conversion increased. The microscopic study [4] showed that the gasification shifts towards the particle surface when carbon conversion achieves >40 % (Figure 5). The reason for the retardation in reaction rate could be carbon deposition on reaction surfaces inside the char particle blocking the pore structure. Other possibilities are mass transfer limitation due to an ash layer on the particle surface or the inhomogeneity of peat. The chars with various conversions from the thermobalance and from a fluidized bed look different. The microscopic analysis shows that in the thermobalance the reaction zone propagates from the edge towards the core except at the beginning of gasification, while no similar zone was observed in the samples taken from the fluidized bed [3]. This indicates that the surface zone of the char, partially reacted in the fluidized bed, is escaping from the bed due to attrition.



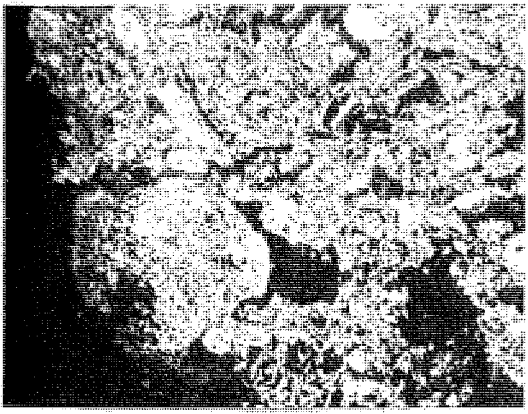
Conversion 0 %



Conversion 25 %



Conversion 40 %



Conversion 50 %

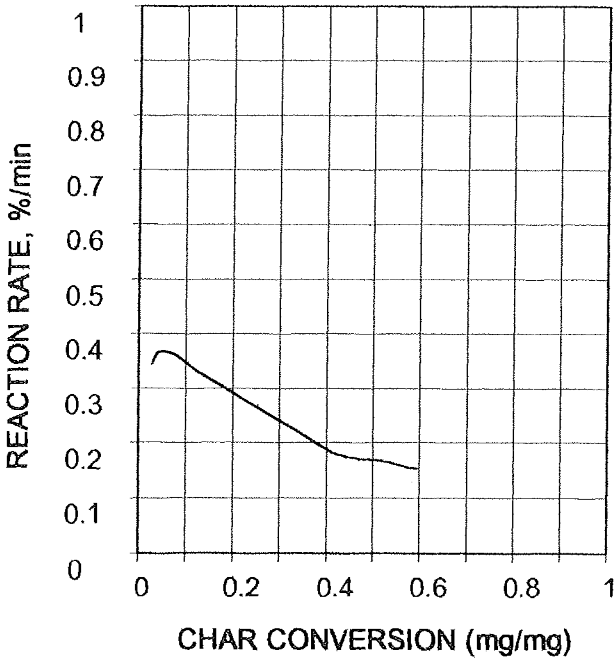


Figure 5. Micrograph showing an unexpected ash zone around a peat char particle in steam gasification at 700 °C, and the graph of the reaction rate of steam gasification as a function of conversion, respectively. The lower end of each picture corresponds to 500 μm.

The pyrolysis temperature has a great effect on gasification rate: the high pyrolysis temperature resulted with peat in a reaction rate, which was one order of magnitude smaller than the reaction rate measured for chars pyrolyzed at 820 °C. With brown coal, respectively, the ratio was about 4:1 (Figure 3).

CONCLUSIONS

Gasification reactivity is easily limited by mass transfer in a thermobalance, especially if only a few points are measured. The limiting mechanism may be studied by light microscopy and fitting the experimental data with curves, taking into account also mass transfer. The authors measured for several solid fuels an activation energy of 230 kJ/mol, ranging from 196 for wood to 265 for peat char. The activation energy for black liquor, which is an extremely reactive fuel, is close to 226 kJ/mol.

The results presented in this work are in agreement with the literature, although data with much lower activation energies have also been presented.

ACKNOWLEDGMENTS

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PAPER II

Gasification reactivities of solid biomass fuels

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GASIFICATION REACTIVITIES OF SOLID BIOMASS FUELS

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Keywords: Biomass, gasification, reactivity

INTRODUCTION

The design and operation of the biomass based gasification processes require knowledge about the biomass feedstocks characteristics and their typical gasification behaviour in the process. In this study, the gasification reactivities of various biomasses were investigated in laboratory scale Pressurised Thermogravimetric apparatus (PTG) and in the PDU-scale (Process Development Unit) Pressurised Fluidised-Bed (PFB) gasification test facility of VTT (Figure 1).

EXPERIMENTAL

In PTG, the effects of individual process parameters (relevant to pressurized fluidised bed gasification) on gasification rate were studied using following parameter ranges: gasification agent (CO_2, H_2O), temperature (700 - 1 000°C), pressure (1-30 bar). With some samples, also the effect of product gas on gasification rate was tested.

The characteristics of the samples are presented in Table 1. The selected samples are part of a biomass sample collection analysed in the EU-project (European Union) belonging JOULE II Program /1/.

The gasification rate measurements were carried out in the pressurised thermobalance (PTG), which is presented schematically in Figure 1. A more detailed description of its operation has been presented in /2/. The tests were carried out isothermally by lowering down the sample of about 50 mg in size to the reactor with the winch system equipped in the PTG. During this time, the sample was pyrolysed when it heated up to the reaction temperature at an estimated rate of above 10K/s. The weight change, which was recorded during this approximately 60 seconds period, was due to, mainly, the pyrolysis of the sample and the buoyancy phenomena. After this period, the weight change due to the gasification (and eventual postpyrolysis) was monitored.

In the fluidized-bed gasification tests, air and a small amount of steam were used as gasification agents. The feedstock and dolomite were fed into the lower part of the bed and part of the fines elutriated from the fluidized-bed were separated in the primary cyclone and recycled back to the bed. The fines separated by the secondary cyclone and the ceramic filter unit were collected, weighed and sampled. The main variable in the tests was the gasification temperature, which was controlled by changing the air-to-fuel ratio.

The carbon conversion data for three biomass fuels are presented together with data for two bituminous coals and Rhenish brown coal. The feedstock analyses are shown in Table 2. Examples of the operation conditions and process data for the different fuels are presented in Table 4.

RESULTS

The gasification rates obtained from the PTG measurements are shown in Table 3 as a function of CO_2 and H_2O pressure measured at 850°C. The gasification rate denoted as r" is indicated as an instantaneous gasification rate, i.e. mass change rate divided by residual ash-free mass (%/min). The conversion used indicates the burn-off of the whole fuel including the mass loss due moisture and pyrolysis release. In Figure 2, the conversion behaviour, i.e. r" vs. conversion, is given for the fuels which were gasified also in the PFB.

The PTG tests show that there are great differences in gasification rates between various fuels. The preliminary correlations between gasification rates and ash composition indicated that, especially, the rates at higher fuel conversions seemed to decrease with increasing silica content in the fuel. This indicates that catalytically active ash components can loose their activity due to reactions with silica, or due to sintering behaviour. Also, adding a product gas component to the gasification gas decreased radically the gasification rate. For example, the gasification rate (r") of wheat straw decreased from 27 %/min to 10%/min when CO was added 10% to CO_2 at 30 bar pressure.

The carbon conversions of the PFB tests shown in Table 4 are calculated from the material balances. The great differences between the gasification behavior of the five feedstocks used in PFB measurements can be clearly seen by comparing the data shown in Figure 3. Only the two bituminous coals seemed to behave more or less similarly and a strong and clear correlation was found between carbon conversion and equivalence ratio (or temperature). With these fuels it took several hours to reach steady state char inventory in the bed and also in the freeboard and in the recycling loop.

The three different biomass fuels had also clearly different gasification behavior. In gasification of pine sawdust, very high carbon conversions could be achieved already at relatively low temperatures, while bark and straw were more difficult to be completely gasified. In the case of straw gasification high conversion efficiencies could be achieved at above 850°C, but unfortunately sintering of the straw ash caused severe operational problems. Pine bark did not have problematic ash sintering behavior, but has a clearly lower reactivity than wood or straw. Consequently high gasification temperatures and efficient recycling of elutriated fines are required with pine bark to reach high conversion efficiencies.

Rhenish brown coal is an excellent feedstock for fluidized-bed gasification and over 95 % carbon conversion could be reached already at about 900 °C temperature. This fuel has also a high reactivity measured in PTG /3/.

The results of this study shows that gasification reactivities of the biomasses can differ greatly from each other. The comparison of the results between PTG and PFB shows that the gasification rates measured in PTG have the same order as the reactivities in PFB based on achieved carbon conversion calculations.

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Table 1a. The characteristics of the feedstock samples, wt%, dry basis

Sample	V.M., %*)	F.C., %*)	Ash, %	C, %	H, %	N, %	O_{diff}, %	S, %
Pine saw dust	83.1	16.8	0.1	51.0	6.0	0.1	42.8	nil
Pine bark	73.1	25.3	1.7	52.5	5.7	0.4	39.7	0.03
Forest residue (pine)	79.3	19.4	1.3	51.3	5.8	0.4	40.9	0.02
Salix	79.9	18.9	1.2	49.7	6.1	0.4	42.6	0.03
Wheat straw	77.7	17.6	4.7	47.5	5.9	0.6	41.5	0.07
Barley straw	76.1	18.0	5.9	46.2	5.7	0.6	41.5	0.08
Reed canary grass	73.5	17.6	8.9	45.0	5.7	1.4	38.9	0.14
Miscanthus	78.5	18.2	3.3	47.9	6.0	0.6	41.6	0.6
Sweet sorghum	77.2	18.1	4.7	47.3	5.8	0.4	41.7	0.1
Kenaf	79.4	17.0	3.6	46.6	5.8	1.0	42.8	0.1

V.M.: Volatile Matter Content, F.C.: Fixed Carbon

Table 1b. The ash compositions of the samples.

Sample	Ash composition, %									
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	SO_3	P_2O_5
Pine saw dust	8.3	4.0	3.7	41.8	11.8	24.6	0.5	0.12	1.9	10.5
Pine bark	1.3	10.6	0.6	40.6	4.5	15.2	1.0	0.12	2.0	9.6
Forest residue (pine)	38.5	9.4	7.4	15.4	4.0	16.6	0.7	0.5	1.6	6.4
Salix	0.4	0.6	0.4	30.8	5.1	53.0	0.5	0.02	3.0	22.9
Wheat straw	59.9	1.6	1.1	7.3	1.8	33.7	0.9	0.04	1.1	4.5
Barley straw	62.0	0.4	0.3	4.5	2.2	38.5	1.0	0.02	1.4	5.0
Reed canary grass	89.8	2.8	2.3	3.5	1.5	6.3	0.3	0.05	1.1	8.2
Miscanthus	42.8	1.0	0.8	7.6	4.8	50.6	1.3	0.03	2.1	10.5
Sweet sorghum	57.8	1.3	1.1	9.0	2.7	16.4	3.0	0.05	3.0	6.0
Kenaf	6.6	3.6	2.4	30.8	6.0	26.5	2.5	0.08	5.7	5.5

Table 2. The analyses of the feedstock materials used in the fluidised bed tests.

	Polish coal	Colombian coal	Rhenish brown coal	Wheat straw	Pine sawdust	Pine bark
Moisture content, wt-%	3.6-6.7	7.6	11.5-12.2	6.1	6.1-16	5.6-6.7
<u>Proximate analysis, wt-% d.b.</u>						
Volatile matter	31.8	34.7	53.0	75.8	83.1	71.8
Fixed carbon	59.9	53.2	42.7	18.2	16.8	26.7
Ash	8.34	12.1	4.3	6.1	0.08	1.6
<u>Ultimate analysis, wt-% d.b.</u>						
C	75.5	71.9	63.8	46.1	51.0	53.9
H	4.7	4.9	4.6	5.6	6.0	5.8
N	1.3	1.5	0.8	0.52	0.08	0.35
S	0.7	1.0	0.3	0.08	< 0.01	0.03
O (diff.)	9.5	8.6	26.2	41.6	42.8	38.4
Ash	8.3	12.1	4.3	6.1	0.08	1.6

Table 3. The instantaneous gasification rates of the samples at the minimum and at the conversion value of 95% measured at 850°C.

Sample	1 bar CO_2		30 bar CO_2		1 bar H_2O		30 bar H_2O	
	r" min.	r" at X=95%	r" min.	r" at X=95%	r" min.	r" at X=95%	r" min.	r" at X=95%
Pine saw dust	27	39	22	43	25	25	50	71
Pine bark	9	16	7	13	7	13	44	71
Forest residue (pine)	18	20	na	na	na	na	na	na
Salix	29	42	23	50	30	130	60	225
Wheat straw	16	19	25	42	13	17	46	58
Barley straw	19	22	na	na	na	na	na	na
Reed canary g.	3	3	10	15	15	19	na	na
Miscanthus	18	25	26	59	24	45	na	na
Sweet sorgh.	20	23	26	51	29	62	na	na
Kenaf	50	83	55	103	67	83	na	na

Table 4. Operational data on typical set points with different fuels.

	Polish Coal	Colombian coal	Rhenish brown coal	Wheat straw	Pine sawdust	Pine bark
Equivalence ratio	0.47	0.49	0.44	0.3	0.39	0.34
Fuel feed rate, g/s	5.33	5.49	11.50	13.30	10.67	11.45
g/s-daf	4.70	4.50	9.70	11.70	9.00	10.40
Air feed rate, g/s	23.67	23.66	35.03	21.2	21.15	23.56
kg/kg-fuel(daf)	5.04	5.26	3.61	1.81	2.35	2.27
Steam feed rate, g/s	4.06	4.50	1.90	3.6	1.77	1.23
kg/kg-fuel(daf)	0.86	1.00	0.20	0.31	0.20	0.12
Purge N_2 feed rate, g/s	3.3	3.4	1.2	4.6	2.1	2.6
Dolomite feed, g/s	0.45	0.45	0	0	0.7	0.39
Pressure, MPa	0.5	0.5	0.5	0.5	0.5	0.5
Bed temperature, °C	1 001	980	824	772	831	871
Freeboard temperature, °C	1023	1014	910	848	968	978
Carbon conversion, wt%						
to gas (C1)	85.0	86.2	95.9	83.4	94.6	87.7
to gas+tars (C2)	85.3	86.7	96.2	93.9	100.3	90.0
incl.dolomite input (C3)	84.2	85.5	96.2	93.9	98.6	89.3
Carbon losses, wt-% of input, Bottom ash	0.5	0.2	0.1	0	0.1	0
Cyclone dust	2.3	3.4	2.4	2.1	0	2.5
Filter dust	13.0	11.1	1.1	2.5	0.8	8.3
Carbon balance closure output, wt % of input	100.0	100.2	99.8	98.5	99.5	100.1
Gas composition, vol%						
CO	8.7	6.9	16.4	9.0	8.8	12.0
CO_2	10.6	10.8	10.0	11.5	13.8	12.8
H_2	8.4	8.1	12.0	4.0	7.8	9.0
CH_4	0.7	0.9	1.1	3.6	3.8	3.1
C_2 hydrocarbons	0.00	0.00	0.02	0.78	0.15	0.20
H_2O	15.6	18.3	7.3	23.9	17.2	12.6
NH_3	0.12	0.14	0.19	0.15	0.026	0.13
H_2S	0.039	0.058	0.017	0.014	0.005	0.009
N_2 (+Ar)	55.8	54.8	53.0	47.1	48.4	50.2

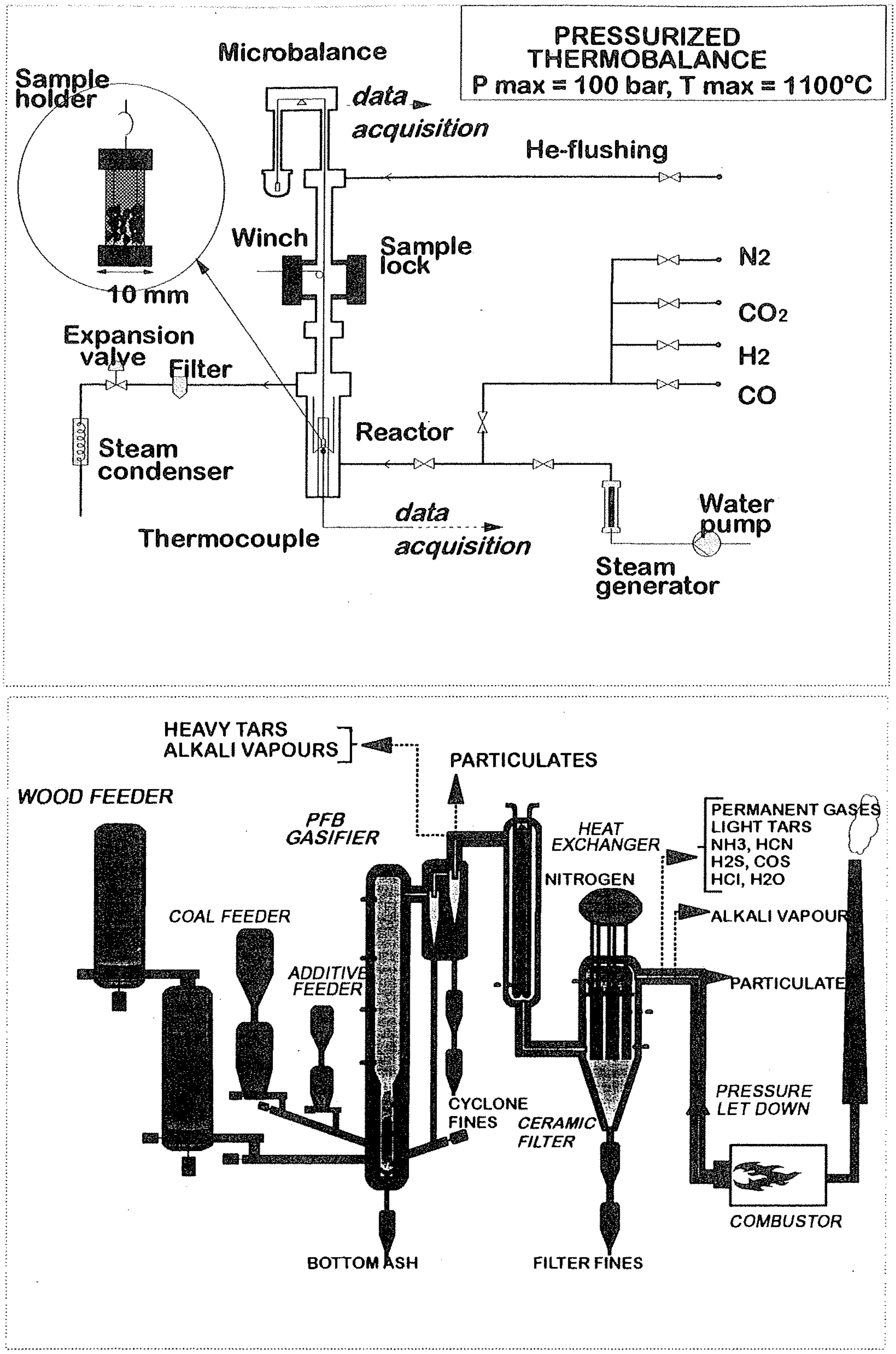

Figure 1. The pressurised thermogravimetric apparatus and pressurized fluidized-bed gasification test facility used in the study.

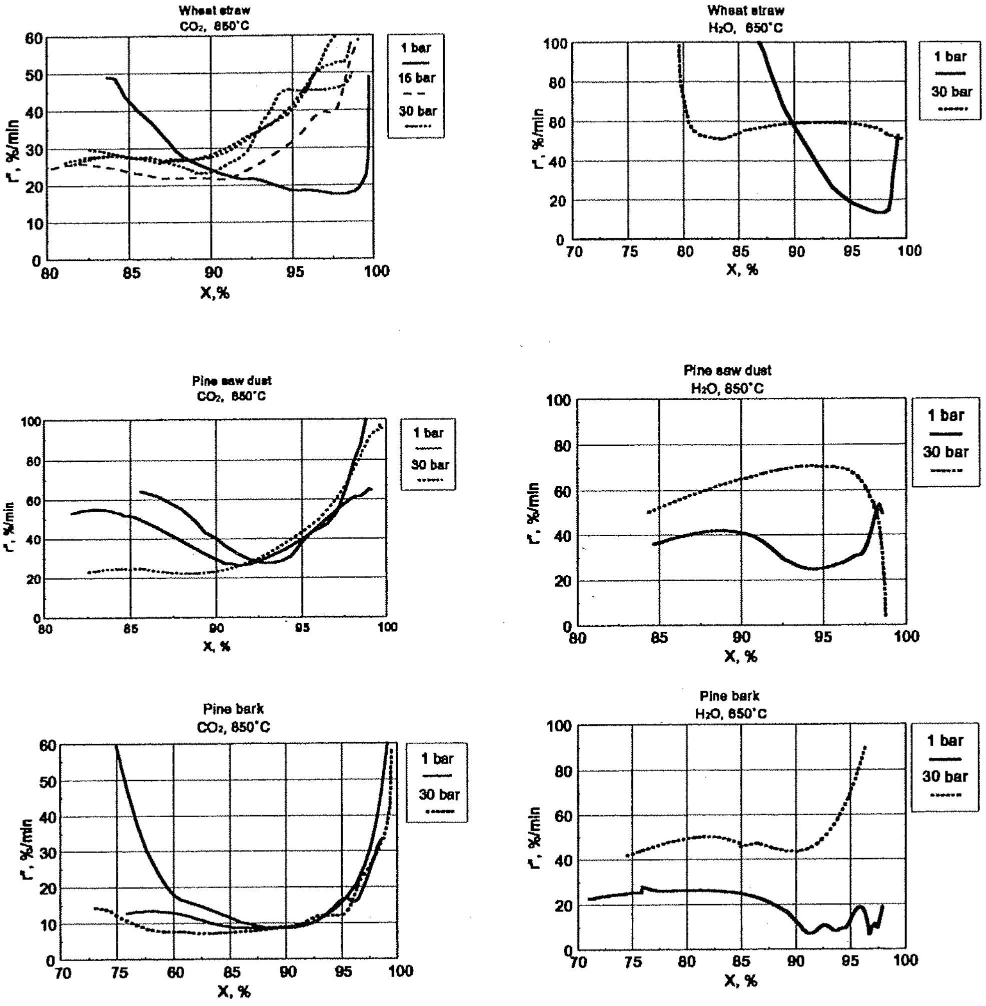

Figure 2. The gasification rate r" vs. fuel conversion X of CO_2 and H_2O gasification in 1 and 30 bar pressures and at 850°C.

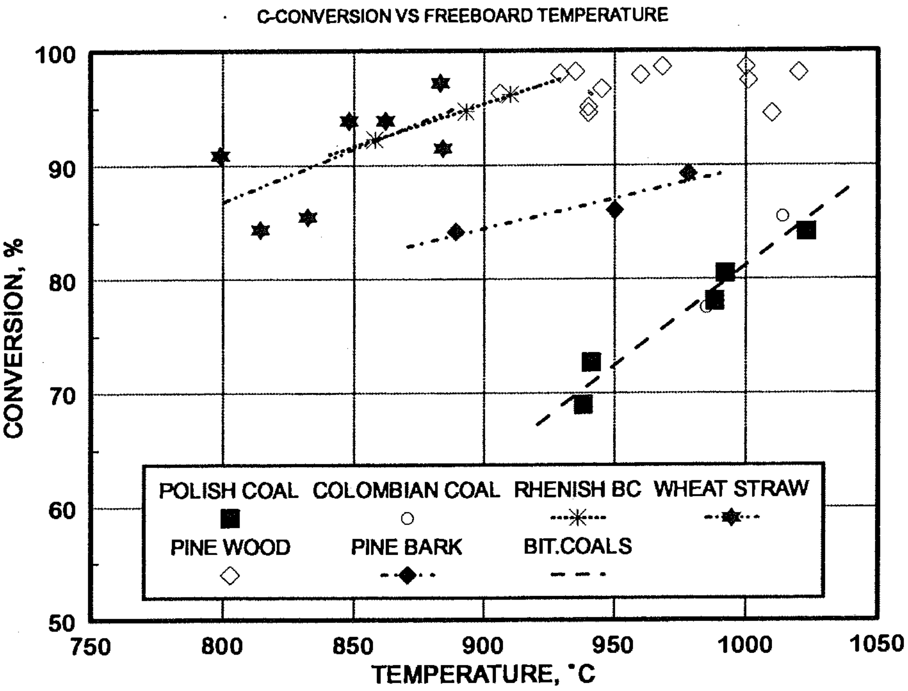

Figure 3. The achieved carbon conversions as a function of freeboard temperature in the PFB.

PAPER III

Characterisation of gasification reactivity of peat char in pressurised conditions

Effect of product gas inhibition and inorganic material

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Characterization of gasification reactivity of peat char in pressurized conditions

Effect of product gas inhibition and inorganic material

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The characteristic effects of the main operating parameters in pressurized fluidized bed gasification, such as pressure and product gas composition, and of inorganic material on peat char gasification reactivity were studied. The measurements were carried out isothermally in a pressurized thermobalance at temperatures between 1023 and 1233 K and pressures up to 1.5 MPa. Steam and carbon dioxide, both pure and mixed with the product gases H_2 and CO, were used as reaction agents. The reactivity was expressed in the form of instantaneous gasification rate vs. char burnoff. The steam gasification rate of peat char was only slightly higher than the CO_2 gasification rate, and the gasification rates decreased at increasing pressure in both steam and carbon dioxide. The steam gasification rate of the peat char increased to a maximum before decreasing with increasing char burnoff. In carbon dioxide, the main trend was that the gasification rate slightly increased with the burnoff. Demineralization of the peat decreased the reactivity and also removed the negative burnoff behaviour observed in steam gasification. The presence of the product gases H_2 and CO inhibited the gasification of the peat char almost entirely. *Copyright © 1996 Elsevier Science Ltd.*

(Keywords: peat char; gasification reactivity; demineralization)

The total carbon conversion achieved in fluidized bed gasification (at temperatures < 1273 K) depends on the reactivity of the fuel and especially of the fuel char. Besides gasification taking place in the bed, the dust phase above the fluidized bed plays an important role in achieving a good carbon conversion. The carbonaceous material of the dust phase comprises residual char particles that are recycled to the bed. Their gasification takes place in the presence of product gases. To improve the quality of the product gas, the freeboard temperature is increased in some gasifiers. Therefore the dust phase can also partly react at temperatures higher than that in the fluidized bed.

The gasification rate of the char formed in pyrolysis, as well as char structure and the catalytic effect of the ash-forming material, is affected by both pressure and the presence of product gases[1]. The product gas components, H_2 and CO, can retard the gasification rate of carbonaceous materials significantly[1–3]. The rate is also affected by the product gas formation in the pore structure, especially in larger char particles. These factors have been considered by Löwenthal *et al.*[4,5] in modelling the gasification of larger char particles, taking into account the gas transport inside the particle by pore diffusion and convective flow. Furthermore, the effect of pressure and gas atmosphere on the gasification behaviour of fuel char is often unforeseen, as Mühlen[6] observed in his studies of lignite and coal gasification, which showed that the gasification behaviour of char, which is catalysed by mineral matter as a function of pressure, cannot be predicted from the measurements made at atmospheric pressure. One reason for this poor predictability is the behaviour of the catalytically active substances of the fuel minerals as a function of pressure, gas atmosphere and temperature. These parameters can affect the catalytic components by deactivating them during gasification, e.g. by clustering or agglomerating the catalyst, or by forming new mineral phases. Hence the behaviour and activity of gasification catalysts contained in the mineral matter as well as in other ash-forming constituents should be considered when determining gasification rates.

Peat is a significant fuel used in Finland for combustion, and it can also be used as gasification feedstock[7]. The background for this study was obtained from the gasification research carried out on coal. Takarada *et al.*[8] and Miura *et al.*[9,10] summarized factors affecting the gasification reactivity of various types of coal and correlations between coal properties and gasification reactivity. Peat gasification reactivity has been studied less extensively. Sipilä *et al.*[11] studied the factors affecting the gasification reactivity of peat char for producing activated carbon from peat. The gasification behaviour of peat (including also biomass) was studied[12–15] under conditions relevant to atmospheric fluidized bed gasification. In these studies, the effects of various factors, such as pyrolysis conditions and pretreatment forms of peat feedstock, on the gasification reactivity of peat char were

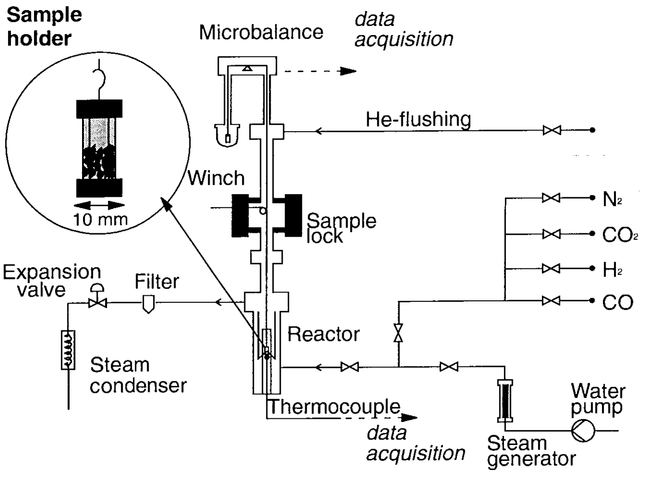

Figure 1 Flow scheme of the pressurized thermobalance

included, as well as changes in char structure as a function of burnoff. The effect of pressure has also been studied by Espenäs[16].

Table 1 Analysis of peat sample

Proximate analysis (wt% db)		Ash composition (wt%)	
Ash	7.8	SiO_2	18
Volatile matter	65.9	Al_2O_3	12
Ultimate analysis (wt% db)		Fe_2O_3	54
C	55.4	CaO	9.6
H	2.0	MgO	1.6
N	5.8	Na_2O	0.5
O_{diff}	29	K_2O	0.6
		TiO_2	0.4
		P_2O_5	3.3

The purpose of the work described in this paper was to characterize first how the addition of the product gas components H_2 and CO affects the gasification reactivity of peat under pressurized conditions, and second how the inorganic material in peat affects the gasification behaviour.

EXPERIMENTAL

The gasification tests were carried out in a pressurized thermobalance system (PTG)[17] (*Figure 1*). The sample was placed in a cylindrical sample holder having a central shaft and walls made of high-temperature alloy wire mesh. The measurements were carried out isothermally at temperatures between 1023 and 1223 K and pressures up to 1.5 MPa. Isothermal test conditions were achieved

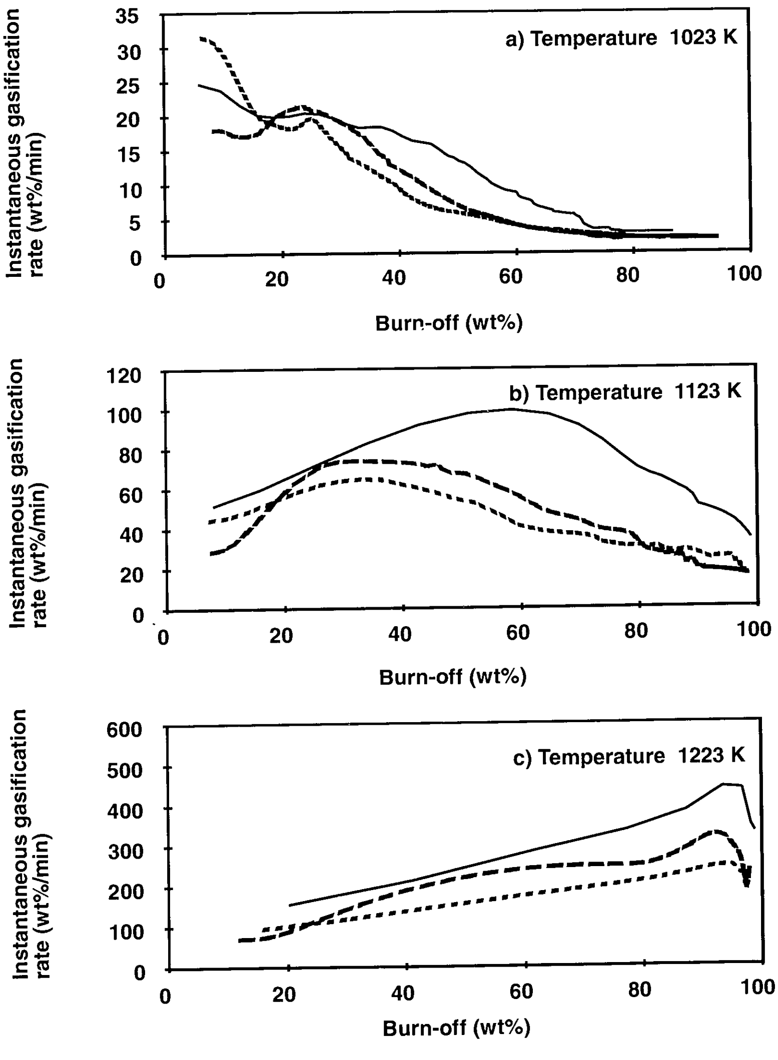

Figure 2 Steam gasification rate of peat char vs. char burnoff at different temperatures and pressures: ———, 0.1 MPa; – – – – –, 0.5 MPa; - - - - - - -, 1.5 MPa

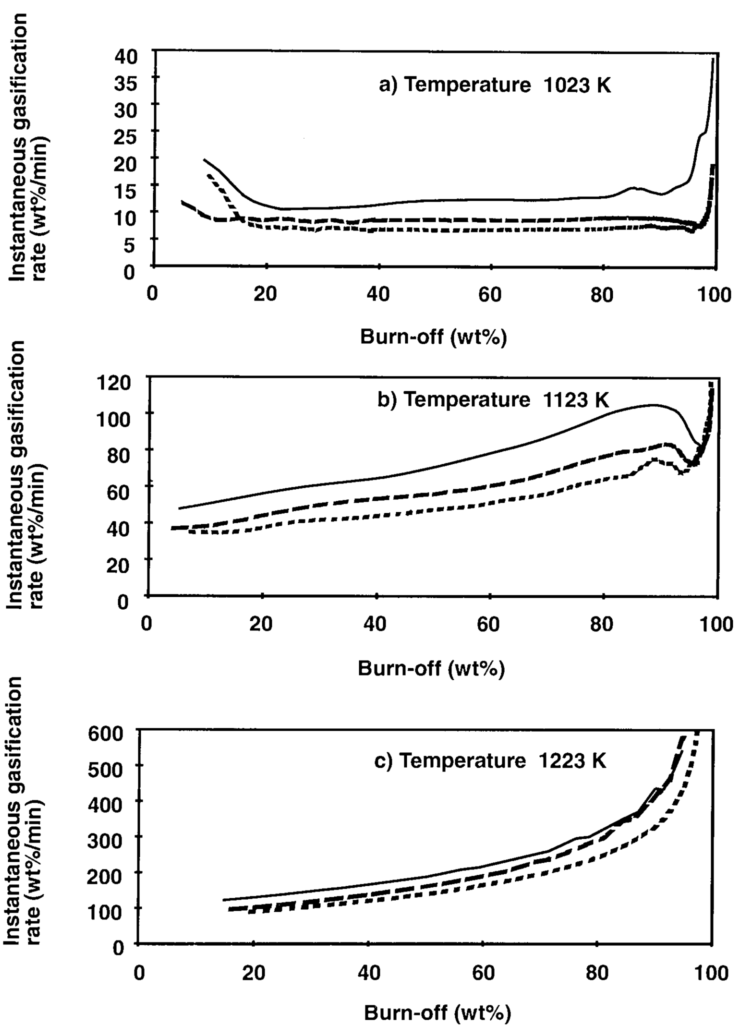

Figure 3 Carbon dioxide gasification rate of peat char vs. char burnoff at different temperatures and pressures: ————, 0.1 MPa; – – – – –, 0.5 MPa; - - - - - - -, 1.5 MPa

by lowering the sample holder into the reactor, into the reaction conditions directly, using a winch fixed in the sample lock of the PTG. During this procedure, the sample was heated up in ~30 s to the reaction temperature. This period was excluded from the beginning of the weight change curve.

The peat sample used in this study was sod peat as used previously[12], which was pulverized to an average particle size of 0.1 mm. The main properties and the ash composition of the sample are given in *Table 1*. Reactivities were measured for peat char, which was produced by pyrolysing the peat precursor at 1223 K in an atmospheric drop tube reactor (DTR), where the residence time was 2 s and the heating rate was estimated to be $10^4\,\mathrm{K\,s^{-1}}$. Steam and carbon dioxide, both pure and mixed with the product gas—H_2 and CO respectively—were used as reaction agents.

RESULTS AND DISCUSSION

The reactivities were expressed in form of instantaneous gasification rate, r'', which was calculated from the experimental weight–time curve obtained from the PTG using the following formula:

$$r'' = \frac{1}{w}\frac{\mathrm{d}w}{\mathrm{d}t} \qquad (1)$$

where $\mathrm{d}w/\mathrm{d}t$ is the weight change rate and w is the instantaneous ash-free weight. This expression was chosen to determine the dependence of the reaction rate on char burnoff, which can vary widely depending on fuel and on reaction conditions.

The effect of steam and carbon dioxide pressure (up to 1.5 MPa) on char gasification was investigated with peat char produced in the DTR. The results are shown in *Figures 2* and *3*. Two main features can be observed: the gasification rates decreased at increasing pressure in both steam and carbon dioxide, and the burnoff behaviour was different in steam and carbon dioxide.

The steam gasification rate of peat char at 0.1 MPa and 1023 K was only 1.1 times the CO_2 gasification rate (the average ratio between char conversions of 20 and 80 wt%). At 20 wt% char burnoff, the ratio was 1.8, and the minimum ratio was 0.2 at 80 wt% char burnoff. With pressure increase, the mean ratio did not differ significantly from that at 0.1 MPa pressure, but the slope of the rate from lower to higher burnoff was sharper. With temperature increase, the mean ratio did not change from 1.1, but the burnoff behaviour was different between low and high conversions. The mean steam gasification rate in the burnoff range from 20 to 80 wt% at 0.1 MPa was 1.6 times that at 0.5 MPa pressure at both 1023 and 1123 K, and 1.3 times that at 1223 K. The ratios between 0.1 and 1.5 MPa were 1.7, 1.8 and 1.6 at 1023,

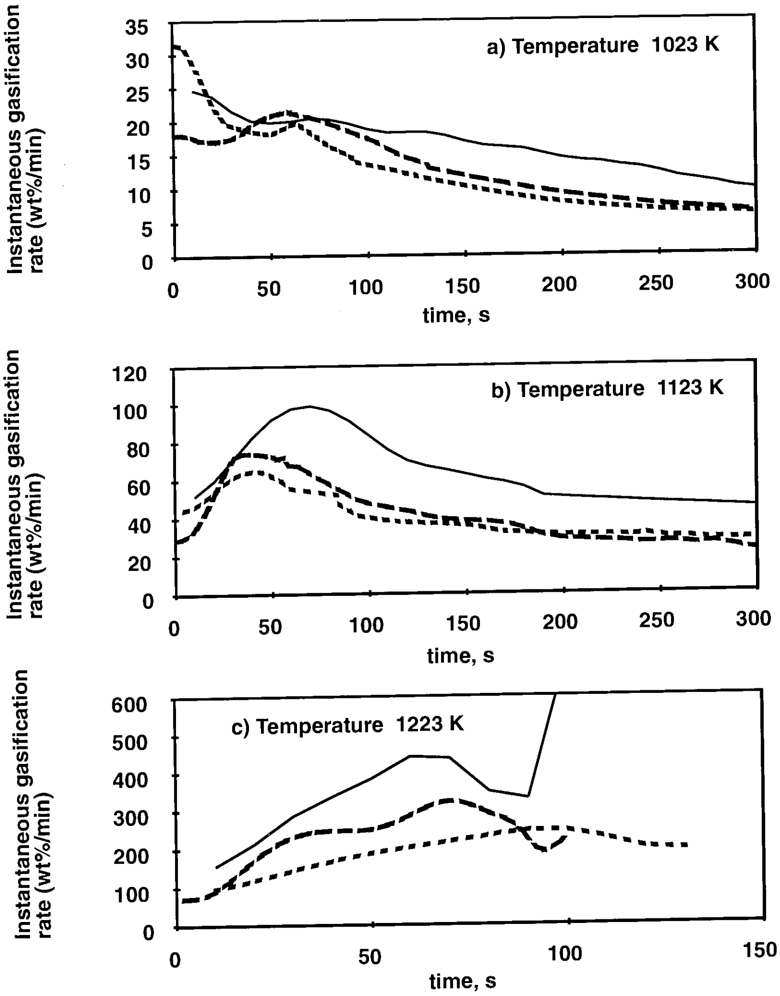

Figure 4 Steam gasification rate of peat char vs. time at different temperatures and pressures: ———, 0.1 MPa; – – – – –, 0.5 MPa; - - - - - - -, 1.5 MPa

1123 and 1223 K respectively. In CO_2 gasification, the ratios for the same temperatures were practically similar: between 0.1 and 0.5 MPa, 1.4, 1.3 and 1.2, and between 0.1 and 1.5 MPa, 1.7, 1.5 and 1.4. These ratios in both steam and CO_2 gasification appeared to decrease slightly with increasing temperature.

In steam at 1023 K (*Figure 2a*), the reaction rate decreased while the burnoff increased. When the temperature was raised to 1123 K (*Figure 2b*) the rate of steam gasification increased and passed through a maximum. At 1223 K (*Figure 2c*), the rate increased up to ~ 95 wt% burnoff. In carbon dioxide, the main trend was that the rate increased slightly with burnoff (*Figure 3a, b, c*). However, at 1023 K and at low burnoff, as seen in *Figure 3a* for CO_2 gasification, some decrease in the rate was observed.

Espenäs[16] also observed a similar burnoff behaviour for peat char in steam gasification. This type of burnoff behaviour in steam is unexpected, as the reaction rate related to the instantaneous mass (r'') usually increases solely due to the development of pore structure. In addition, this effect should be enhanced by the catalytically active material among the ash-forming constituents, as its amount remains constant during burnoff, leading to an increase in the catalyst/carbon ratio.

To study this negative burnoff behaviour of steam gasification more closely, the rates were plotted against time. *Figure 4* shows that the maximum rate occurred at a reaction time below < 100 s in all cases. At 1023 K the maxima were at 60–70 s (after the initial decreasing stage) at all pressures. At 1123 K the maximum rate was at 70 s at 0.1 MPa, and 40 s at both 0.5 and 1.5 MPa. At 1223 K the maximum was at 60 s at 0.1 MPa and 90 s at 1.5 MPa. This observed behaviour leads to the assumption that, practically, the deactivation reaction depends only on time, and not so much on temperature and pressure. The faster the gasification, the greater the amount of catalyst still active. At high conversions the catalyst seems to lose its contact with carbon and consequently its activity.

To investigate the role of the catalytically active substances in the burnoff behaviour of peat char, the inorganic material was extracted by acid treatments (HCl, HF), both from the peat char prepared in the DTR and from the original peat. The ash content was thus reduced by ~ 50% in both cases. In this case, the demineralized peat was pyrolysed in the PTG at 1223 K. Therefore the absolute values of reaction rate cannot be compared with those shown in *Figures 2–4*, as the pyrolysis was carried out under different conditions. The burnoff dependence of the reaction rate in steam and carbon dioxide gasification was determined.

The results for the demineralized char showed that the reaction rates were significantly lower than those of the original char in both steam and carbon dioxide (*Figure 5*).

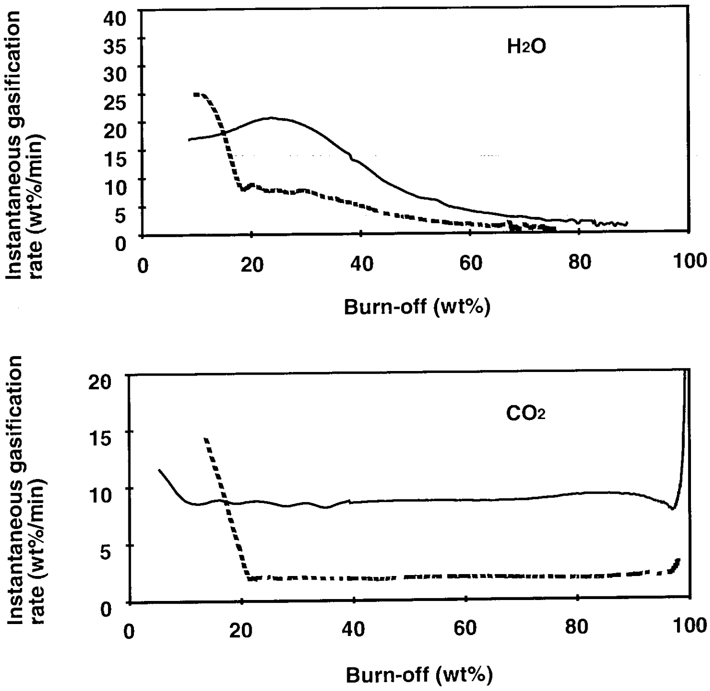

Figure 5 Effect of demineralization of peat char on the steam and carbon dioxide gasification of char at 0.5 MPa and 1023 K: ————, original char; - - - - - -, demineralized char

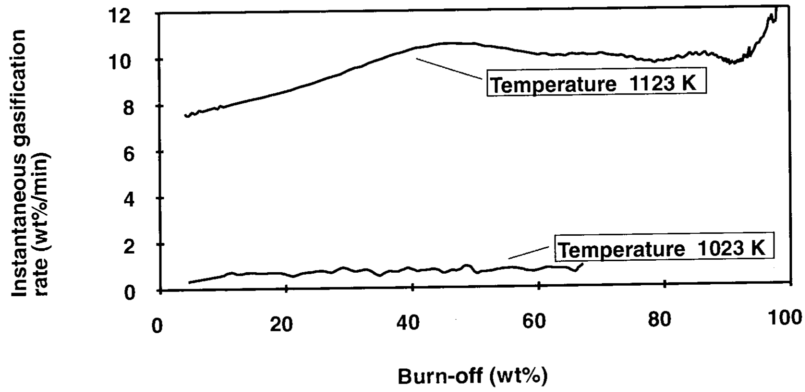

Figure 6 Effect of demineralization of peat on the steam gasification of char at two temperatures and 0.5 MPa

In steam gasification, the reaction rate of the demineralized char still showed a negative burnoff behaviour, i.e. the rate still decreased as a function of burnoff. The char of the demineralized peat however showed a different behaviour: the gasification rate increased while the burnoff increased, as shown in *Figure 6*. The observation made after the extraction of the char leads to the conclusion that inorganic material has significance in catalysing the gasification of peat char. Espenäs[16] also found similar reductions in the steam gasification reactivity of peat char after demineralization. In addition, the observation made after the extraction of the parent peat shows that the inorganic material also has an influence on the burnoff behaviour in the steam gasification of peat char. The fact that after char extraction the negative burnoff behaviour was not affected could result from a difference in or selectivity of the extraction procedure.

The observed behaviour in steam gasification can be explained on the basis of the results obtained in earlier studies with coal, which imply that the catalytically active substances contained in the fuel are deactivated with increasing burnoff. Mühlen[6] reported on deactivation in lignite gasification, in which the catalytically active substances, e.g. calcium, can react and lose activity during gasification. This deactivation can result from e.g. sintering and agglomeration of catalytically active substances. Other possible reasons for the deactivation could be the formation of new mineral phases or reactions with the gasifying agent, as suggested by the difference in burnoff behaviour between steam and carbon dioxide gasification of peat char. In addition to calcium, iron could also play a role in peat gasification. The peat used in the test exhibits an exceptionally high iron content (*Table 1*). The iron present in Finnish peat can be in finely divided form[18]. This catalytically active iron can lose its activity, for instance, due to the effects discussed by Ohtsuka and Asami[19], who concluded that the catalytic activity of iron correlates with the dispersion of Fe_3O_4 particles in char and that the agglomeration of this highly dispersed iron catalyst during gasification reduces the gasification rate. This role of

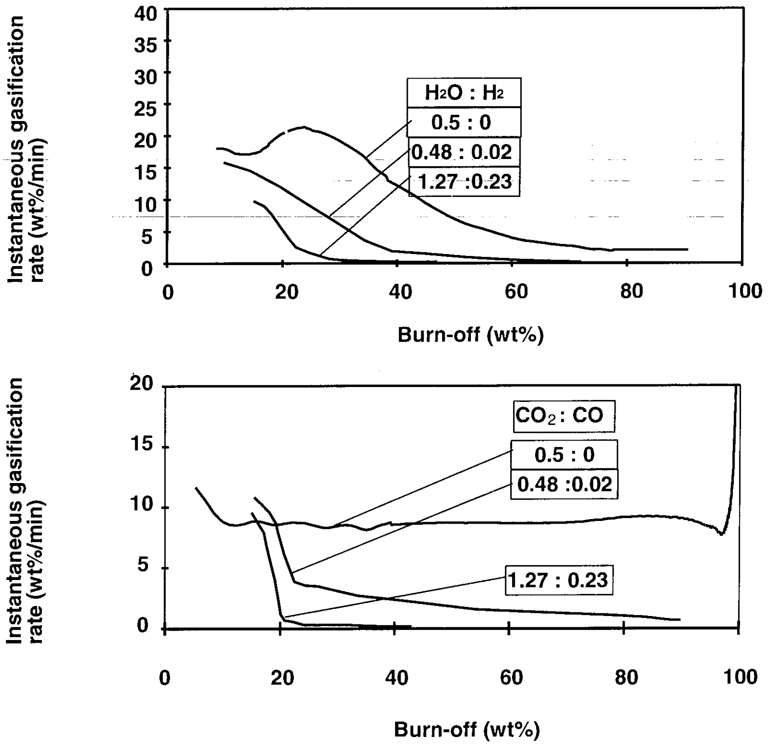

Figure 7 Inhibiting effect of H_2 in steam gasification (upper) and CO in carbon dioxide gasification (lower) of peat char at 1023 K (the numbers indicate partial pressures in MPa)

iron (as well as other inorganic material) needs further investigation to be proved valid for this peat sample.

To determine how the product gas components H_2 and CO affect the gasification rate and the burnoff behaviour, the reactivity of the peat char was also determined in the presence of these gases. In these tests, the binary gas mixtures H_2O–H_2 and CO_2–CO^{20} were used. The peat char sample used was that prepared in the DTR. The results shown in *Figure 7* indicate that the addition of both product gases H_2 and CO to the pure gasification agents leads to a considerable reduction in the reaction rate of peat char. The decrease in the rate depended on the partial pressure of the component added. In steam gasification, the negative burnoff behaviour intensified when H_2 was added to steam. The addition of CO to CO_2 also caused a strong negative burnoff behaviour.

When the partial pressure of hydrogen was 20 kPa and the total pressure 0.5 MPa, the rate decreased from the initial value of 16 wt% min^{-1} to almost zero at a burnoff > 70 wt% at 1023 K (*Figure 7*, upper). The decrease was even sharper when the partial pressure of H_2 was 0.23 MPa and the total pressure 1.5 MPa: the rate decreased from 10 wt% min^{-1} to almost zero beyond 40 wt% char burnoff. When CO was added to CO_2 (*Figure 7*, lower), the decrease was not as sharp as that after hydrogen addition at the lower partial pressure; when the CO pressure was 20 kPa, the rate decreased from 11 to 1 wt% min^{-1} (at 90 wt% burnoff). At 0.23 MPa CO pressure however, the decrease seemed to be sharper than that at the corresponding pressure of H_2: the rate decreased sharply from ~9 wt% min^{-1} to almost zero beyond 40 wt% char burnoff.

CONCLUSIONS

The following conclusions can be drawn:

(1) the steam gasification rate of peat char is only slightly higher than the CO_2 gasification rate;
(2) gasification rates decrease with increasing pressure in both steam and carbon dioxide;
(3) the steam gasification rate of peat char decreases from a maximum as char burnoff increases;
(4) demineralization of peat decreases the reactivity, and also eliminates the negative burnoff behaviour observed in steam gasification;
(5) the presence of the product gases H_2 and CO inhibits the gasification of peat char almost entirely.

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PAPER IV

Gasification reactivities of biomass fuels in pressurised conditions and product gas mixtures

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GASIFICATION REACTIVITIES OF BIOMASS FUELS IN PRESSURISED CONDITIONS AND PRODUCT GAS MIXTURES

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Abstract

Measuring data required for describing the reactivity of biomass-based fuels for pressurised gasification, like various straws (wheat, barley, reed canary grass) and wood-based feedstock (pine, willow, forest residues, miscanthus, sweet sorghum, kenaf), are discussed. The measurements were carried out isothermally in a pressurised thermobalance by determining the gasification rates of char. The main variables were temperature and partial pressures of H_2O and H_2, and CO_2 and CO. The reaction rates were determined in binary gas mixtures H_2O-H_2, and CO_2-CO as well as in product gas mixtures H_2O-H_2-CO_2-CO. The total pressure range was 1-30 bar and the temperature range 650-950 °C. The char samples were produced by pyrolysing the samples in a thermobalance in the gasification conditions by placing the sample in the reactor in the reaction conditions adjusted.

In the paper, the characteristic gasification behaviour of the samples in the presence of product gases is discussed. For wood kinetic parameters were determined using the Langmuir-Hinshelwood kinetics, which takes into account the effect of the product gases on the reaction rate. The results indicated that the H_2O-H_2 system was well in conformity with this kinetics, while the reaction rates measured for the CO_2-CO system required the description of the catalytic effects of the ash-forming material. In the gasification of wood as well as of other biomasses, the behaviour of catalytically active ash components is more complex during char gasification.

Keywords: biomass, gasification, reactivity, pressure, product gas

1 Introduction

The basis of this study was in the need of adding knowledge of the behaviour of various biomass-based fuels, especially, for the development work on pressurised gasification processes based on fluidised-bed technique. In coal gasification, a lot of fundamental research has been carried out to create the scientific background required for the commercialisation of new and quite complex power production systems such as pressurised IGCC technique. Characteristics of various biomasses have been studied much less.

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In the present study, the gasification behaviour of biomass feedstocks was characterised for pressurised fluidised-bed gasification. The testing conditions chosen were typical of a pressurised fluidised-bed gasification process, i.e. temperature range max. 1000°C and pressure max. 30 bar. The aim was to produce measuring data for the assessment of carbon conversion in pressurised gasification of solid fuels. The factor affecting the carbon conversion is the reactivity of the char residue after the feedstock material is pyrolysed in the reactor. There are fairly many articles in literature on the characteristics of biomass gasification reactivity and the role of the inorganic material in catalysing it, e.g., [1, 2, 3].

To evaluate the behaviour of biomass in the fluidised-bed gasification, the conditions involved in the reactivity of char material are those existing in the bed and in the freeboard. In this context, particularly the presence of the product gas components must be taken into account, especially for the char material circulating in the freeboard. The product gas components have been found to significantly reduce the gasification rate for coal and peat [4, 5, 6, 7]. The biomass-derived fuels differ from coal, i.e., with regard to the high content of volatile substances (i.e. small amount of residual char) and other type of ash-forming material, which can catalyze the char gasification reactions.

Gasification rates of residual char formed in pyrolysis in the presence of the product gas of gasification were determined on a pressurised thermobalance (PTG) for pine sawdust. The most significant variables were temperature, pressure and H_2O - H_2 and CO_2 - CO ratios. The measurements were carried out for these gas mixtures as a function of partial pressures of the components and of temperature. Kinetic parameters were determined on the basis of the reaction rate values obtained with the aid of Langmuir-Hinshelwood formulas. Gasification reactivities of other biomass types determined in the PTG were compared to the results obtained for pine sawdust.

2 Experimental

The measurements were carried out in the pressurised thermobalance system. The principle of the testing method has been presented previously [7]. The tests were carried out in the temperature range of 700-900 °C and in the pressure range of 1-30 bar (abs.). Pine sawdust was mainly used as sample, the average particle size being 0.1 mm. For characterising the gasification behaviour of different biomasses the samples presented in Table 1 were used [8].

The sample was pyrolysed by lowering it by the winch of the thermobalance direct into the reactor, into gasification conditions. The aim was to get rapid pyrolysis that to some extent corresponds to process conditions. The average heating rate of the sample obtained in this way was some 10 °C/s. The conditions for measuring the char gasification were stabilised after 60 seconds from the input of the sample, including the pyrolysis stage. This part of the weight-time signal recorded by the thermobalance system was removed in the data evaluation. The results obtained for mass change and for the rate of mass change with this treatment are shown in Fig. 1. The rate of mass change due to char gasifying and pyrolysis was given as a so-called instantaneous rate of reaction r" (%/min). It was calculated by dividing the rate of mass change of the sample by the residual ash-free mass. X (%) is the conversion of the total ash-free sample.

Table 1. The characteristics of the feedstock samples, wt%, dry basis

Sample	Volatile matter, %	Fixed carbon, %	Ash %	C %	H %	N %	$O_{diff,}$ %	S %
Pine saw dust	83.1	16.8	0.1	51.0	6.0	0.1	42.8	nil
Pine bark	73.1	25.3	1.7	52.5	5.7	0.4	39.7	0.03
Forest residue (pine)	79.3	19.4	1.3	51.3	5.8	0.4	40.9	0.02
Salix	79.9	18.9	1.2	49.7	6.1	0.4	42.6	0.03
Wheat straw	77.7	17.6	4.7	47.5	5.9	0.6	41.5	0.07
Barley straw	76.1	18.0	5.9	46.2	5.7	0.6	41.5	0.08
Reed canary grass	73.5	17.6	8.9	45.0	5.7	1.4	38.9	0.14
Miscanthus	78.5	18.2	3.3	47.9	6.0	0.6	41.6	0.6
Sweet sorghum	77.2	18.1	4.7	47.3	5.8	0.4	41.7	0.1
Kenaf	79.4	17.0	3.6	46.6	5.8	1.0	42.8	0.1

Ash chemical composition, wt%

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	SO_3	P_2O_5
Pine saw dust	8.3	2.0	1.8	41.8	11.8	12.3	0.3	0.12	1.9	5.2
Pine bark	1.3	5.3	0.3	40.6	4.5	7.6	0.5	0.12	2.0	4.8
Forest residue (pine)	38.5	4.7	3.7	15.4	4.0	8.3	0.4	0.5	1.6	3.2
Salix	0.4	0.3	0.2	30.8	5.1	26.5	0.3	0.02	3.0	11.5
Wheat straw	59.9	0.8	0.5	7.3	1.8	16.9	0.5	0.04	1.1	2.3
Barley straw	62.0	0.2	0.2	4.5	2.2	19.3	0.5	0.02	1.4	2.5
Reed canary grass	89.8	1.4	1.1	3.5	1.5	3.1	0.1	0.05	1.1	4.1
Miscanthus	42.8	0.5	0.4	7.6	4.8	25.3	0.7	0.03	2.1	5.3
Sweet sorghum	57.8	0.7	0.5	9.0	2.7	8.2	1.5	0.05	3.0	3.0
Kenaf	6.6	1.8	1.2	30.8	6.0	13.3	1.3	0.08	5.7	2.7

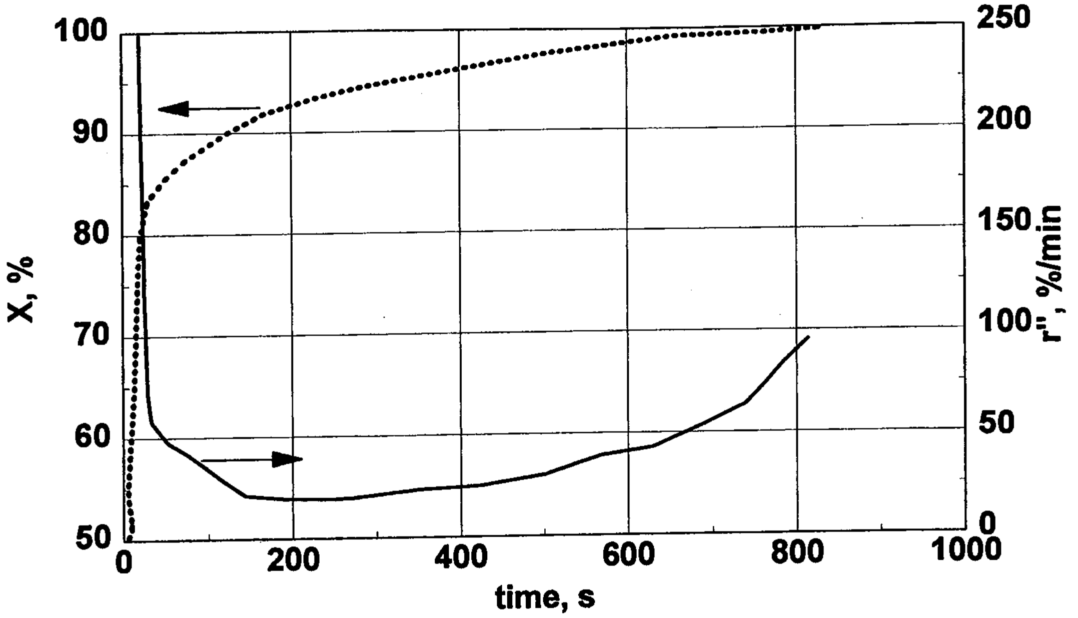
The kinetic parameters were calculated on the basis of the minimum reaction rates of the gasification rate vs. fuel conversion curve, see point A in Fig. 1.

3 Results

Fig. 2 shows the dependence of the reaction rate of wood residual char on temperature, measured in 1 bar pressure of CO_2 and H_2O. The activation energy was 217 kJ/mol for steam gasification and 229 kJ/mol for CO_2 gasification. These values are of the same magnitude range as those measured earlier [9].

The dependence of gasification of wood char on pressure can be seen from Fig. 3, measured in the pressure range of 1-15 bar CO_2 and H_2O at temperatures of 750 and 850 ^{o}C. When the pressure was raised in the range under study, the rate of CO_2 gasification was reduced slightly at both temperatures, while the rate of H_2O gasification increased clearly.

The effect of the product gas on the gasification reactivity of wood residual char was studied using binary gas mixtures CO_2- O and H_2O-H_2. The dependence of reaction rate on the partial pressure of product gas components were described with Langmuir-Hinshelwood formulas as used for coal [5].



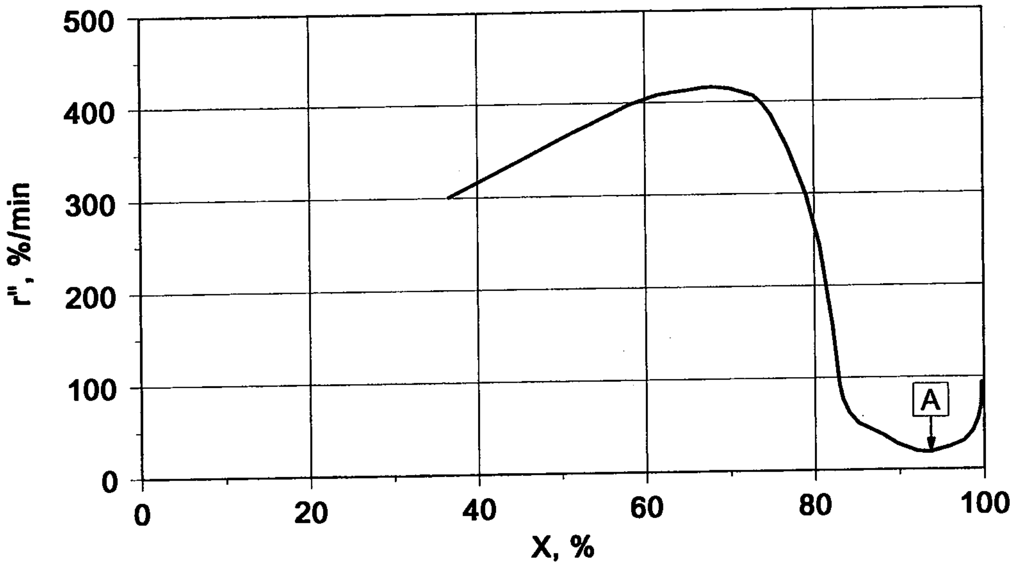


Fig. 1. Fuel conversion (X, %), and gasification rate (r", %/min), as a function of time (upper graph) and r" as a function of fuel conversion (X, %) (lower graph). Point A shows the minimum gasification rate.

According to the Langmuir-Hinshelwood kinetic expression, the reciprocal of the reaction rate should have a linear correlation with the ratio of the partial pressures, e.g., P_{CO}/P_{CO2}. The measurements indicated that the reciprocal of the reaction rate in the gasification of wood residual char in the CO_2-CO system was dependent linearly fairly well on the ratio of partial pressures, while the level of dependence was dependent on the total pressure (Fig. 4).

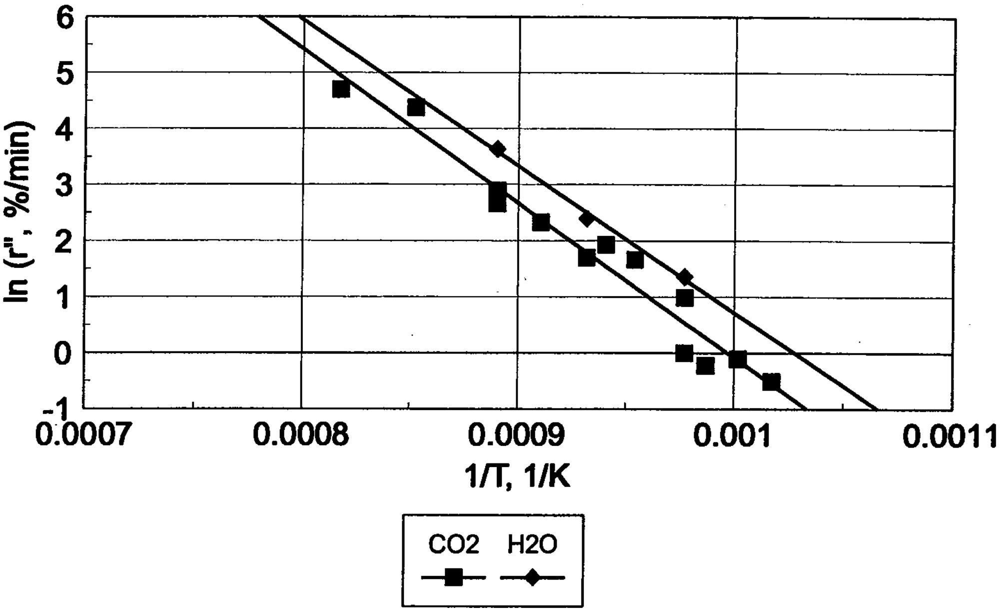


Fig. 2. Dependence of the gasification rate of wood char on temperature at 1 bar CO_2 and H_2O pressure.

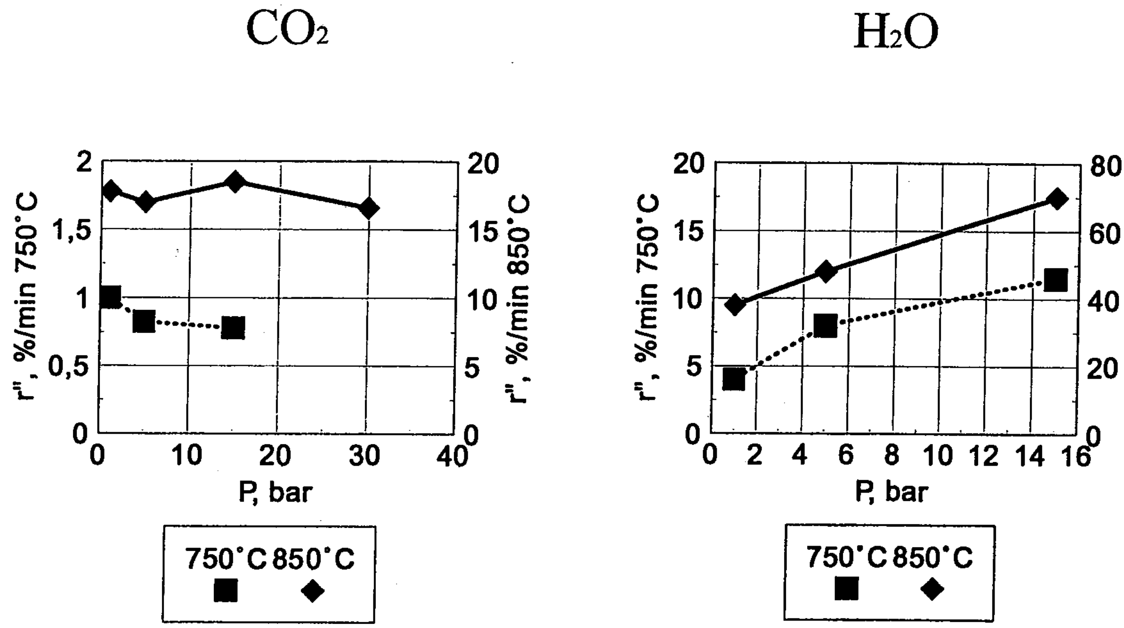


Fig. 3. Dependence of the gasification rate of wood char on CO_2 and H_2O pressure at 750 and 850 ^{o}C.

In the H_2O-H_2 mixtures the corresponding dependencies were significantly better and the total pressure was of no great significance, as can be seen from Fig. 5.

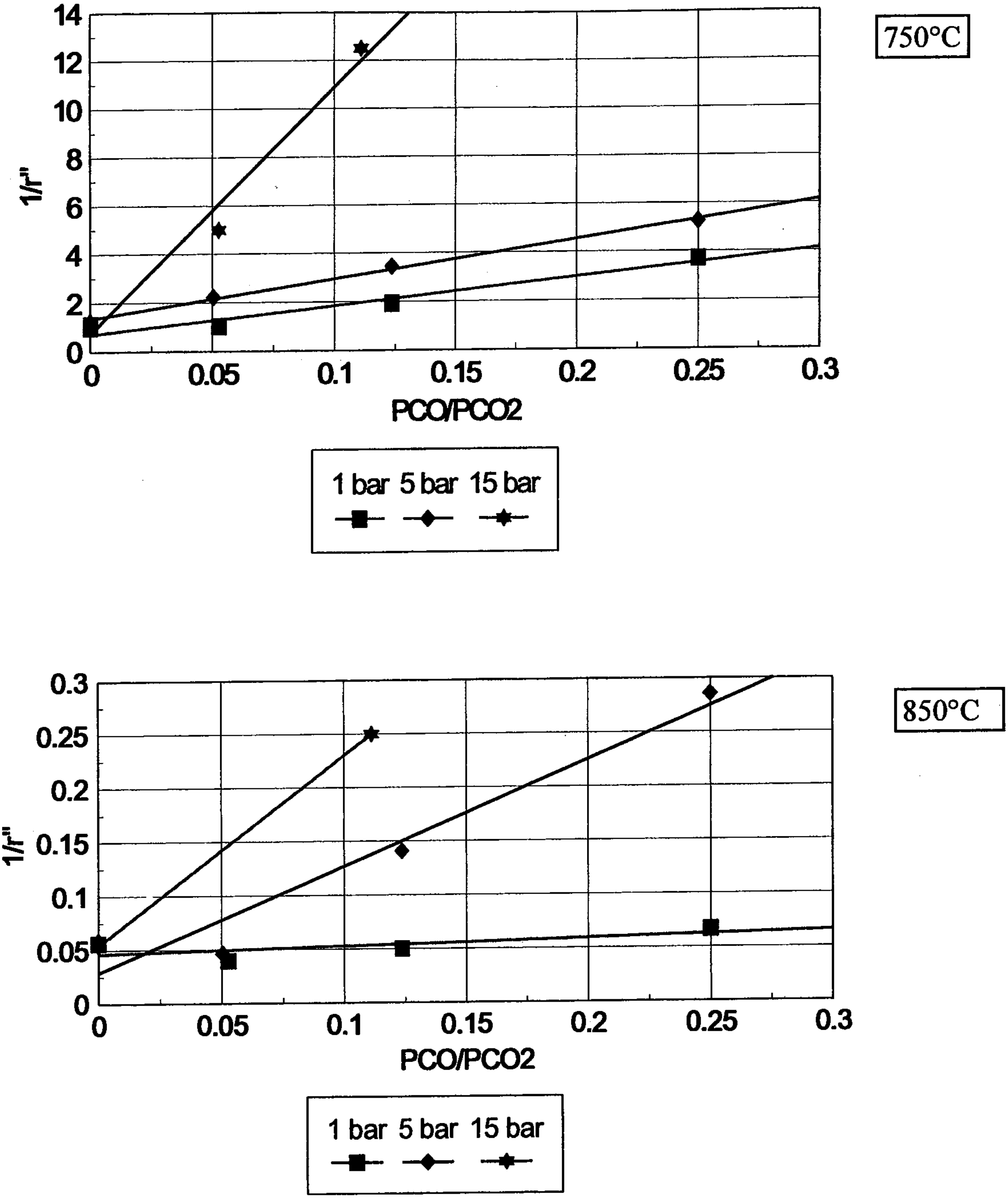
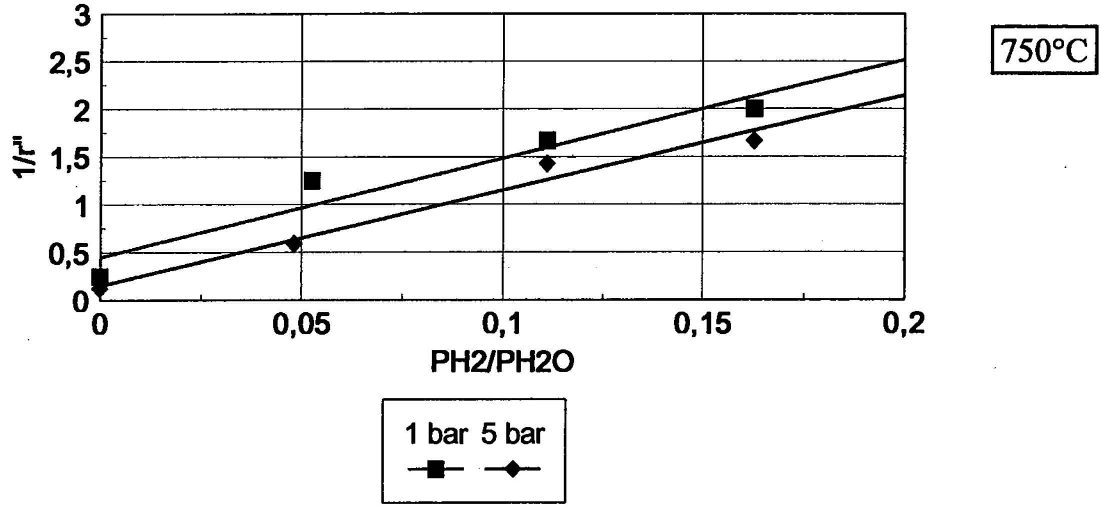
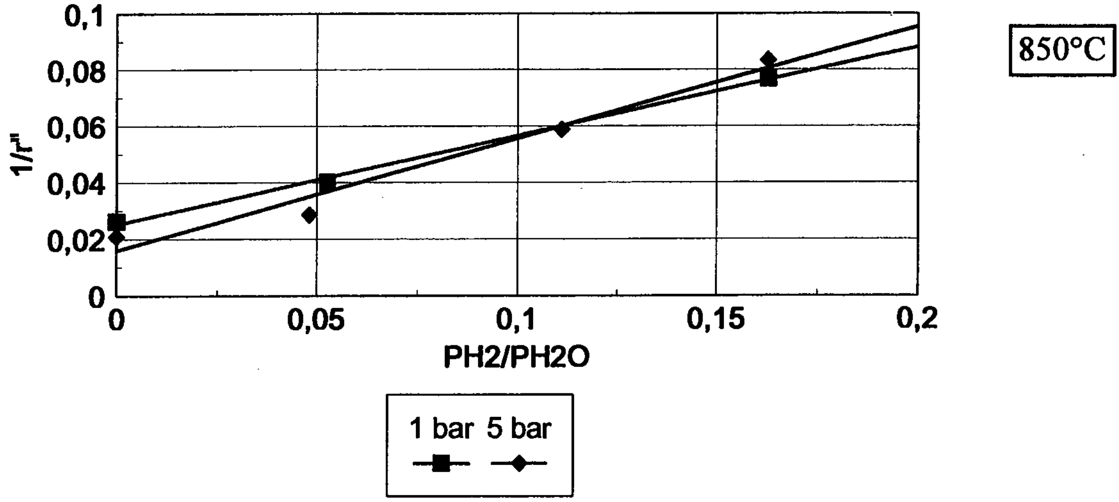


Figure 4. Dependence of the gasification rate of wood char and the P_{CO}/P_{CO2} ratio at 750 and 850 ^{o}C in the pressure range of 1-15 bar.



1 bar: $y = 10{,}346\,x + 0{,}4471$
5 bar: $y = 9{,}961\,x + 0{,}1500$



1 bar: $y = 0{,}3146\,x + 0{,}0252$
5 bar: $y = 0{,}3974\,x + 0{,}0159$

Figure 5. Dependence of the gasification rate of wood char and the H_2/H_2O ratio at 750 and 850 ^{o}C in the pressure range of 1-15 bar.

The reason for the differences observed seems to be the complexity of pressure dependence, which is possibly due to the behaviour of ash-forming substances during gasification. The catalytic effect of the ash-forming substances on the gasification reactivity of solid fuels is well-known, e.g., for lignites [10], and the gasification reactivity behaviour of low-rank coals is dependent on the behaviour of these substances [11, 12, 13] . Metals contained in biomasses have also been found to have a significant effect on their gasification reactivity [1-3, 7]. Thus, the behaviour of these substances during gasification can affect also the reactivity behaviour.

The behaviour of ash-forming substances during gasification can be very complicated. Possible effective behaviour models are an increase in diffusion resistance caused by ash or a decrease in catalytic activity of the ash-forming substances. In fuels with a low silicon content, the reaction rate correlates with the K + Ca content [2]. Biomasses, however, can contain very variable, even high, amounts of silicon [14], as shown in Table 1. Silicon occurs in plants dominantly as amorphous silicahydrate SiO_2nH_2O or as polymerised silicic acid [15]. Silicon distribution is highly dependent on the plant species. Silicon flocculates in cell structures protecting and supporting the plant. In fuel use, silicon can affect the reactivity by reducing it. The effect of silicon has been observed in the gasification of rice husk as a reduction in carbon conversion [3]. Research on silicate formation in gasification indicates an increase in diffusion resistance as the gasification reactions progress, when silicate ash sinters with alkali metals and carbon is encapsulated inside it. Kannan et al. [2] found out the reactivity-reducing effect of silicon by adding fine quartz powder to well-gasifiable biomass, when its gasification reactivity collapsed. Ash-forming substances may also react with each other or with the gas phase, when new compounds, different in catalytic effect can form [16].

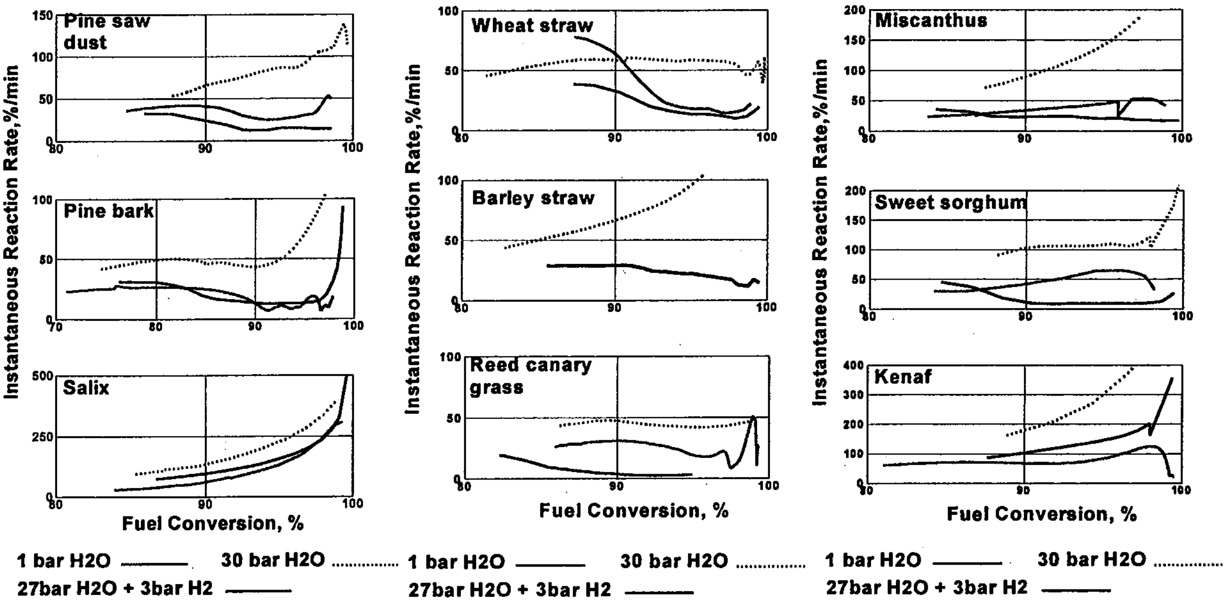
The reactivity results obtained with other biomasses indicate great scattering compared to the results obtained with wood. As can be seen from Fig. 6, the pressure dependence between various biomasses in steam and CO_2 gasification can be rather different and unpredictable. As an example, the effect of the presence of 3 bar hydrogen in steam on the gasification rate was determined at 30 bar total pressure. The results show that the presence of hydrogen reduces the gasification rate, and differently for different biomass types.

4 Conclusions

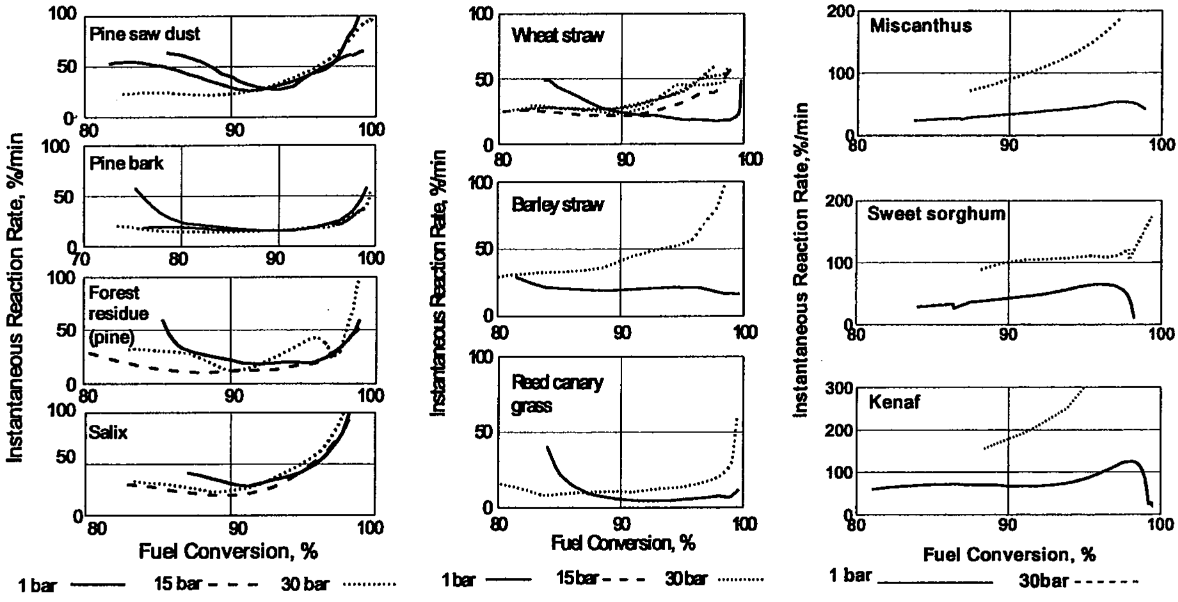
The most significant conclusion from this study is that the determination of characteristics that describe gasification requires detailed knowledge of fuel structure and ash chemistry. A hypothesis is that the deviations found out in this study, such as the reduction of reaction rate at increasing pressure and differences in the gasification behaviour of CO_2-CO and H_2O-H_2 mixtures are due to the behaviour of ash-forming substances in gasification.

5 Acknowledgements

This research was part of the gasification research programme of VTT Energy. The study was funded by the Finnish National Research Programme LIEKKI 2, Academy of Finland, Ministry of Agriculture and Forestry and VTT.



H_2O



CO_2

Fig. 6. Gasification behaviour of various biomasses measured in 1-30 bar pressure and at 850°C.

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PAPER V

New high-pressure gasification rate data for fast pyrolysis of black liquor char

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New High-Pressure Gasification Rate Data for Fast Pyrolysis of Black Liquor Char

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It has been customary, when measuring the gasification rate of black liquor char, to add CO during the preceding temperature equilibration period in order to suppress the loss of sodium by the char before gasification is started. The present study shows that this hot treatment *before gasification leads to a reduction in the pressurized CO_2 gasification rate data. It is proposed that a thin layer of soot, deposited during the hot pretreatment, reduces the catalytic activity of sodium sites for carbon gasification by CO_2. Surprisingly, the pressurized* hot treatment *has no effect on the pressurized H_2O gasification rate. Atmospheric* hot treatment *has also no effect on the gasification rate. New high-pressure CO_2 gasification rate data are presented for fast pyrolysis black liquor char which has not been subjected to the* hot treatment.

INTRODUCTION

Modern pulp mills produce steam and power for their own use. The heat in fuels — bark, sludges and black liquor — can be converted into power in a condensing steam turbine. The steam pressure and the temperature of the turbine are limited by the requirement to keep the corrosion rates in the recovery boiler at an acceptable level.

A more efficient way to utilize the fuel heating value is to apply combined-cycle technology which requires pressurized gasification of fuels [1–3]. Since black liquor is the dominant fuel in pulp mills, its pressurized gasification is of key importance for the introduction of combined-cycle technology [4]. A gasifier can in principle operate either below or above the melting point of the salts. The temperature window where operation would be difficult due to plugging problems [5] is somewhere between 700 and 850°C.

One of the key issues affecting gasifier design in the low temperature regime is char reactivity, i.e. how quickly the pyrolyzed char can be gasified. The cheapest gasifying agent is air which reacts quickly with volatiles of black liquor, producing an atmosphere where N_2, H_2O, H_2, CO_2 and CO are the main components, with some hydrocarbons and sulphur compounds. The char is subsequently gasified in this atmosphere. The gasification reaction is a rate-limiting step for the carbon conversion. The gasification rate of char under pressurized conditions is thus a very important parameter for implementation of the combined-cycle technology. However, this rate is very difficult to determine experimentally, since the production of the char and its actual gasification can only be done at conditions which approach those expected in industrial practice. Pioneering work on pressurized CO_2 and H_2O gasification of black liquor char has been carried out at Åbo Akademi, Finland [6–9] using a thermobalance set-up.

In order to obtain good gasification data, a uniform and constant temperature of the sample is required. This is obtained if the sample is kept in an inert atmosphere for a certain time, e.g. 400 s, before introducing the gasifying atmosphere. This has been the procedure in previous studies of pressurized gasification of black liquor as well as of atmospheric gasification [10–14].

To prevent the carbothermic decomposition of sodium carbonate through the proposed reactions (1) and (2) [18],

$$Na_2CO_3 + 2C \rightleftarrows 2Na + 3CO \qquad (1)$$

$$Na_2CO_3 + C \rightleftarrows 2Na + CO + CO_3 \qquad (2)$$

carbon monoxide has been added to the "inert" atmosphere during temperature equilibration [15–17]. However, since this particular pretreatment may affect the char reactivity, the present study addresses the question of what the effect is of time and atmosphere (in particular the pressure of CO) of the pretreatment on the carbon gasification rate.

EXPERIMENTAL

Black liquor was obtained from laboratory-scale digestion of *Pinus sylvestris*. The liquor was spray dried and particles larger than 105 µm were removed by screening. The composition of the dried black liquor is presented in Table I.

This liquor was pyrolyzed in a pressurized heated-grid unit shown in Fig. 1. The equipment is described in detail by McKeough [19]. The temperature history of the char during pyrolysis is shown in Fig. 2. The pyrolysis pressure was 100 kPa (absolute N_2), the temperature 675 or 710°C (standard deviation 10°C), and holding time 10 s for all the chars produced. The composition of the resulting char is presented in Table II. The numbers in brackets show that 35% of the sulphur and a negligible amount (5%) of sodium is released during pyrolysis.

The gasification reactivity measurements were carried out in a pressurized thermobalance (PTG) which is of the same make (DMT) as that used at Åbo Akademi. The schematic diagram is shown in Fig. 1. A more detailed description of its operation has been presented by Mühlen [20]. The flow of the reaction gases to the PTG are controlled with mass flow controllers. The

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TABLE I
COMPOSITION OF DRIED BLACK LIQUOR

	% of dry matter
Elemental analysis	
Carbon	38.5
Hydrogen	4.1
Sodium	17.3
Sulphur	3.5
Nitrogen	0.2
Oxygen (by difference)	36.4
Organic material	
Lignin	42.0
Aliphatic acids	27.4
Other	5.2
Total organics	74.6
Inorganic material	
NaOH	3.6
Na_2CO_3	2.5
Na_2S	2.4
$Na_2S_2O_3$	4.7
Na_2SO_4	0.2
Sodium bound to organics	11.2
Sulphur bound to organics	0.6
Other	0.2
Total inorganics	25.4

TABLE II
COMPOSITION OF CHAR

		% of char	%of dry black liquor
Sulphur (% of the original)		3.7	2.3 (65)
Sodium (% of the original)		26.4	16.5 (95)
Inorganics			
Na_2CO_3	93.5	52.2	
Na_2S	0.5	0.3	
$Na_2S_2O_3$	3.8	2.1	
Na_2SO_3	0.9	0.5	
Na_2SO_4	1.3	0.7	
Total inorganics	100	55.8	34.9
Gasifiable char (by difference)		44.2	27.6

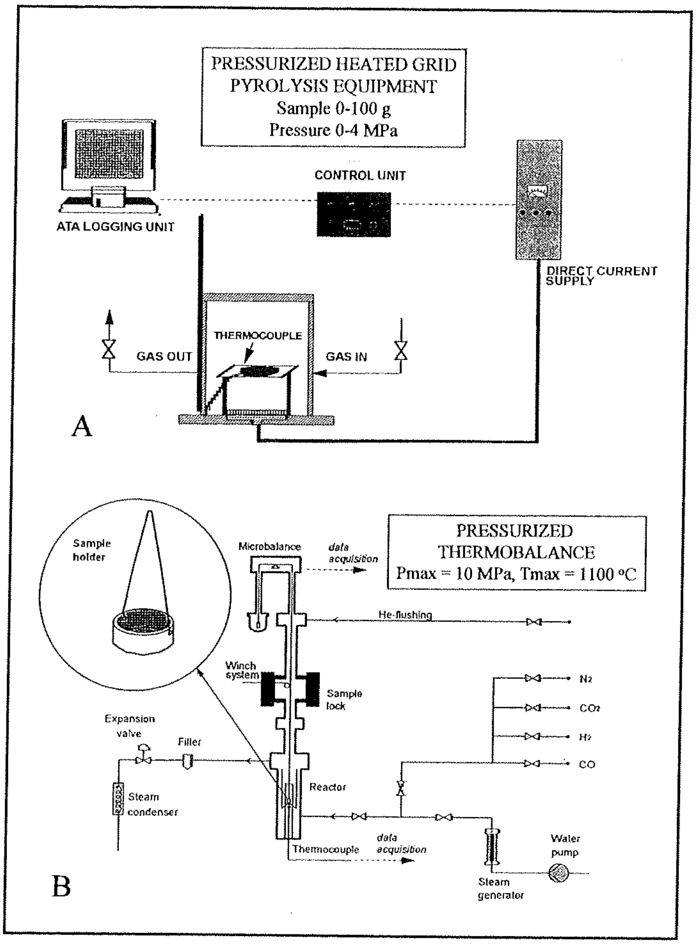

Fig. 1. (A) Heated grip pyrolysis and (B) thermobalance equipment.

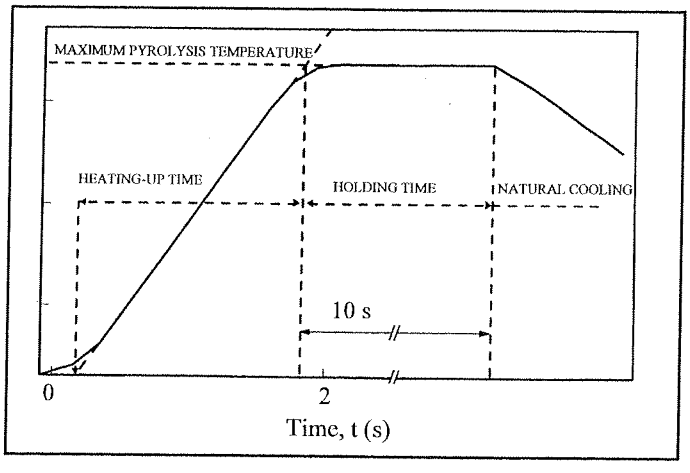

Fig. 2. Pyrolysis heating profile (heating rate 750 K/s).

gases are preheated to the reaction temperature in the jacket around the reactor tube before entering the reaction chamber. Helium is purged from the top of the reactor to prevent air from entering the microbalance compartment. The sample is placed in the helium-purged sample lock at ambient temperature while the reaction conditions are established. When the adjustments have been completed, the sample is lowered into the reaction chamber with a winch system. The gasification temperature and weight of the sample are monitored continuously with a computer. In our experiments, the gasification temperature is measured as well as controlled by a thermocouple placed beneath the sample holder.

A char sample of approximately 10 mg was weighed in a laboratory balance and put into the sample holder made of alumina (Fig. 1). After the gasification test, the sample holder was removed and the residue was again weighed immediately with a laboratory balance. If the residue had a greyish or black colour, or the weight curve still showed a decreasing trend, the ash content of the residue was determined by burning it in air in the thermobalance at 675°C (the temperature of the sample was not measured, but it undoubtedly was higher than the temperature of the thermobalance). The amount of gasifiable char was then obtained as the difference between the initial char sample weight and the weight of the residual ash.

When the sample is lowered into the reactor, it heats up to the reaction temperature at an estimated rate of more than 10°K/s. The weight change recorded during this period of approximately 60 s is due to several effects including buoyancy and gasification. Due to the uncertainty in the sample mass during these first 60 s, the initial char weight was obtained by extrapolation of the subsequent linear portion of the weight-loss curve (Fig. 3), for all the mass-time graphs. The initial char weight is needed in order to calculate the conversion of the total gasifiable material. The extrapolated part of the weight-loss curve was not used for the calculation of the gasification rate, so that the rates at 0–20% char conversion are omitted in the subsequent graphs.

In order to compare the above-mentioned procedure with those used in previous studies, a *hot treatment* period was added prior to the gasification in a number of experiments. During this period of typically 400 s, the sample was kept at the gasification temperature and a certain gas atmosphere. The atmosphere was N_2 with or without CO.

V/2

TABLE III

HOT TREATMENT AND GASIFICATION CONDITIONS

Sample		*Hot treatment* (400 s)				Gasification						
		P_{N_2}	P_{CO}	P_{tot}	T	P_{tot}	T	P_{CO_2}	P_{CO}	P_{H_2O}	P_{H_2}	P_{N_2}
Run no.	mg	kPa	kPa	kPa	°C	kPa	°C	kPa	kPa	kPa	kPa	kPa
329	9.9	no *hot treatment*				100	675	20	4	0	0	76
330	10.6	90	10	100	675	100	675	20	4	0	0	76
331	10.6	no *hot treatment*"				2000	675	400	80	0	0	1520
334	9.7	1800	200	2000	675	2000	675	400	80	0	0	1520
345	10.2	1800	200	2000	735	2000	735	400	80	0	0	1520
346	10.4	no *hot treatment*				2000	735	400	80	0	0	1520
392	10.0	no *hot treatment*				2000	735	0	0	400	80	1520
393	10.1	1800	200	2000	735	2000	735	0	0	400	80	1520

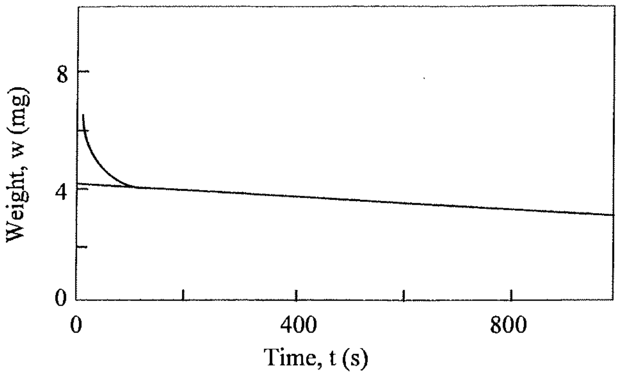

Figure 3

Fig. 3. Determination of initial char weight (A).

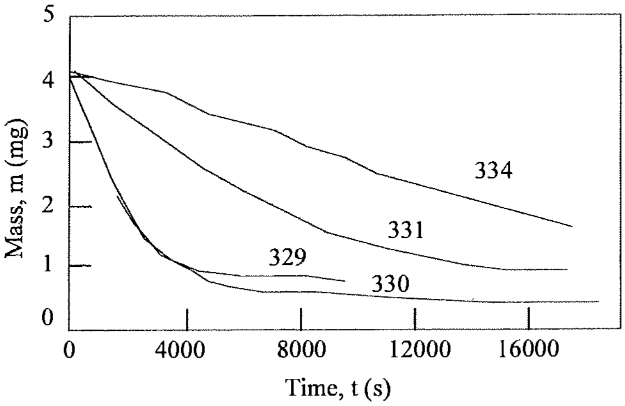

Figure 4

Fig. 4. Typical weight-time curves for gasification at 675°C. For legend, see Table III.

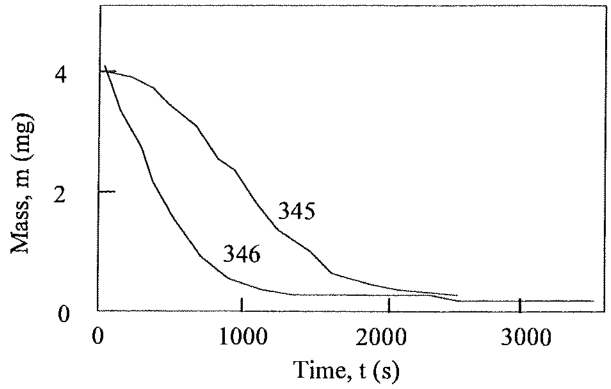

Figure 5

Fig. 5. Typical weight-time curves for gasification at 735°C. For legend, see Table III.

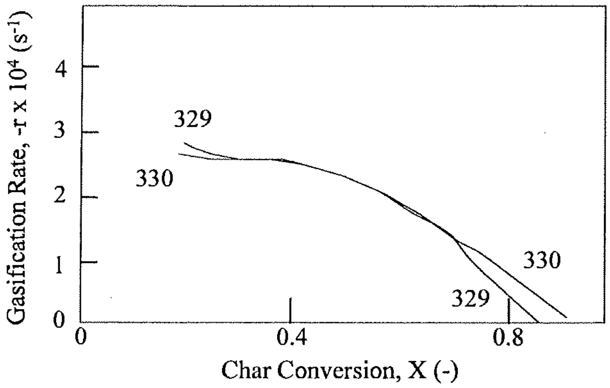

Figure 6

Fig. 6. Effect of *hot treatment* at atmospheric pressure on atmospheric gasification at 675°C. For legend, see Table III.

After the *hot treatment*, the sample was lifted up into the sample lock. After adjustment of the gasification atmosphere, the gasification procedure described above was again followed.

RESULTS

The weight–time (m–t) CO_2 gasification curves of the char with or without *hot treatment* are shown in Figs. 4 and 5 at, respectively, 675 and 735°C. Table III gives the different conditions for *hot treatment* and for gasification. It can be seen from these two figures that the *hot treatment* under a CO pressure of 10% retards the pressurized CO_2 gasification rate of the black liquor char, especially at the beginning. However, Fig. 4 also shows that the "*hot treatment*" has an insignificant effect on atmosphere gasification by 20% CO_2.

In order to better compare the char reactivities, the gasification rate, r, was determined as

$$r = -\frac{dm_c}{dt} \Big/ m_{c,o} \tag{3}$$

where

$$-\frac{dm_c}{dt}$$

is the measured weight-loss rate (mg/s), and

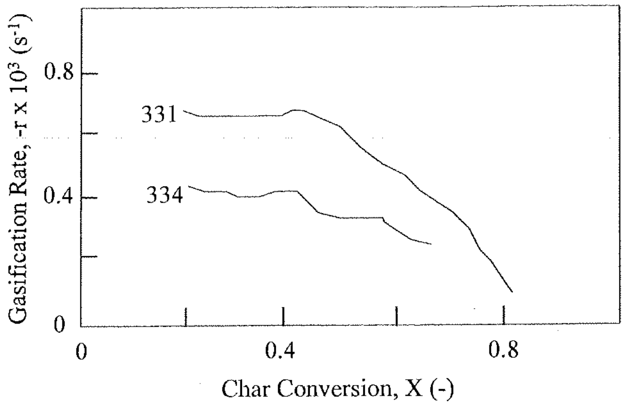

Figure 7

Fig. 7. Effect of pressurized *hot treatment* on pressurized gasification with CO_2 at 675°C. For legend, see Table III.

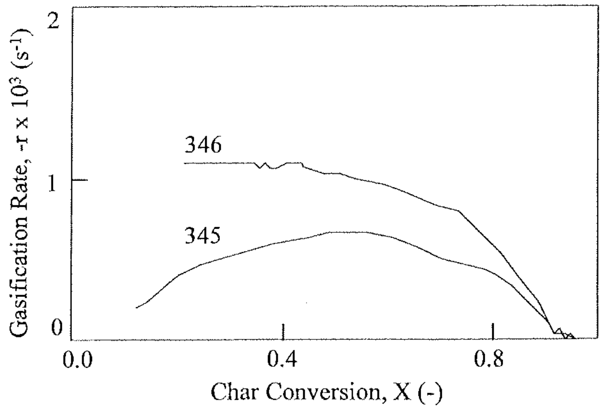

Figure 8

Fig. 8. Effect of pressurized *hot treatment* on pressurized gasification with CO_2 at 735°C. For legend, see Table III.

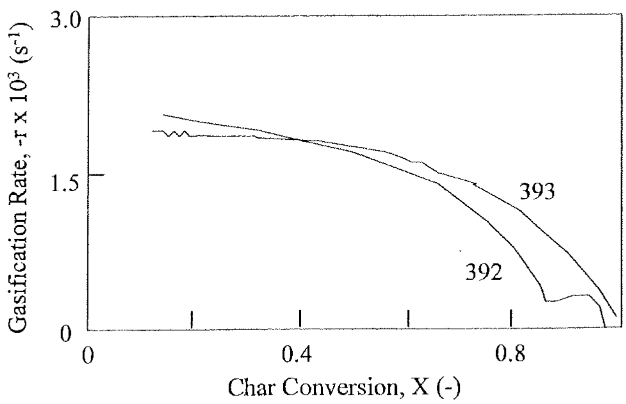

Figure 9

Fig. 9. Effect of *hot treatment* on the H_2O gasification rate at 735°C. For legend, see Table III.

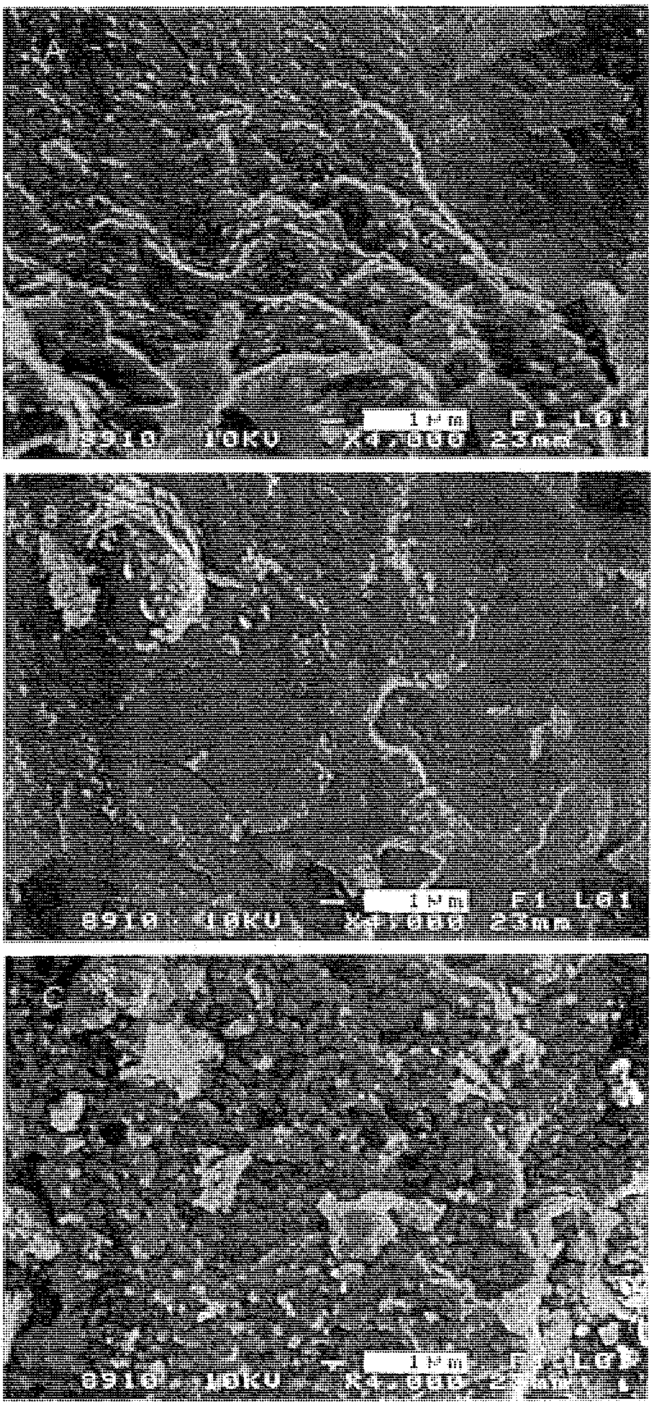

Fig. 10. SEM photomicrographs showing the effect of the *hot treatment* on char morphology. (A) Char after pyrolysis. (B) *hot treatment* at 100 kPa (P_{CO} = 10 kPa, P_{N_2} = 90 kPa); (C) *hot treatment* at 2000 kPa (P_{CO} = 200 kPa, P_{N_2} = 1800 kPa).

$m_{c,o}$ is the total gasifiable amount of char defined earlier. The gasification rate calculated for the experiments shown in Figs. 4 and 5 are plotted vs char conversion $X (= 1 - m/m_{c,o})$ in Figs. 6–8. The results in Fig. 6 confirm that the *hot treatment* has no effect on the char gasification rate at atmospheric conditions and 675°C. It can also be seen that the gasification rate is independent of char conversion up to $X \approx 0.45$. This behaviour has been noticed earlier for catalyzed gasification of quickly pyrolyzed black liquor char at atmospheric pressure [14]. Huhn [21,22] has concluded from coal gasification studies that the zero-order reaction is a sign of catalyst mobility in the char.

The effect of *hot treatment* on the $r-X$ behaviour of pressurized (2000 kPa) gasification by 400 kPa CO_2 and 80 kPa CO (the balance being N_2) at 675 and 735°C is

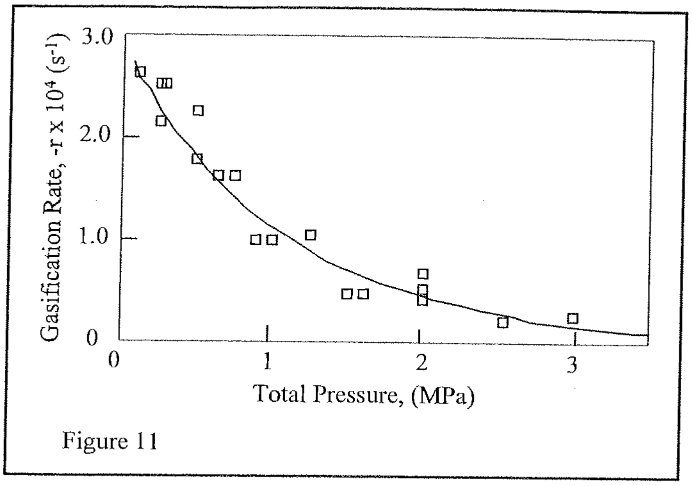

Fig. 11. Effect of total pressure on CO2 gasification rate at 675°C.

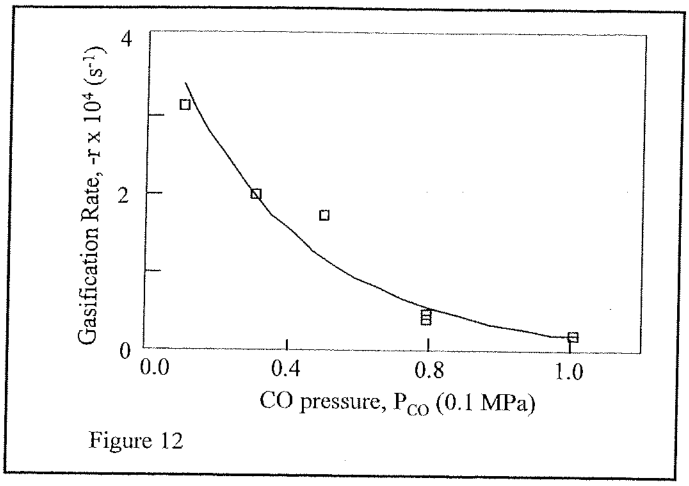

Fig. 12. Effect of CO partial pressure on CO2 gasification rate at 675°C when P_{CO_2} = 400 kPa.

shown in Figs. 7 and 8, respectively. These results quantify the decrease in the gasification rate due to *hot treatment* as 40 = 60% for conversions up to about 0.6. It is interesting to note that at 735°C the pressurized gasification of hot-treated char does not follow the zero order in char kinetic behaviour. The behaviour whereby the rate *r* first increases and then decreases has been reported previously as typical of pressurized gasification of black liquor char with CO_2 [9]. In our experiments, this type of behaviour is obtained at 735°C but not at 675°C.

When gasification is performed with H_2O, the effect of pressurized *hot treatment* under a CO atmosphere (10% CO, rest N_2) on the gasification rate is almost negligible, as can be seen in Fig. 9. At atmospheric pressure, the effect is also found to be negligible. Finally, *hot treatment* (400 s) without CO prior to gasification had only a minor effect on the gasification rate behaviour, both under atmospheric and at 2000 kPa total pressure for CO_2 and H_2O gasification.

EXPLANATION OF THE EFFECT OF HOT TREATMENT

It was found that the sample weight increased during *hot treatment* in the presence of CO. This was also the case with an empty sample holder, which became covered with soot. This behaviour can be explained by the reverse of the Boudouard reaction :

$$C + CO_2 \rightleftarrows 2\,CO \quad (4)$$

which produces CO_2 and carbon from CO. The weight increase rate observed with the empty sample holder is shown in Table IV (P_{CO} = 200 kPa, P_{N_2} = 1800 kPa). It can be inferred from Table IV that the amount of soot deposited at 735°C is significant, while that at 675°C is not.

TABLE IV
SOOT FORMATION RATE WITH EMPTY SAMPLE HOLDER

T,°C	Deposition rate, 10^{-4}, mg/s
675	0
735	1.2

Subsequent gasification of the soot deposited on the hangdown wire and empty sample pan with 100% CO_2 at 2000 kPa and 735°C gave a gasification rate of 1.3 × 10^{-4} (s^{-1}), which is an order or magnitude smaller than that for kraft black liquor char (see Fig. 8) considering the difference in CO_2 partial pressure (respectively 2000 and 400 kPa). Therefore, we propose that a thin layer of soot is deposited on the catalytically active sodium sites in black liquor char during pressurized *hot treatment*, which protects the char from gasification when CO_2 is subsequently introduced. In other words, the pressurized gasification rates at 735°C shown in Fig. 8 after *hot treatment* are significantly biased until the soot layer is removed by gasification. This also explains why the gasification rate, *r*, in Fig. 8 first increases with increasing conversion, *X*. The absence of this behaviour in Fig. 7 for pressurized gasification at 675°C is most likely due to the fact that the soot formation is much smaller at this lower temperature (see Table III). Microscopic evidence of soot deposition during *hot treatment* is presented in Fig. 10. It shows the char surface before and after *hot treatment*, the latter both at atmospheric and 2000 kPa total pressure. Mercury porosimetry showed that the soot deposition did not change the size distribution and volume of pores with a diameter less than 1 µm, indicating that the internal pore structure was unaffected by the soot formation.

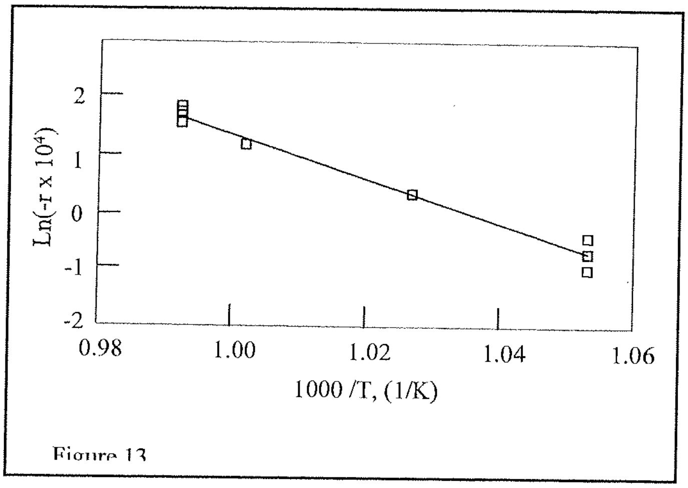

Fig. 13. Arrhenius plot of CO2 gasification rate for P_{CO_2} = 400 kPa, Pco = 80 kPa and P_{N_2} = 1520 kPa.

It is important to notice that *hot treatment* at atmospheric total pressure has no significant effect on the (pressurized) gasification rate. This means that the atmospheric gasification rate data reported for fast pyrolysis char following atmospheric hot treatment [11] are not affected by the *hot treatment*. Finally, it is surprising that the pressurized *hot treatment* has no effect on the subsequent pressurized steam gasification rate (see Fig. 9). This would suggest that the deposited soot does not form a barrier for H_2O, while it does for CO_2.

Gasification Kinetics

Because the previously reported pressurized gasification rate data are affected by the soot formation during *hot treatment*, a series of pressurized gasification experiments were performed without the *hot treatment* to determine the unbiased CO_2 gasification kinetics. These gasification rate data obtained at 675°C are shown in Figs. 11 and 12. In Fig. 11, the composition of the gasification gas is kept constant (P_{CO} = 4%, P_{CO_2} = 20%, balance N_2) while the total pressure is varied from 100 to 3000 kPa. It can be seen that the unbiased rate data show a dramatic decrease with increasing pressure, just as was shown earlier by Frederick et al. [9]. Actually, the data of Frederick et al. [9] are comparable to the present, presumably because in the latter study the maximum gasification rate was reported. In Fig. 12, the CO partial pressure is varied while the CO_2 partial pressure is kept constant at 400 kPa. The data in this figure clearly show the strong inhibiting effect of CO on the CO_2 gasification rate. The effect of temperature on the gasification rate is shown in Fig. 13. From this Arrhenius plot an activation energy of 368 kJ/mol is obtained, which is much higher than the value of 205 kJ/mol measured by Frederick and Hupa [7] for their high-pressure data. It is also much larger than the activation energy of 250 kJ/mol obtained by Li and van Heiningen [11] for atmospheric CO_2 gasification of kraft black liquor. Further work is needed to explain why the activation energy in the present investigation is different from these earlier studies.

ACKNOWLEDGEMENTS

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ABSTRACT: It has been customary, when measuring the gasification rate of black liquor char, to add CO during the preceding temperature equilibration period in order to suppress the loss of sodium by the char before gasification is started. The present study shows that this *hot treatment* before gasification leads to a reduction in the pressurized CO_2 gasification rate data. It is proposed that a thin layer of soot, deposited during the hot pretreatment, reduces the catalytic activity of sodium sites for carbon gasification by CO_2. Surprisingly, the pressurized *hot treatment* has no effect on the pressurized H_2O gasification rate. Atmospheric *hot treatment* has also no effect on the gasification rate. New high-pressure CO_2 gasification rate data are presented for fast pyrolysis black liquor char which has not been subjected to the *hot treatment*.

RÉSUMÉ: Lors du mesurage du taux de gazéification de la liqueur noire résiduelle, il est d'usage d'ajouter du CO durant la phase d'équilibrage antérieure de la température de manière à éviter que la liqueur noire résiduelle ne perdre son sodium avant que la gazéification ne soit amorcée. Notre présente étude montre que ce *traitement à chaud* effectué avant la gazéification amène une réduction des données du taux de gazéification du CO2 sous pression. Nous croyons qu'une mince couche de suie, déposée au cours du pré-traitement à chaud, réduit l'activité catalytique des emplacements de sodium au regard de la gazéification du carbone par le CO_2. Il est étonnant par ailleurs de constater que ce *traitement à chaud* sous pression n'a aucun effet sur le taux de gazéification du H_2O sous pression. À la pression atmosphérique, ce même *traitement à chaud* n'a pas non plus d'effet sur le taux de gazéification. Nous reproduisons ici de nouvelles données de taux de gazéification à haute pression du CO_2 aptes à assurer la pyrolyse rapide de la liqueur noire résiduelle qui n'a pas été soumise au *traitement à chaud*.

KEYWORDS: GASIFICATION, PYROLYSIS, BLACK LIQUORS.

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PAPER VI

Gasification reactivity of large biomass pieces

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Gasification reactivity of large biomass pieces

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ABSTRACT: The development of the reliable kinetic model for the development and design of fluidised bed gasifiers (FBG) requires knowledge about the char oxidation relevant to the gasifier. The biomass feedstock can have a large particle size distribution (maximum 50 – 100 mm). Char oxidation depends mainly on char porosity and catalytic material in char, which again depend on fuel reactions in pyrolysis. The pyrolysis conditions are therefore essential when gasification reactivity of solid fuels is determined. The behaviour of fuel in pyrolysis depends on the heating rate of fuel particles, which is dependent on the particle size. In large pieces, the centre heats up slower than the surface, which forms a layer of char after a fast reaction in the surrounding heat. In this work, the effect of particle size on gasification reactivity was studied in two ways: 1) the reactivity of char material formed when large wood pieces were pyrolysed, and 2) large pieces were gasified directly. Birch wood was used as sample material and particle/piece sizes varied below 0.5 mm to 10 mm. The reactivity tests were carried out isothermally in a thermobalance, in steam and at temperatures from 750 °C to 850 °C. The chars formed from the pyrolysis of the large wood pieces were crushed and their reactivity was measured normally. The other procedure was to insert the wood pieces in the gasification reactor and gasify it directly (*in situ* pyrolysis). According to the results, in both cases the gasification rate of chars showed a declining tendency with the increasing size of the wood pieces (maximum dimension or outer surface area of the wood piece).

INTRODUCTION

The development of the reliable kinetic model for the development and design of fluidised bed gasifiers (FBG) requires knowledge about the char oxidation relevant to the gasifier[1,2]. Char oxidation depends on char porosity, catalytic material (i.e. ash forming material) in char, which again depends on pyrolysis conditions. The behaviour of fuel in pyrolysis depends on the heating rate of the fuel particle, which is dependent on the particle size. The gasifier feedstock can have a large particle size distribution (maximum 50–100 mm). In larger particles the centre of the particle heats up slower than the surface, which forms a layer of char after a fast reaction in the surrounding heat. This layer is also subjected to attrition in the fluidised bed. Therefore, the effect of pyrolysis conditions is essential to know when gasification of solid fuels is modelled.

For coal, a lot of research is carried out on this subject, but less for biomass[3]. Zanzi[4] studied the effect of biomass particle size on gasification reactivity, but he used a smaller particle size range (less than 1 mm) than in this work. He observed that the char yield increased with particle size. In general, the temperature has a major role in pyrolysis as high temperature decreases char reactivity though affecting positively the heating rate in pyrolysis. Development and quality of internal surfaces of a particle are influenced by the reactor temperature and residence time of a fuel particle in the reactor. With large particles and pieces, the heating rate is different on the surface and inside the particle. Chen *et al.*[5] have compared the gasification reactivities of chars from free-fall reactor with fast heating rate and thermobalance with slow heating rate, and they concluded that the former had higher reactivity. According to Cazorla-Amorós *et al.*, the heating rate used in the pyrolysis treatment produces different initial dispersions for calcium[6], which act as catalyst in char gasification reactions[7]: higher pyrolysis heating rate produces higher dispersion for calcium, and thus higher reactivity. Calcium is an abundant element in biomass ashes, especially in woody biomasses (Table 1)[8].

At high temperatures exceeding 1000 °C, also the char structure becomes more ordered and hence results in a lower reactivity[9]. Zolin *et al.* have studied the effect of thermal deactivation of various solid fuel chars on oxidation reactivity[10]. They compared the deactivation-leached straw to a.o. coals and observed that the straw char deactivated with the increasing heat treatment temperature (temperatures 973–1673 K) but it had a higher reactivity than coal chars.

Inside large char particles and pieces, gas atmosphere containing product gas components (H_2, CO) is formed, which inhibit gasification reactions and thus should be taken into account in the modelling [1,11].

The objective of this work was to study, how gasification reactivity is affected by large piece sizes, which are relevant in the biomass feedstock material used in fluidised bed gasifiers. The results are applicable for wastes, too, since they contain a significant part of biomass[12]. The effect was studied in two principles: how large biomass feedstock pieces affect the char quality related to the gasification reactivity, and how fast the char with large piece sizes is gasified.

EXPERIMENTAL

The sample material used in the study was birch wood, which was the same as used by Barrio[13]. Table 1 presents the fuel characteristics of the birch wood.

Table 1 Properties of birch wood [13,14].

Proximate analysis	%, dry matter
Moisture	11.1
Volatile matter*)	78.7
Fixed carbon	20.9
Ash	0.37
Ultimate analysis	**%, dry matter**
C	48.7
H	6.4
N	0.078
O (by diff.)	44.5
Ash analysis	**% in ash**
Si	0.03
Al	0.01
Fe	0.17
Ca	30
Mg	4.8
K	28
Na	0.08
Ti	0.007
S	0.64
P	3.4

*) Pyrolysis conditions: heating at 24 °C/min until 600 °C, held for 30 min and natural cooling

Different piece sizes of birch wood were used as the sample material as presented in Fig. 1. The sizes used were sawdust (particle size below 0.5 mm) and wood pieces with several dimensions as presented with the results in Tables 2 and 3. Also symmetrical cubic pieces and round spheres were used in some test runs. The tests were carried out in the same thermobalance as used previously[15]. Gasification tests were mainly conducted isothermally in 1 bar steam pressure at temperatures from 750 °C to 850 °C.

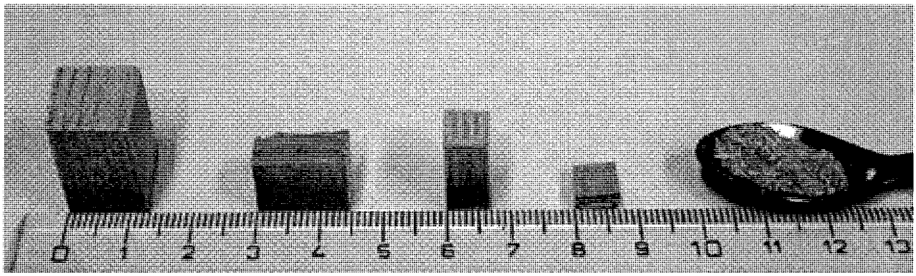

Fig. 1 Birch wood pieces used in the gasification tests.

To compare the results with the studies carried out by Barrio[13] with the sample material, the birch wood was subjected to heat treatments prior to the gasification tests. The treatments were divided into slow and fast heat treatments. It is common that the slow heat treatment is used when char gasification is characterised in a thermobalance. Barrio has used this slow heat treatment (SHT) in their research, which was simulated in this study according to the following: a sample of birch wood sawdust was heated in an inert gas phase of nitrogen (N_2) at a heating rate of 24 °C/min to 600 °C and kept in this temperature for 30 minutes. After that, the sample was held at 200 °C for 10 min, after which it was heated at a heating rate of 24 °C/min to 1000 °C and kept there for 30 minutes[14].

The heat treatments to simulate fast pyrolysis were carried out in a furnace as it takes place in fluidised bed gasification when the fuel enters the reactor. This was carried out with two methods a) VM method and b) *in situ* pyrolysis. The VM method was used to test the effect of the particle size on char quality. Accordingly, birch wood of different piece sizes was put in a crucible, which is used in the measurement of the volatile matter content[16]. The crucible was introduced at the temperature of 850°C, at which the sample was kept two holding times; 1–2 minutes and 3 minutes. The weight loss was about 86–87%. The large char pieces formed in this way were crushed and sieved to the particle size of 0.25–1 mm for the gasification measurements in the thermobalance. In the *in situ* method, the pyrolysis of large pieces took place by subjecting large pieces directly to the gasification surroundings in the thermobalance. The reactivity of char formed was measured directly thereafter. In these experiments, a sample holder of a cup form was used. The effect of the sample holder form on reactivity was tested and compared with the cylindrical sample holder, which is usually used in the reactivity tests[15]. With the cup, it was observed that the reaction rate was too fast for the cup holder at the temperature of 850 °C compared to that measured in the wire mesh sample holder. Therefore, the lower temperature of 800 °C was selected for the reactivity tests with the cup.

RESULTS AND DISCUSSION

The reactivities in the figures of this study are expressed in a form of instantaneous reaction rate, r" (%/min) *vs.* conversion, similarly as presented in reference[15]. In Tables 2 and 3, the reaction rate r" is presented as an average value covering the conversion range from about 10% to 80% for chars, and from 90% to 98% for fuels. In the fuel conversion values, the conversion caused by pyrolysis was included.

The heat treatment applied by Barrio gave similar result in our study, too, as shown in Fig. 2. Accordingly, the heat treatment affects the char so that it becomes significantly less reactive, and furthermore unsuitable for predicting fuel behaviour in

FBG. In the figure, it can be seen that the char produced *in situ* and in VM method have higher starting reaction rates than the SHT char. The prolongation of the holding time from 1 minute to 3 minutes of the VM chars had a negligible effect on char quality, as shown in Fig. 2. The gasification reactivity of char produced *in situ* was also similar to these chars.

Fig. 3 depicts the reaction rates of the VM chars that were subjected to the 1-minute heat treatment (compare Fig. 7). Tables 2 and 3 present the sizes of the sample pieces and the resulted gasification rates of the chars prepared with VM method and *in situ*, respectively.

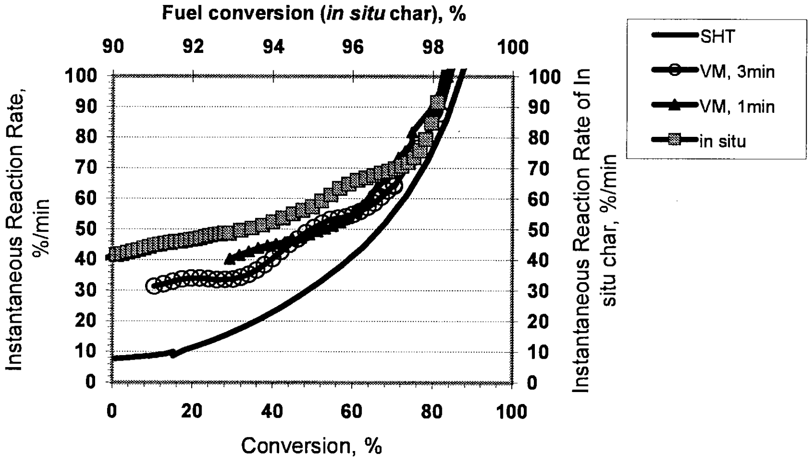

Fig. 2 Gasification reactivity of birch chars (particle size less than 0.5 mm) measured in 1 bar steam and at 850 °C. (Note: the conversion axis of the *in situ* char is scaled to correspond the SHT char).

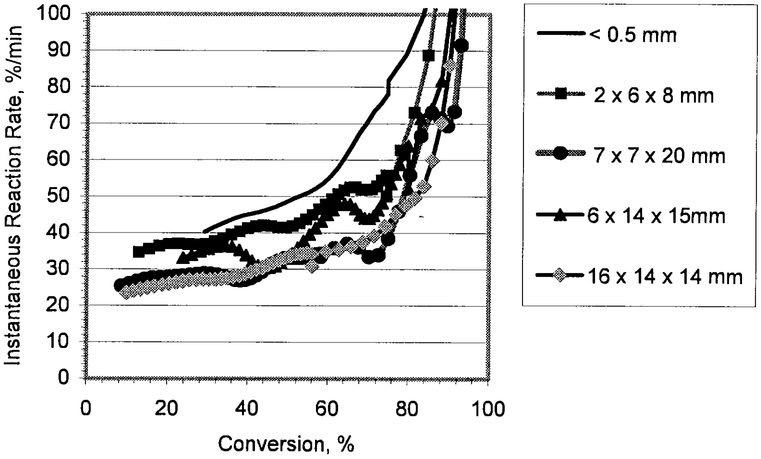

Fig. 3 Gasification reactivities of chars made from birch wood pieces of different sizes; chars were prepared with VM method, and the holding time was 1 min; gasification was carried out in 1 bar steam and at 850 °C.

According to the results, it is evident that pyrolysis of large pieces produced less reactive char as shown in Fig. 4, which presents the dependency of the gasification reactivity with the maximum dimension of the wood pieces. The reason for this can be connected with transportation of pyrolysis products (tars) formed during the pyrolysis of the large pieces. During the pyrolysis of large wood pieces, Chan *et al.* and Grønli[17,18] measured a significant temperature gradient from the hot surface to the cooler inner parts of the piece, and also the capillary tubes of wood were observed to affect the temperature profile. Thus, the volatile products released at the surface and transported to the cooler inner part could be condensated and form char, which can be assumed to have different properties than the rest of the char: This char material has lost contact with the char catalysing ash material, thus leading to a lower reactivity. However, this assumption would need to be studied further.

Table 2 The sizes of the birch wood pieces and the holding times used in the VM method; the gasification rates of the resulting chars; gasification was carried out in 1 bar steam and at 850 °C.

Dimension, mm				
Min.	Middle	Max.	Holding time, min	r" (10%–80%), %/min
saw dust		< 0.5	3	46
3	6	7	3	36
6	6	15	3	38
7	10	15	3	40
10	15	20	3	30
saw dust		< 0.5	1	57
2	6	8	1	45
7	7	20	1	31
7	7	20	1	33
6	14	15	1	40
6	14	15	1	41
14	14	16	1	31
6	14	14	1	41
11	11	11	1	45
9	9	9	1	38

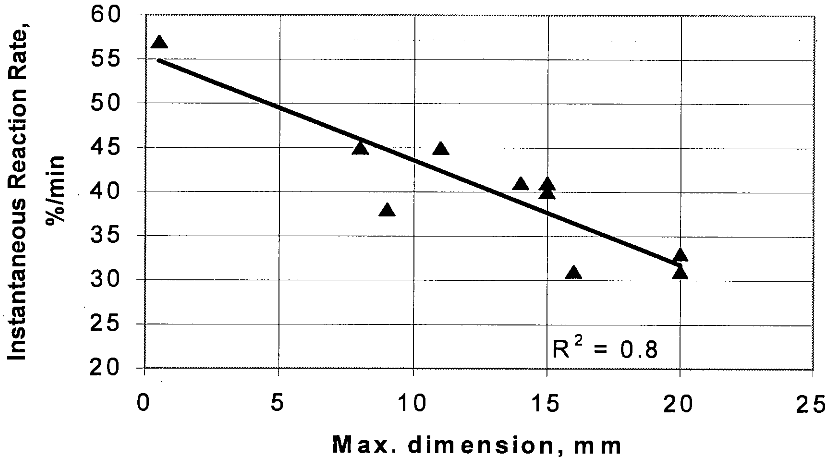

Fig. 4 The dependence of the gasification rate of the VM chars (holding time 1 min) on the maximum dimension of the wood piece; gasification was carried out in 1 bar steam and at 850 °C.

The pyrolysis of symmetrical pieces seem to produce little more reactive chars than the elongated, but this result was not very distinct, as presented in Fig. 5.

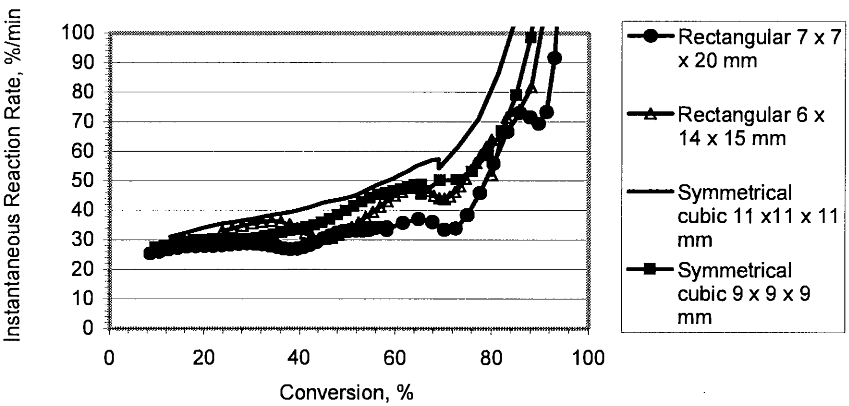

Fig. 5 Gasification reactivities of chars made from symmetrical and elongated birch wood pieces of different sizes; chars were prepared with VM method, and the holding time was 1 min. Gasification was carried out in 1 bar steam at 850 °C.

According to Fig. 6, the reactivity of birch char was comparable to those chars prepared from chipboards and cardboards (these components exist in wastes). The chars were made with VM method from birch wood of the size 10 x 15 x 20 mm, from chipboard of the size 20 x 12 x 8 mm and from the cardboard of the size 20 x 18 x 2 mm.

The results of the *in situ* chars are presented in Table 3 and in Figures 7–9. Here the sizes are given for different birch wood pieces, not for chars. It has to be noted that significant shrinkage takes place in the pyrolysis of wood pieces[19]. Accordingly, the gasification rates of these chars had the best dependency on the outer surface area of the original wood pieces as shown in Fig. 8: the higher the area, the lower the gasification rate. This result seems to correspond with the results obtained for modelling of char particle gasification by Konttinen *et al*[1], which showed a decreasing reactivity trend with the increasing piece dimension.

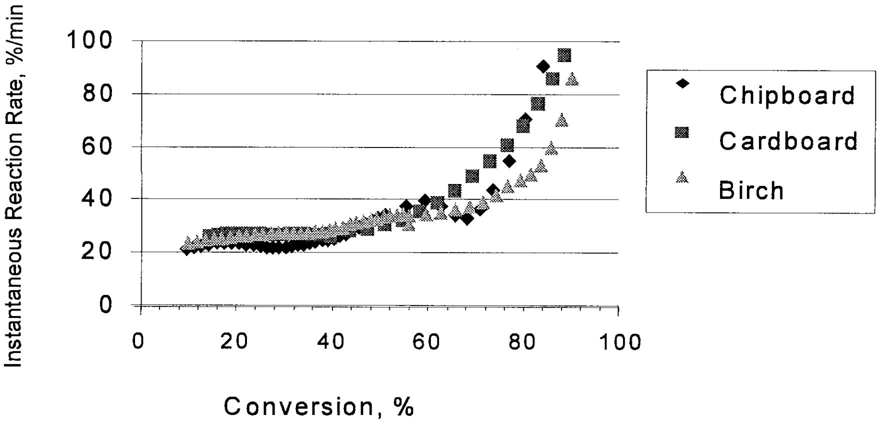

Fig. 6 Comparison of the gasification reactivities of the chars made from birch wood and pieces of wood waste; chars were prepared with VM method and the holding time was 1 min. Gasification was carried out in 1 bar steam at 850 °C.

Table 3 The gasification reactivities of the *in situ* chars measured in 1 bar steam at 750 and 800 °C.

	Dimensions, mm Min.	Middle	Max.	Max/Min	Area, mm^3	T, °C	r" (90%–98%), %/min
sawdust	< 0.5					800	26
sphere	10.5	10.5	10.5	1	346	800	17
cuboid	6	7	9	1.5	318	800	14
cuboid	3	4	5	1.7	94	800	35
crumbs	0.5	2	3	6	17	800	33
sticks	1	1	7	7	30	800	39
chips	1	6	9	9	138	800	20
sawdust	< 0.5					750	10
cuboid	6	7	9	1.5	318	750	4.4
cuboid	6	7	10	1.7	344	750	4.0

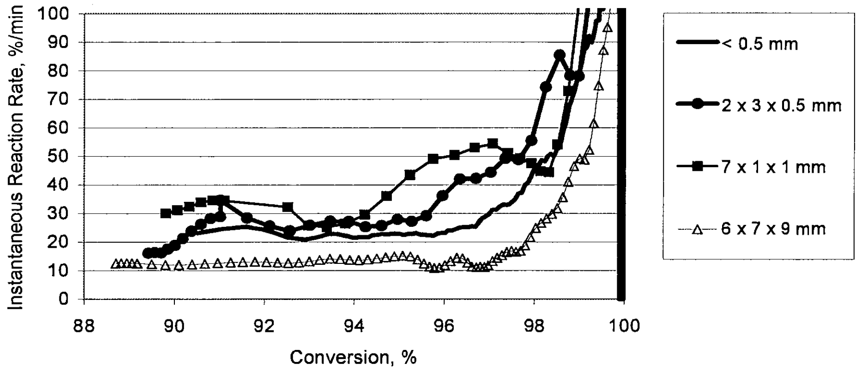

Fig. 7 Gasification reactivities of chars of different sizes made from birch wood pieces, respectively, with the *in situ* method; gasification was carried out in 1 bar steam at 800 °C (Note: the conversion presented on x-axis is the conversion of the whole fuel including pyrolysis).

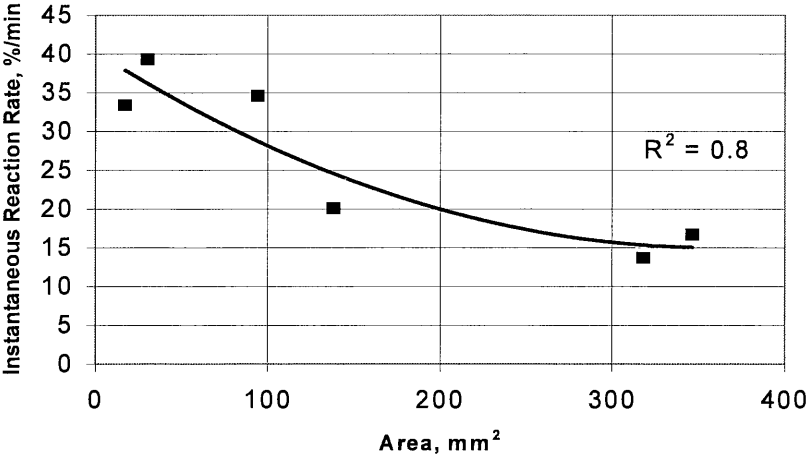

Fig. 8 The dependence of the gasification rate of the *in situ* chars on the outer surface area of the wood pieces; measured at 800 °C in 1 bar steam.

The effect of piece form was also tested. As it can be seen in Fig. 9, the form does not seem to be of importance at least when it comes to roundness. However, elongation seems to be a significant factor, as it can be seen in Fig. 7 from the result obtained with a 7 x 1 x 1 mm piece. The gasification rate of the char produced from the wood piece of this size was 1.5 times than that of sawdust. The reason for this might be related to the direction of the capillary tubes in the piece, but however, it needs further study.

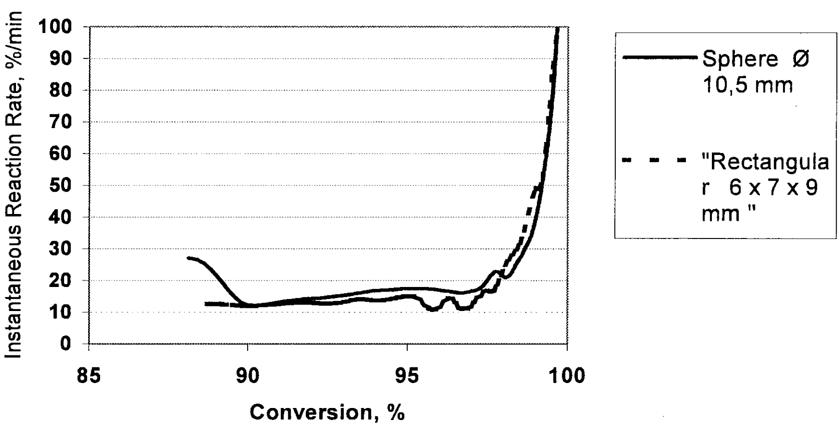

Fig. 9 Comparison of the gasification reactivity of a spherical and a rectangular birch piece measured in 1 bar steam at 800 °C, *in situ* pyrolysis.

CONCLUSIONS

In the study, gasification reactivity of biomass chars was measured in a thermobalance as a function of piece size and heat treatment. The study aimed at a support for the modelling of char gasification, which was needed in addition to the chemical kinetics[1,2]. The heat treatments were carried out in a furnace to simulate fast pyrolysis as it takes place in fluidised bed gasification. Firstly, it was tested how feedstock piece size affects char quality related to the reactivity, and secondly, how fast the chars prepared with *in situ* pyrolysis in the thermobalance reacted as a function of their size. Also, the effect of a high temperature heat treatment with slow pyrolysis rate on the reactivity was verified.

According to the results, high temperature (1000 °C) treatment with slow pyrolysis produced char, which was significantly less reactive at low conversion. In the pyrolysis of large wood pieces, char with slower reactivity was developed. The large char pieces reacted also slower with the increasing dimension, which is understandable due to the inhibiting effect of the product gases formed inside the pieces. In both cases, correlations between the dimension and the outer surface area of the original wood pieces and the gasification rate were found.

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PAPER VII

Ash behaviour in biomass fluidised-bed gasification

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ASH BEHAVIOUR IN BIOMASS FLUIDISED-BED GASIFICATION

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1. INTRODUCTION

In biomass combustion, ash deposit formation is a common problem and has been studied by a number of researchers [Miles *et al.*, 1995; Baxter and DeSollar, 1995; Nordin *et al.*, 1995; Bryers, 1996; Miles *et al.*, 1996; Moilanen *et al.*, 1996]. There are also some observations about operational problems in fluidised-bed gasification processes, caused by ash. In pressurised steam-oxygen gasification of peat, ash deposits have been formed in the upper part of the gasifier and in the cyclones [Moilanen, 1993]. Furthermore, straw ash has been found to cause both bed sintering and deposit formation in air-blown gasification [Kurkela *et al.*, 1996]. These problems were difficult to overcome in straw-alone gasification. In fact, the gasification temperature had to be reduced to below 800–850 °C, which resulted in poor carbon conversion and high tar concentrations. On the other hand, co-gasification of coal and straw (up to 50wt% straw) could be carried out without any signs of ash problems in spite of high operation temperatures of the order of 950–980 °C [Kurkela *et al.*, 1996].

One variable of significance that was observed to prevent the detrimental behaviour of ash in the gasification process was carbon conversion and measures to achieve this [Kurkela *et al.*, 1996; Skrifvars *et al.*, 1995]. The completeness of fuel carbon conversion is dependent on the reactivity of residual char and the operating conditions. If the reactivity is high, ash is formed rapidly and, consequently, deposits are also formed rapidly. The gasification reactivity of the biomasses has been observed to vary within wide limits [Moilanen and Kurkela, 1995; Moilanen and Saviharju, 1997]. Ash and its composition can be regarded essential in this respect and they vary significantly in different biomasses [Wilén *et al.*, 1996]. The ash components, mainly alkaline metal, contribute catalytically to the rate of gasification, which may increase or decrease as a function of conversion depending of the behaviour of catalytically active substances. However, it is rather unknown, in detail, how these substances react during the gasification of biomass chars.

Impact of Mineral Impurities in Solid Fuel Combustion, edited by Gupta *et al.*
Kluwer Academic / Plenum Publishers, New York, 1999.

The aim of this study was to obtain data on the detrimental ash behaviour of different biomass types in fluidised-bed gasification, and on the basis of these data to determine the process conditions and measures of preventing this kind of behaviour. Different types of biomass fuel relevant to energy production, such as straw and woody biomasses were used.

2. MATERIALS AND METHODS

Two different experimental methods were used in this study: laboratory thermobalance studies and bench-scale fluidised-bed gasification.

2.1. Laboratory Studies

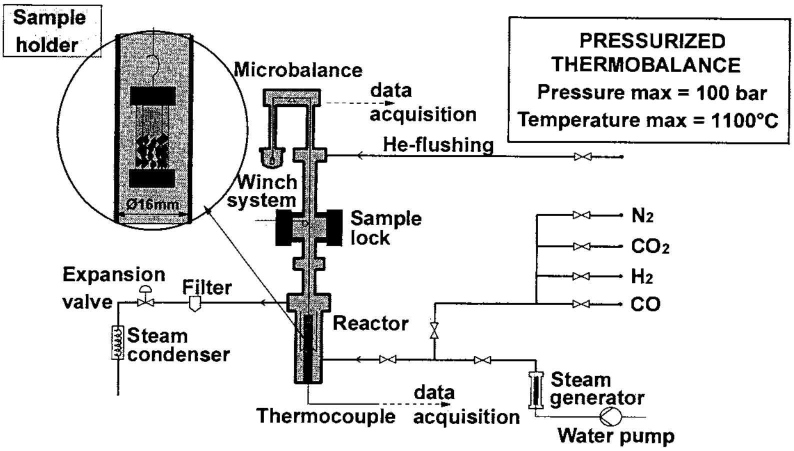
Different woody biomasses and straws were used as sample materials in this study. The samples are listed in Table 2. Analytical data on these biomasses have been published previously by Wilén *et al.* [1996] and Kurkela *et al.* [1996]. The most detailed studies were carried out with willow, wheat straw and alfalfa. The ash compositions of these feedstocks are presented in Table 1.

A pressurised thermobalance (PTG, Fig. 1) was used to study the characteristic reaction behaviour of the fuel and its ash. Elevated pressure was applied, as the elevation of pressure has been proven to contribute to ash sintering at lower temperatures than in ambient pressure [Moilanen and Kurkela, 1997]. In the present tests, the effect of temperature and pressure as well as the gasification agent on gasification reactivity and ash sintering were determined using the following reaction conditions: temperature 850 °C (isothermal measurement), pressure 1 or 30 bar, steam as gasification agent. If needed tests were also carried out at lower temperature of 750 °C. With some feedstocks also CO_2 was used as gasification agent.

For a test, the fuel sample (particle size below 0.2 mm, sample amount 100–200 mg) was placed in the cylindrical sample holder having the wall made of wire mesh. In an isothermal test, after the adjustments were completed (i.e. temperature, pressure, gas composition), the sample was lowered into the reactor with the winch system (Fig. 1). During

Table 1. Ash chemical composition of the wheat straw –95, willow and alfalfa ash.

Oxide	Danish wheat straw –95	Willow	Alfalfa
SiO_2	34.2	7.5	3.0
Al_2O_3	0.3	1.6	0.3
Fe_2O_3	0.2	1.1	0.7
CaO	8.4	35.0	22.4
MgO	2.16	3.5	9.0
K_2O	30.1	9.6	27.7
Na_2O	<0.5	0.8	1.9
TiO_2	0.02	0.1	0.02
SO_3	3.2	1.9	3.0
P_2O_5	3.9	7.8	8.0
Carbonate (as CO_2)	—	21	16
Sum	83	90	92
Ash content, % d.	4.8	1.3	6.9



the measurement, the gasification temperature and weight of the sample were monitored. The weight change recorded during the first 60 second period was due to several effects including buoyancy and gasification, and this part of the weight-time curve was removed in the evaluation process of the results. The sintering degree of ash residue after the reaction was inspected under microscope.

2.2. Fluidised-bed Reactor Studies

The behaviour of ash in fluidised-bed gasification was studied in the bench-scale atmospheric fluidised-bed reactor (AFB, fuel feed rate 0.5 kg/h, bed diameter 5 cm, freeboard diameter 10 cm, electrically heated jackets, Fig. 2). In this reactor, ash agglomeration and deposit formation was monitored both in the bed and freeboard by collecting samples from the reactor after the tests. The operation parameters of the reactor were selected to obtain differences in the ash agglomeration behaviour both in the bed zone as well as in the freeboard. The main operational parameters comprised temperature, bed material and the use of steam. The gasification agent was introduced only as the primary fluidization gas and no secondary or tertiary air was used. The selected operation conditions were in many respects similar to those of real large-scale gasifiers. Temperatures varied from 750 to 840 °C, and aluminium oxide, limestone, dolomite and coal coke were used as bed materials. Most of the tests were carried out with Danish wheat straw –95.

3. RESULTS AND DISCUSSION

3.1. Thermobalance Tests

The ash residues from the thermobalance experiments were studied by microscopy using the following classification criteria (Fig. 3, Table 2):

1. Non-sintered ash residue: ash structure resembling the original fuel particles, easily crumbling when touched (no asterisk: o)

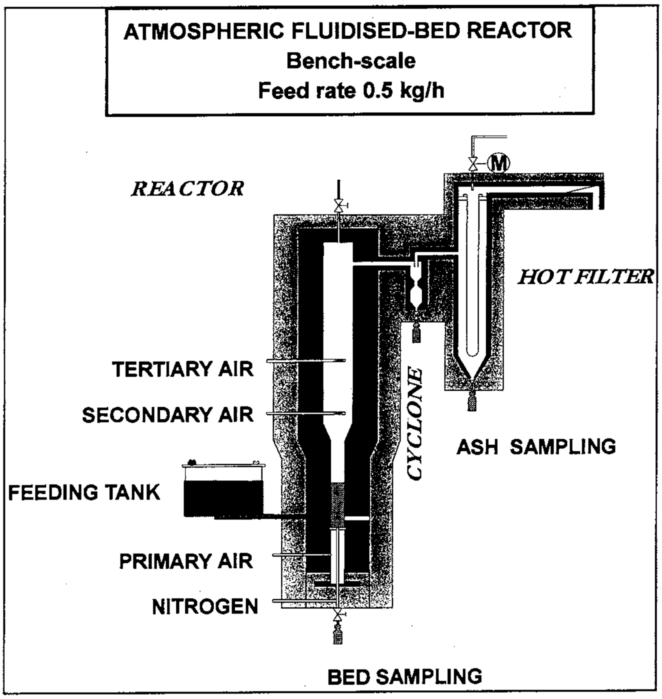


Figure 2. Bench-scale fluidised-bed reactor (AFB).

2. Partly sintered ash (different degrees in this group): particles contained clearly fused ash (1 or 2 asterisks: *, **);
3. Totally sintered ash: the residue was totally fused to larger blocks (3 asterisks: ***).

The thermobalance tests carried out in high pressure steam showed that under pressure ash sintering with some of the feedstocks was much stronger than in atmospheric pressure. Willows (Finnish and Swedish), spruce bark and alfalfa had this type of behaviour. The ash residues were totally sintered when willow and spruce bark samples were gasified under 30 bar steam and at 850 °C, and the same result was obtained even at 750 °C. With alfalfa, the ash residue was completely sintered even at 700 °C. On the other hand in atmospheric pressure, no sintering was observed at 850 °C with willow and spruce and clearly weaker sintering with alfalfa.

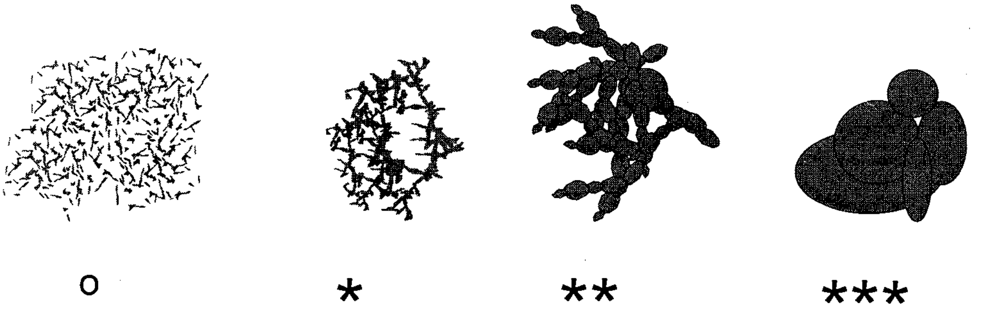


Figure 3. Classification of the ash residues with increasing sintering.

Table 2. Conditions in the thermobalance and the sintering degree of ash residue determined by microscopy.

	Temperature and gasification agent				
	850 °C			750 °C	
	H_2O		CO_2	H_2O	
Biomass	1 bar	30 bar	1 bar	1 bar	30 bar
Pine bark	o	o	na.	na.	na.
Pine saw dust (ash amount small)	***	***	o	o	o
Spruce bark	o	***	*	na.	***
Forest residue **B**, total	o	o	na.	o	na.
Forest residue **B**:					
— bark	na.	***	na.	na.	***
— needles	o	*	na.	na.	o
— stem	o	o	na.	na.	na.
Finnish willow	o	***	***	o	***
Swedish willow	o	***	**	o	**
Finnish wheat straw	***	***	**	@	***
Danish wheat straw A	***	***	na.	na.	**
Danish wheat straw B	***	***	*	*	*
Danish wheat straw –95	***	***	*	**(*).	na.
Alfalfa	**	***	*	*	***

o no sintering; *slightly sintered; **moderately sintered; ***completely sintered; @not totally gasified; na.: not analysed.

When gasifying in CO_2 at 850 °C, a different sintering behaviour was observed: the ash residues of the willow were strongly sintered, but the ash of spruce bark sintered less in these conditions. The sintering of alfalfa was also weaker under CO_2 than in steam gasification. The reason for this behaviour is assumed to be connected with the lack of silicon in these ashes (see Table 1).

The ash of pine bark differed from that of spruce bark in having no sintering tendency in these tests. This observation is in consistence with the tests in the fluid-bed gasifier in which pine bark has shown no ash problems. The other biomasses, like pine saw dust indicated strong sintering after gasification in the thermobalance. This was somewhat surprising, because the saw dust ash had not shown any deposition or agglomeration problems in the fluidised bed gasification. The reason for this can be that the ash content of saw dust is very small, and hence, ash problems are avoided due to the dilution of ash in the process.

In earlier fluidised-bed gasification tests of forest residues at VTT (mainly spruce based), ash deposits were formed in the cyclones of the gasifier. To find out the reason for this behaviour, this feedstock was characterised by separating different parts: needles, bark and stem. According to the results, the bark seemed to be the most critical component of forest residue feedstock. The bark ash of forest residue B in Table 2 showed strong sintering under pressure, similarly as measured with the separately studied spruce bark sample. The ash from needles seemed to have only a weak sintering tendency in pressurised gasification, and stem ash indicated no signs of sintering.

The wheat straw ash generally showed strong agglomeration in gasification tests performed earlier at VTT, but this behaviour seemed to be dependent on the quality of the straw used as feedstock [Kurkela *et al.,* 1996]. In the thermobalance tests of this study, the wheat straw ashes sintered strongly when gasified at 850 °C both under 1 bar and also under 30 bar steam. Even at 750 °C strong sintering was observed in some samples. The use of CO_2 as gasification agent resulted in less sintering.

To find out the reason for the differences observed in the ash behaviour of wheat straws, the relationship between the chemical composition, sintering and gasification reactivity of ash was studied in further detail for this biomass. Table 1 presents the chemical composition of the ash of Danish wheat straw (= 95), willow and alfalfa. Accordingly, the potassium content of this straw ash was very high; 30.1% of K_2O in ash. The wheat straw samples previously used in the gasification tests (indicated as Danish wheat straws A and B) had a K_2O content of 8.1 and 18.1% in ash, respectively [Kurkela *et al.* 1996]. Their gasification reactivity behaviour, i.e., gasification rate vs. conversion, is shown in Figs. 4 and 5. The reactivity is expressed in form of instantaneous gasification reaction rate, %/min (i.e. mass change rate divided by residual ash-free mass), and the conversion (given as fuel conversion, % ash-free) is the reacted part of the whole biomass including pyrolysis. The reactivity behaviour of wheat straws showed that the gasification rate can be increasing or decreasing as a function of conversion, depending on the quality of wheat straws B and = 95 showed an increasing trend and straw A a decreasing trend. This difference seems to be associated with the potassium and silicon ratio in the ash. Potassium is known to be a strong catalyst in gasification reactions, and the potassium silicate formation could decrease its activity, as indicated e.g. by Kannan and Richards [1990].

The gasification reactivity behaviour has been shown to affect the sintering of ash in such a way that the retarding gasification rate prolongs the achievement of the total conversion and, as a consequence, ash is also formed slower and the carbon material prevents ash particles from agglomerating. This phenomenon indicates that the control of carbon conversion may contribute to ash sintering in gasifiers [Moilanen and Kurkela 1995; Kurkela *et al.*, 1996]. Figure 4 shows that for wheat straw A, which had a retarding trend of gasification rate, the time required for achieving the ash conversion of 100% was more than four times longer than for straw B (which had the trend upwards). But, when straw A was gasified totally the resulting ash residue was also totally sintered (Table 2).

The effect of potassium content on the reactivity behaviour was studied more closely by washing the straw samples with water. The theory behind this was that rain

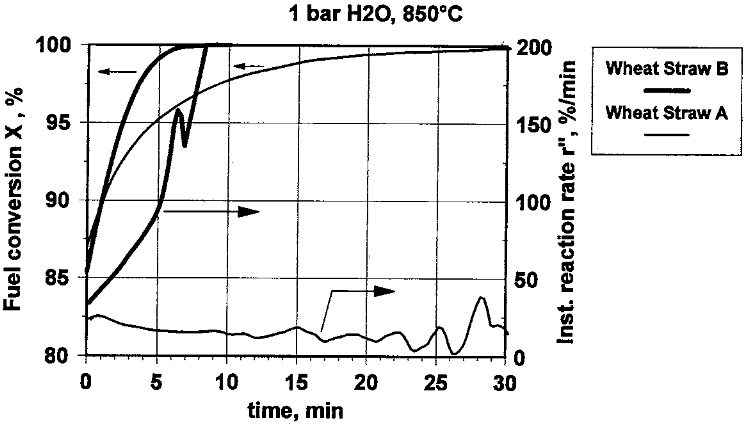


Figure 4. Development of the gasification rate of straw A and straw B and conversion as a function of time measured at 1 bar H_2O and 850 °C.

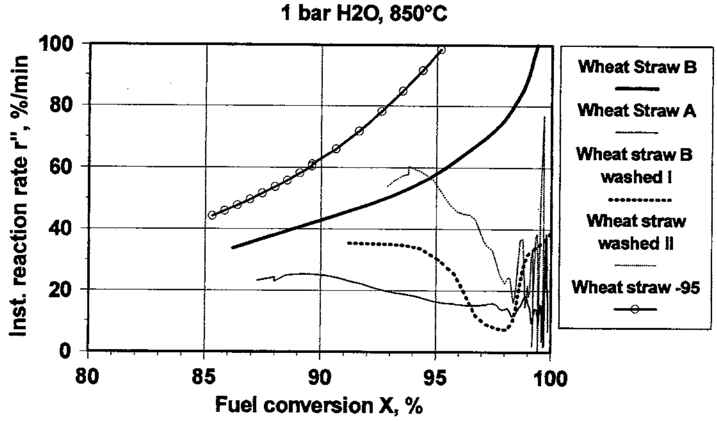


Figure 5. Gasification reactivity of unwashed and washed straws measured at 1 bar H_2O and 850 °C.

had probably influenced straw A by leaching out potassium. Henriksen *et al.* [1997] have also reported decreasing gasification reactivity after washing straw. Thus, straw B was washed with distilled water, and a result similar to straw A was obtained (Fig. 5). The effect of the intensity of water leaching was also tested: the washing procedure was carried out with two methods (indicated as I and II in Fig. 5). Sample I was washed with water at ambient temperature and sample II with boiling water. The potassium content after washing was not determined, but the ash content was reduced from 4% to 3% in sample I and to 2.2% in sample II (the amount of ash was taken from the thermobalance tests). The reactivity reduced clearly to the same level as that of straw A after washing independent of washing intensity.

3.2. Results of the Fluidised-bed Reactor Tests

In the bench-scale fluidised-bed reactor (AFB), nine gasification tests were carried out. Danish wheat straw =95 was used as the fuel in tests AFB1-8, while test AFB9 was carried out with spruce bark. A mixture of air and steam was used as the gasification agent in all tests except test AFB2, which was carried out without air. The air to fuel ratio was selected so that it corresponded to 31–33% of the air to fuel ratio of stoichiometric combustion. Approximately 45 vol% of the fluidising gas was steam in all experiments. The use of relatively high air ratio and high steam feed was necessary to achieve high enough carbon conversion (typical to real-scale gasifiers) without recycling the cyclone fines. The test conditions and the main results are presented in Table 3.

The total test time used for the steady state gasification set point is given in Table 3. The time when the first changes in process parameters (i.e. sudden variations in the bed temperature and/or a pressure rise in the reactor) during the test indicated that agglomeration took place is also given.

Attention was paid to deposit formation in the freeboard and in the bed. The size and strength of agglomerates were different in every test depending on the operating conditions. Some test runs had to be interrupted, because so large agglomerates were deposited in the bed that fluidising was no more possible. Examples of such agglomerates are shown in Fig. 6. The agglomerates were mainly large and irregular, except for one test, in which they were quite regular in size (AFB6).

Table 3. The test conditions and characterisation of ash behaviour in the AFB test runs (× describes the intensity of agglomeration (d_p feedstock 0.6–0.9 mm, d_p alumina bed 0.6–0.7; limestone and dolomite 0.7–1.0; coke 1.2–1.5 mm; U(bed) 0.8 m/s, U(freeboard) 0.3 m/s; T(freeboard) almost the same as T bed +/– 5 °C.

Set point	AFB1	AFB2	AFB3	AFB4	AFB5	AFB6	AFB7	AFB8	AFB9
Feedstock	Straw	Straw	Straw	Straw	Straw	Straw	Straw	Straw	Spruce bark
Bed material	Al_2O_3	Al_2O_3	Limestone	Limestone	Limestone	Precalcined limestone	Dolomite	Coke	Dolomite
T (bed), °C air ratio	840 0.31	830 0[2]	840 0.33	795 0.31	750 0.32	835 0.31	830 0.31	710–840[1] 0.31	830 0.31
C-conversion, wt%	97.2	90.0	98.4	95.7	93.2	97.8	96.5	89.7	81.6
Freeboard deposits mg/g fed feedstock	3.5	43	1.3	0.8	0.6	4.2	3.8	<0.5	<0.5
Visual characterisation of deposit	molten ash	molten ash	molten ash	molten ash	molten ash and char	molten ash	molten ash	unreacted char + molten ash	some molten ash
Total amount of fed feedstock, g used bed material, g	2,494 556	1,410 555	2,972 411	2,967 411	4,769 411	1,512 411	2,648 425	1,410 160	3,880 425
Total test time, min	240	420	285	240	360	120	225	130	360
Initiation sign of bed sintering, min	57	—	117	185	—	70	225	53	—
Bed sinters after the test	xxx	xxx	xx	xxx	0	xx(x)	x	xxx	0
Visual characterisation of bed agglomerates	solid	porous	porous	porous		spherical, quite equal in size			

[1] during the test, temperature varied due to unstable fluidisation (light weight bed material).

[2] this test was carried out without air using a mixture of steam and nitrogen as fluidizing gas.

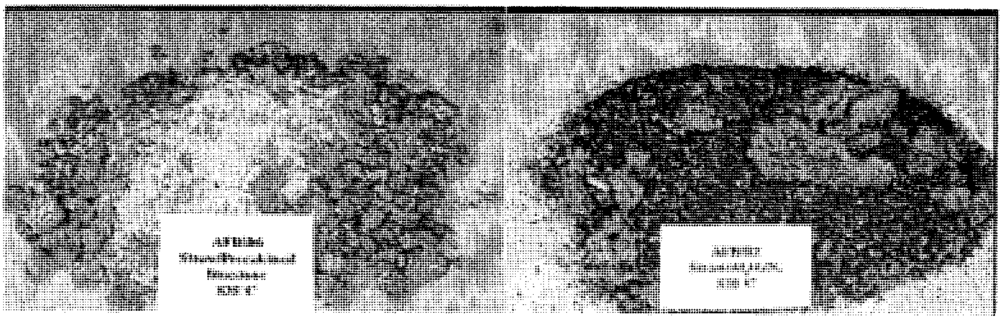


Figure 6. Examples of two types of bed agglomerate: large agglomerates (left, set point AFB2) and regular-size agglomerates (right, set point AFB6). Scale: the long side of the figure about 15 cm.

In every test, some agglomerates or deposits were found either in the bed or on the freeboard walls (or both). The material deposited on the freeboard wall was not strongly sticked in any of the tests, and it was easy to brush off from the wall (Fig. 7). The amount of freeboard deposit was determined after each test. The amounts are given as milligrams against gram of fed feedstock in Table 3. In test AFB2, the amount was highest and in tests AFB4, 5, 8 and 9 the amounts were very small, in fact almost negligible.

The microscopic study of the deposits indicated that in all cases the deposits consisted of particles containing molten ash particles, fine bed material particles sticked to this ash, and also unreacted char particles were present in different amounts. An example of this type of molten ash particle (cross section) is shown in Fig. 7.

At test runs AFB1 and 2, the effect of gasification agent with alumina bed material was tested. The use of steam prevents peak temperatures which can lead to ash melting. In the test runs AFB3-5, limestone bed material was tested at various temperatures, and in tests AFB6-8, different bed materials were compared. In AFB9 spruce was used as feedstock.

In both tests carried out with alumina bed, AFB1-2, large agglomerates were collected from the bed. The agglomerates were less porous in test AFB1, where air was used. Freeboard deposits also occurred in large amounts in these tests. When limestone bed material was tested (AFB3-5) at various temperatures, bed agglomerates were formed at temperatures of 800 °C and above. No agglomeration was detected at

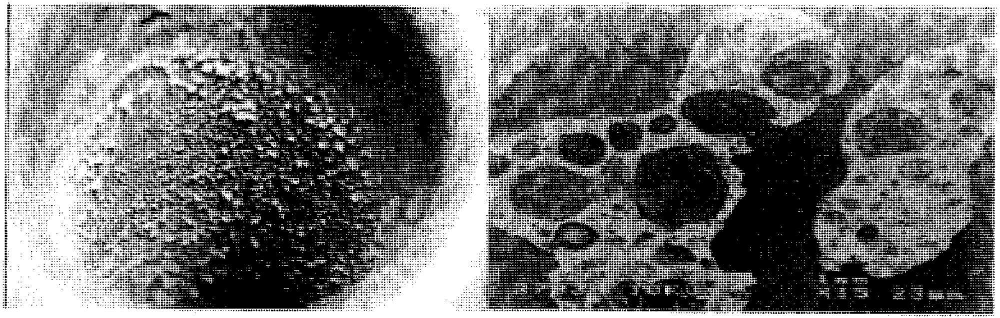


Figure 7. An example of a freeboard deposit in the upper zone of the AFB reactor (left, the reactor i.d. 102 mm) and a cross-section of molten structures contained in the deposit (right, the long side of the figure about 5 mm).

750 °C, although particles containing molten ash were seen in the fairly thin freeboard deposit. In the limestone test series, most severe bed agglomeration occurred at about 800 °C (AFB4). The freeboard deposits in these tests were clearly thinner than in the previous runs.

Tests AFB6 and 7 were carried out at the same temperature level as the tests AFB1-3. In test AFB6, performed with precalcinated limestone at 830 °C, round agglomerates of regular size were obtained, the size of which was growing to such an extent that fluidising was no more possible (Fig. 6). In test AFB7 dolomite was used as bed material and only a few small agglomerates were formed. The temperature level was the same as in the previous test. When using coal coke (AFB8) large bed agglomerates were obtained. These phenomena indicate that the interaction of ash and bed material in the fluidised bed contributes significantly to the agglomeration. No bed agglomerates were detected in the gasification test with spruce bark (AFB9). However, some particles containing fused ash were also seen in the fairly thin freeboard deposit.

3.3. Discussion of AFB Results

The tests with alumina bed material resulted in strong agglomeration in the bed. In the first test (AFB1), applying a mixture of air and steam, it was difficult to maintain the temperature steady at 830 °C and large variations were observed in the bed temperature. This was a sign of starting fluidising malfunctions due to agglomeration (in about 1 hour after start). However, fluidisation did not collapse totally until after four hours, when there were already large agglomerates in the bed. The second test (AFB2) assured that no temperature peaks occurred, and therefore the air feed was excluded (heating only with electric resistances) and only steam was used as gasification agent. Gasification continued for a longer time, but large agglomerates were detected also in this test. However, these agglomerates were porous and very permeable by gas, which probably was the reason for that no dramatic changes in the process parameters were detected during the test run. The contact between straw ash and alumina bed particles forming agglomerates was studied more closely with microscopy. An example of bed agglomerate formed when gasifying straw in the aluminium oxide bed is shown in Fig. 8. In the agglomerate, the bed material particles were glued relatively strongly to each other by molten ash. SEM analyses taken from the bed material moving from the bed material grain towards the sticking ash material indicate the composition at different locations. Point 3 (Fig. 8) presents an analysis of the gluing zone and indicates that it consisted mainly of potassium and silicon, and some calcium. According to the chemical composition of ash (Table 1) potassium and silicon are the major CO components in this wheat straw ash. According to the phase diagrams the K_2O-SiO_2 binary system has the lowest melting temperature of 740 °C (with the composition of 33 wt% K_2O and 68 wt% SiO_2) [Levin *et al.*, 1985].

In the next test, alumina was changed to limestone bed material. In AFB3, the temperature level was the same as in the previous two runs. Also in this test, large agglomerates were formed in the bed already within 2 hours after the start. Despite the fact that agglomeration took place also in the limestone bed, the contact between ash and bed material differed from that in alumina bed. The agglomerates in the limestone bed were more brittle due to the friable structure of limestone particles (but firm enough to resist bed attrition). In test AFB4 (limestone bed material), bed agglomeration was even more intense than in AFB3 although the test temperature was lower (795 °C). An explanation for this could be the formation of fused carbonate between uncalcined limestone and straw ash, which can be connected with the slower rate of calcination in this run. The

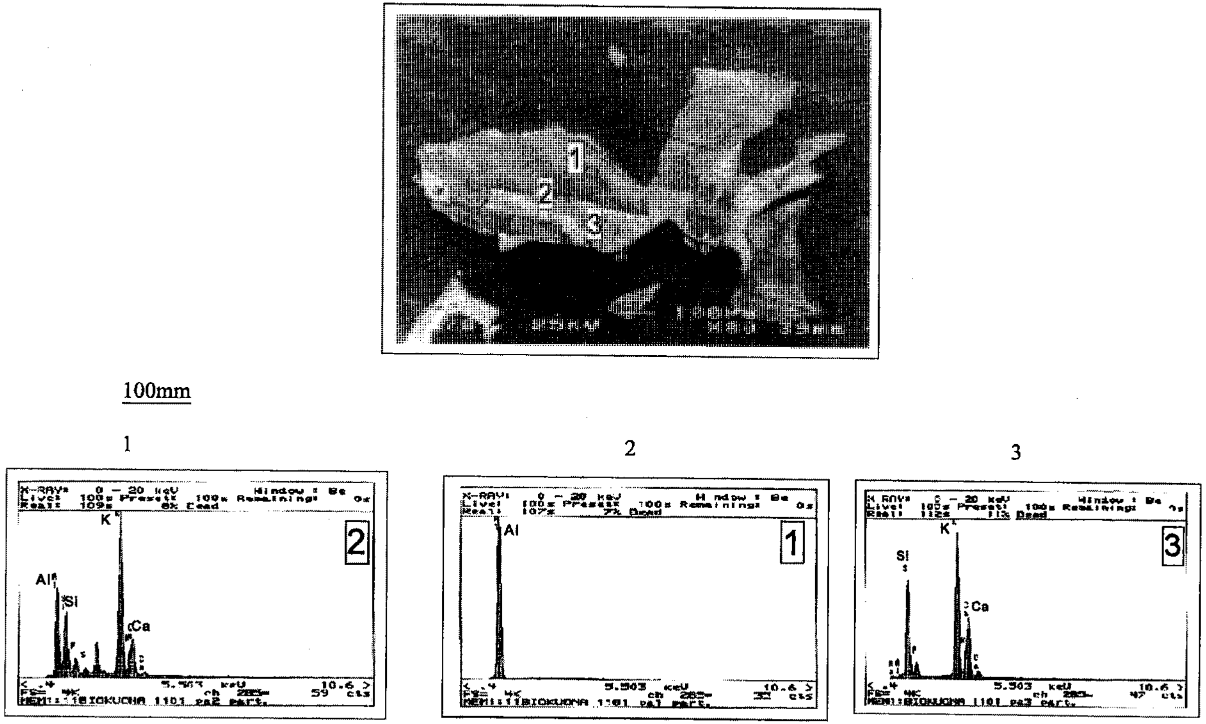


Figure 8. SEM figure of bed agglomerate and analyses of numbered points. The bar indicates the scale.

eutectic temperature of the mixture of potassium carbonate and calcium carbonate is about 750 °C [Levin *et al.*, 1985]. However, this theory of carbonates need to be investigated in further detail with bed materials and ashes. When pre-calcined limestone was used (AFB6), a large amount of round ash agglomerates of fairly regular size was formed in the bed (Fig. 6). The agglomerates were formed by molten ash, which encapsulated bed material particles inside. In this run, there was an increase in the amount of freeboard deposit due to easy attrition on calcined limestone. The deposit contained, in addition to molten ash particles, relatively high amounts of limestone particles sticked to them. When dolomite was used (AFB7) only slight agglomeration was observed in the bed. This was probably due to the calcination of $MgCO_3$ forming MgO, and therefore affecting the structure of bed particles.

The coke bed material was selected as the co-gasification of coal and straw had earlier been successful [Kurkela *et al.*, 1996]. The preventive mechanism in this test was supposed to be due to that ash melt could be absorbed by the porous coke. However, this was not the case in this test. This can be understood on the basis of the measurements by Raask [1985], who observed that ash melt does not wet carbon surfaces. Possible reasons for the difference in the agglomeration behaviour may lay in differences in the operational conditions of these gasification tests. The co-gasification test was carried out under pressure and at higher temperature (around 1,000 °C). At this temperature the gasification reactivity of coal char is significantly higher than at the temperature used in this study (abt 800 °C). This low reactivity was also seen in the bed material (removed after the test), which consisted mainly of unreacted coke. In the co-gasification test, however, the coal reacted totally, so that coal ash was able to become mixed with straw ash. Furthermore, the fluidisation and bed agitation conditions were more intense in the pressurised PDU gasifier, which may have inhibited agglomerate formation.

4. CONCLUSIONS

Characteristic data on ash behaviour can be obtained by laboratory tests and can be used for planning, for example, run conditions for tests with pilot or PDU equipment. Ash sintering can be much stronger in pressurised conditions than under atmospheric pressure. This phenomenon seems to be related to the silicate content in ashes: when the silicon content was low the ash sintering was stronger in pressurised conditions than in atmospheric conditions. However, the chemistry need to be studied more in detail to understand the behaviour observed. The water-soluble constituents of straw (potassium, calcium) affect the relationship of ash sintering and reactivity.

Both bed agglomeration and deposit formation in the freeboard occurred in the tests carried out using straw with problematic ash. The intensity of agglomeration was dependent on operational parameters. It was possible to affect the formation rate of agglomerates and deposits by the choice of gasification conditions and bed material.

The agglomeration of bed particles is a combination of the chemical characteristics and the particle sizes of bed material and ash. The strength of the agglomerates seems to be dependent on the friability of the bed material particles. The alumina bed material particles were firm enough to form strong agglomerates resisting fluidisation, while the limestone particles (depending on the quality and the calcination degree) were friable leading to brittle agglomerates or large regular size particles in the fluidising bed.

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PAPER VIII

Characterisation method of biomass ash for gasification

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Characterisation method of biomass ash for gasification

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ABSTRACT Tendencies for ash agglomeration and deposit formation in biomass gasification were studied in two atmospheric-pressure fluidising bed reactors together with reactivity tests carried out using a thermobalance. Various herbaceous and woody biomasses of different origin and a selection of Danish straws were tested. The measurements were carried out as a function of temperature, and H_2O and CO_2 were used as gasification agents. The reaction gas pressure was varied between 1 and 30 bar, and the temperature range was 650 - 950 °C. The appearance of the ash residues after the gasification reaction was examined by microscopy. Bed agglomeration and freeboard deposit formation were monitored by collecting samples after test runs. Samples were analysed by using a computer-controlled scanning electron microscopy (CCSEM) technique developed for ash deposit analyses. The thermobalance measurements gave results comparable to the ash behaviour in the fluidised-bed reactor. The strongest ash sintering was observed for wheat straw both in the thermobalance and in the fluidised-bed reactor. The effect of additives to prevent agglomeration formation was included in the study.

INTRODUCTION

Many potential biomass feedstocks, such as straw, have a problematic ash composition, which causes sintering and fouling problems in combustors. In biomass combustion, ash deposit formation is a common problem and has been studied by a number of researchers [1 - 5]. There are also some previous observations about operational problems in fluidised-bed gasification processes, caused by ash. In pressurised steam-oxygen gasification of peat, ash deposits have been formed in the upper part of the gasifier and in the cyclones [6]. Furthermore, straw ash has been found to cause both bed sintering and deposit formation in pressurised air-blown bubbling fluidised-bed gasification [7]. These problems were difficult to overcome in straw-alone gasification. In fact, the gasification temperature had to be reduced to below 800 - 850 °C, which resulted in poor carbon conversion and high tar concentrations. On the other hand, co-gasification of coal and straw (up to 50 wt% straw) was carried out without any signs of ash problems in spite of high operation temperatures of the order of 950 - 980 °C.

Char reactivity and ash behaviour are factors limiting possible operation conditions in all gasification processes when planning the use of new fuels. Thus, the purpose of this work was to create data that can also be used in the development projects of gasification of various biomass feedstocks. The ash sintering behaviour was characterised using a thermobalance, and larger-scale tests were performed in two atmospheric-pressure fluidised-bed reactors, a bubbling bed reactor (AFB) and a circulating fluidising bed reactor (CFB). Bed agglomeration and deposit formation in the freeboard were monitored by collecting samples after test runs. These samples were analysed by computer-controlled scanning electron microscopy (CCSEM). The effect of additives to prevent agglomeration was also included in the study. The sintering part of the study was a continuation for a work reported previously [8].

LABORATORY STUDIES

The samples used in the study comprised various biomasses and a selection of Danish straws. The analyses of the fuels used in the study are presented in Tables 1 and 3, and the chemical composition of ash, together with a summary of the thermobalance sintering tests, in Tables 2 and 4. The Danish wheat straw qualities were selected on the basis of growth site, fertilising and weathering conditions [9].

ASH SINTERING

The ash sintering behaviour was determined in a thermobalance according to the method described in [8]. The ash residues from the thermobalance experiments were studied by microscopy using the following classification criteria:

1. Non-sintered ash residue: ash structure resembling the original fuel particles, easily crumbling when touched (no asterisk: o)
2. Partly sintered ash (different degrees in this group): particles contained clearly fused ash (1 or 2 asterisks: *, **);
3. Totally sintered ash: the residue was totally fused to larger blocks (3 asterisks: ***).

The results are given in Tables 2 and 4 completed with the data of ash chemical composition [8]. Accordingly, the results showed that ash sintering was dependent on the pressure of steam. For spruce bark, willows and alfalfa, as shown in Table 2, ash sintered stronger in pressurised conditions than at atmospheric pressure.

When the ash composition data of Table 2 are compared to the observed degree of sintering, it seems to be evident that in the samples (i.e. spruce bark, willow and alfalfa), having a higher sintering tendency under pressure than at atmospheric pressure, the silica content was very low (<10%) and calcium as well as potassium contents were relatively high. Pine bark and spruce bark are very similar with respect to ash chemical composition. No sintering was observed in pine bark, but very strong sintering took place in spruce bark under pressure. We should suggest that this be due to the high alumina content (or the ratio alumina/potassium) in pine bark ash.

The behaviour observed under pressure can be due to the carbonate chemistry involved in the ash. According to phase diagrams presented in literature [11], the mixture of calcium and potassium carbonate forms a eutectic at about 750 °C. This behaviour provides, of course, that carbonates are formed in the ash. During gasification, carbonates can be formed, and they decompose slowly, especially at higher CO_2 partial pressures. To confirm this, gasification tests were also carried out at 1 bar CO_2, which is above the CO_2 equilibrium pressure at 850 °C [8]. For willow and spruce bark samples, the sintering was pronounced when measured at 1 bar CO_2 while in 1 bar steam there was no sintering at 850 °C. However, alfalfa had not the same behaviour and indicated only weak sintering at 1 bar in CO_2, while it strongly sintered under pressure in steam even at the temperature of 600 °C (Figure 1).

To see the effect of temperature on the melting of carbonates, additional tests were carried out for spruce bark and willow in 30 bar steam and at 700 °C, which was clearly below the eutectic. The results showed that the spruce bark had no ash sintering but the willow ash was clearly sintered. This observation and the behaviour of alfalfa indicate that chemical compounds other than carbonates are also involved in ash sintering. One explanation could be found in the chlorine chemistry: Below 700 °C the major part of chlorine remains in ash. The chlorine content of Danish straw ashes, which were prepared at 550 °C in a laboratory furnace, is shown in Table 4. Mixtures of compounds CaCl and KCl, and also KCl and K_2CO_3 are possible. The former mixture has the eutectic of 595 °C and the latter 640 °C [11].

In the major part of the Danish straw samples, the sintering behaviour was fairly similar, between ** and ***, as shown in Table 4. In straws #4, #9 and #11, the degree of sintering was less severe, from * to o. This behaviour is related to the ratio of the potassium and silicon contents in the sample. Very low SiO_2/K_2O ratios cause a high reactivity and a low inherent sintering tendency, while very high SiO_2/K_2O ratios cause a low reactivity and also a low agglomeration tendency. Medium-value SiO_2/K_2O ratios cause a medium reactivity and a high inherent sintering tendency [9].

Table 1 Analyses of various biomass feedstocks (dry basis).

Sample	Ash %	Volatile matter %	Fixed carbon%	LHV* MJ/kg	C %	H %	N %	O(diff) %	S %	Cl ppm
Pine bark	1.7	73.0	25.3	19.7	52.5	5.7	0.4	40.0	0.03	85
Pine saw dust	0.08	83.1	16.8	19.0	51.0	6.0	0.1	42.8	0	<50
Spruce bark	2.3	75.2	22.5	18.5	49.9	5.9	0.4	41.4	0.03	279
Needles**	3.6	75.3	21.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Finnish willow	1.2	79.9	18.9	n.d.	49.7	6.1	0.4	42.6	0.03	n.d.
Swedish willow	1.3	80.5	18.2	n.d.	49.4	6	0.5	42.7	0.03	130
Danish wheat straw A (-93)	4.9	77.4	17.7	17.7	47.3	5.8	0.5	41.4	0.07	1 770
Danish wheat straw B (-93)	4.5	76.9	18.5	17.5	47.1	5.9	0.6	41.9	0.07	3 190
Danish wheat straw -95	4.8	76.1	19.1	17.4	47.5	5.9	0.7	41.2	0.16	5 200
Danish wheat straw -97	6.1	75.8	18.1	17.3	46.5	5.7	1.4	40.1	0.12	4 360
Alfalfa	5.0	75.8	19.2	18.4	45.8	5.4	2.2	41.5	0.1	3 920

* Low Heating Value, MJ/kg, n.d.: not determined, **half pine half spruce

Table 2 Ash chemical composition of the various biomass feedstock, and ash sintering test results ($Sint_{750}$ = sintering degree at 750°C, $Sint_{850}$ = sintering degree at 850°C).

Sample	Ash	Ash chemical composition, % in ash										$Sint_{850}$		$Sint_{750}$	
	%	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2C	TiO_2	SO_3	P_2O_5	1bar H_2O	30bar H_2O	1bar H_2O	30bar H_2O
Pine bark	1.7	1.3	5.3	0.3	40.6	4.5	7.6	0.5	0.1	2.1	4.8	o	o	n.d.	n.d.
Pine saw dust	0.08	8.3	2	1.8	41.8	11.8	12.3	0.3	0.1	1.9	5.2	***	***	o	o
Spruce bark	2.3	1.5	1.1	0.1	39.2	5.1	7.6	0.4	0	1.0	4.1	o	***	n.d.	***
Needles	3.6	34.2	0.5	0.2	23.8	3.32	7.7	0.1	0.02	1.5	5.0	o	*	n.d.	o
Finnish willow	1.2	0.4	0.3	0.2	30.8	5.1	26.5	0.3	0	3.0	11.5	o	***	o	***
Swedish willow	1.3	7.5	1.6	1.1	35	3.5	9.6	0.8	0.1	1.9	7.8	o	***	o	**
Finnish wheat straw	7.4	68.4	0.85	0.45	4.3	2	13.2	0.25	0.04	0.9	2	***	***	slow	***
Danish wheat straw A (-93)	4.9	72.7	0.7	0.5	7.3	1.6	8.1	0.4	0	n.d.	n.d.	***	***	n.d.	**
Danish wheat straw B (-93)	4.5	49.2	0.4	1	9.7	2.2	18.1	0.3	0	n.d.	n.d.	***	***	*	*
Danish wheat straw -95	4.8	34.2	0.3	0.2	8.4	2.2	30.1	<0.5	0.02	3.2	3.9	***	***	**(*)	n.d.
Danish wheat straw -97	6.1	29.9	0.8	1.3	10.6	5.6	27.7	1.5	0.07	5.5	10.8	***	n.d.	**(*)	n.d.
Alfalfa	5.0	3.0	0.3	0.7	22.4	9.0	27.7	1.9	0.02	3.0	8.0	**	***	*	***

o no sintering; * slightly sintered; ** moderately sintered; *** completely sintered; n.d.: not measured; slow: low reactivity

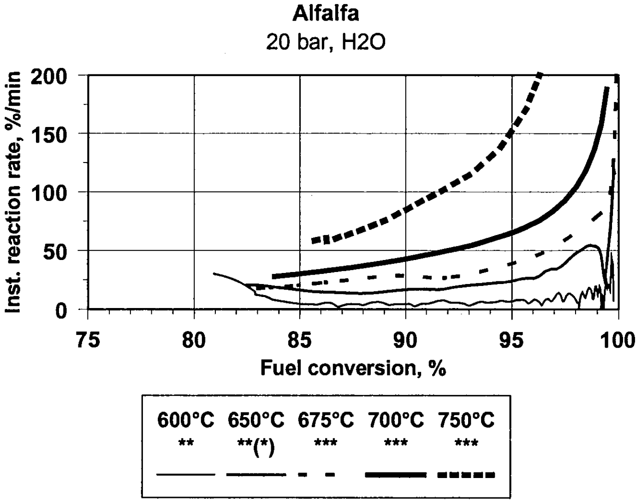

Fig. 1 The gasification reactivity and ash sintering behaviour of alfalfa in 20 bar steam at different temperatures.

Table 3 Proximate and ultimate analysis of Danish straws (dry basis).

Sample	Ash %	Volatile matter %	Fixed carbon %	LHV, MJ/kg	C %	H %	N %	O %	S %
#1 Wheat	5.4	76.5	18.1	17.27	46.9	5.8	0.8	40.9	0.18
#2 Wheat	5.4	77.1	17.5	17.36	46.4	5.9	0.6	41.6	0.13
#3 Wheat	5.3	76.2	18.5	17.13	46.9	5.8	0.7	41.2	0.13
#4 Wheat	3.5	78.2	18.3	17.53	47.2	5.9	0.5	41.5	0.13
#5 Barley (W)	5.7	76.2	18.1	17.16	46.4	5.7	0.7	41.4	0.13
#6 Grass	5.2	75.9	18.9	16.89	46.7	5.9	1.0	41.1	0.15
#7 Barley (S)	5.5	76.2	18.3	17.07	46.5	5.7	0.5	41.7	0.12
#9 Wheat98/rib	15.5	68.0	16.5	15.76	42.1	5.2	1.2	35.9	0.14.
#11 Wheat/rib+	8.0	75.3	16.7	17.13	46.1	5.5	0.9	39.4	0.10

Table 4 Ash chemical composition (wt% dry), and ash sintering test results (Sint$_{750}$ = sintering degree at 750 °C, 1 bar of steam, Sint$_{850}$ = sintering degree at 850 °C, 1 bar of steam).

Sample	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	SO_3	P_2O_5	Cl	Sint$_{750}$	Sint$_{850}$
#1 Wheat	38.5	0.2	0.3	9.1	3.8	27.7	0.4	0.03	6.2	4.6	10	**(u)	**(u)
#2 Wheat	29.9	0.2	0.2	10.4	4.1	32.5	0.5	0.03	6.0	3.9	11	**	***
#3 Wheat	27.8	0.3	0.4	10.4	4.5	34.9	0.4	0.03	5.2	3.7	12	**(*)	***
#4 Wheat	16.3	0.2	0.6	15.4	4.1	41.0	0.4	0.03	7.5	1.8	12	*	*
#5 Barley (W)	34.2	0.6	0.5	12.7	3.2	30.1	2.4	0.05	5.0	5.0	6.3	**(*)	***
#6 Grass	29.9	0.1	0.2	8.3	3.8	36.1	0.3	0.03	5.0	5.7	11	**(u)	***
#7 Barley (S)	32.1	0.2	0.3	11.9	2.7	30.1	2.4	0.03	4.7	3.4	13	**(u)	***
#9 Wheat98/rib	59.9	1.8	1.1	7.7	2.5	14.5	0.5	0.17	3.2	3.9	4.1	n.d.	*(*)
#11 Wheat/rib+	70.6	0.3	0.3	8.1	3.3	9.0	0.5	0.03	2.7	4.6	0.4	n.d.	(o)

n.d.: not determined, u: unburned carbon present

BEHAVIOUR OF POTASSIUM IN GASIFICATION

The behaviour of the most abundant alkaline metal in straw, i.e. potassium was studied during gasification in the thermobalance. Another abundant element is silicon. Potassium and silicon react easily to form potassium silicate (glass), which is water-insoluble. The objective of this task was to detect the relationship between water-soluble potassium and insoluble potassium, and also possible evaporation of potassium during gasification. In the tests, the gasification was stopped at certain conversion levels in the thermobalance. Afterwards, the samples were extracted by water to analyse the water-soluble potassium and the total potassium (the total alkaline metal analysis was carried out by neutron activation analysis INAA). Steam, CO_2 and their mixture were used as gasification agents in these tests. The difference between the total potassium content and water-soluble potassium described the amount of insoluble potassium, which is in form of potassium silicate.

The results of this study are summarised in Figure 2. The results were calculated so that the amount of potassium was normalised to one either in the char (immediately after pyrolysis, i.e. at 0% char conversion), or in the original straw. Hence, the water-soluble potassium and the total potassium were compared, as shown in Figure 2.

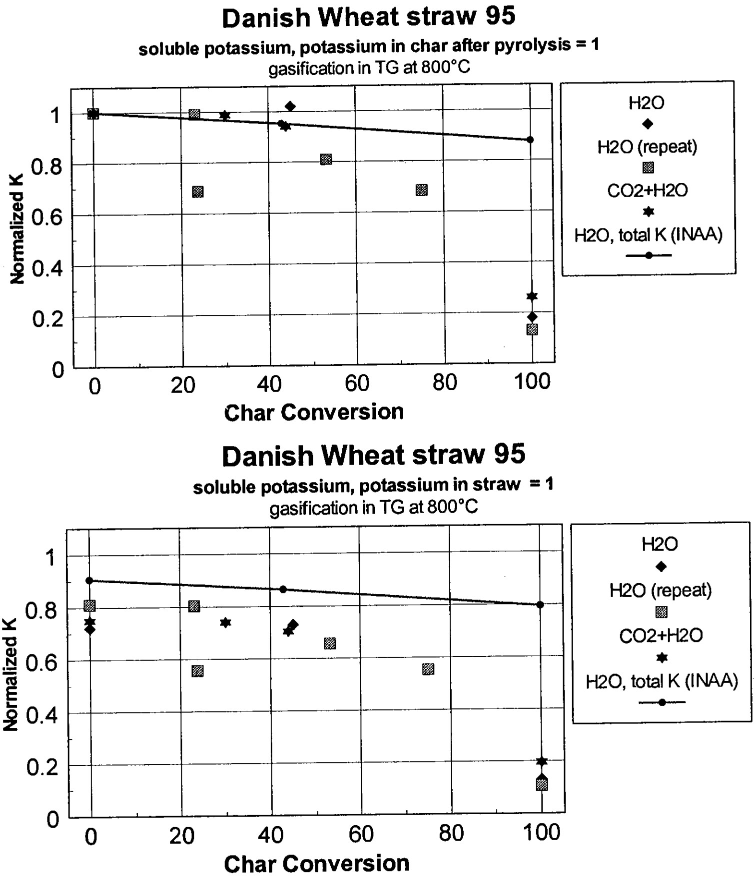

Fig. 2 The amount of potassium in straw char as a function of char conversion. Symbols without line: amount of water-soluble potassium (normalised values); sym-bols with the solid line: amount of total potassium. In the upper graph, potassium is de-noted as 1 in char after pyrolysis; in the lower graph in straw dry matter, respectively.

Accordingly, it shows that the repeatability of the determinations was acceptable, and no dependence on the gasification agent was observed. The amount of soluble potassium was relatively constant to the conversion level of 50%, after which it decreased to the value of about 15% of the origin. The total potassium content decreased by about 10% as a function of char conversion The results indicated that the major part of potassium had reacted to the water-insoluble form, i.e. potassium silicate, and this reaction started after the char conversion of 50%.

In addition, the total potassium level apparently was reduced during pyrolysis: at the char conversion of 0%, the total potassium content was 10% and the soluble potassium content 20% lower than that in straw, respectively. This indicated that during pyrolysis, a part of potassium would have been reacted to insoluble potassium, and moreover a part was evaporated during pyrolysis. However, due to the relatively large scatter of the measuring points, a more detailed study is needed to verify this observation.

BENCH-SCALE FLUIDISED-BED GASIFICATION TESTS

The behaviour of straw ash was studied further in a bench-scale atmospheric-pressure fluidised-bed reactor (AFB). This study completed the test series reported in [8]. The Danish wheat straw -95 (Tables 1 and 2) was used as the fuel in the 7 set points AFB/B24-31 (Tables 5 and 6). In these test series, the effect of bed material mixtures, a different limestone grade, freeboard cooling and fuel additives were tested. A selection of Danish wheat straws was also tested (set points 98/1 - 98/5, Table 7). Each test was carried out in one day.

TESTING OF DIFFERENT BED MATERIALS AND ADDITIVES

Previously [8], different bed materials (Al_2O_3, dolomite and coke) were tested, and this work was continued by carrying out four additional tests, in which another limestone and a dolomite as well as mixtures of limestone and sand were used. Data for these tests are given in Table 4.

The bed material mixtures were tested at two set points: AFB/B24-25. Two mixtures (50/50 wt% basis) were used: a) sand and limestone Parfil, b) sand and dolomite Myanit. The test temperature at these set points was 800 °C. As soon as the temperature signal deviated from the steady state indicating poor fluidisation, the test was stopped. The test periods are given in Table 5. However, in these tests no large agglomerates were found in the sampled bed material. Still the bed contained agglomerates having diameters of a few millimetres, which were too large to be fluidised. This caused temperature gradients in the bed. The amount of freeboard deposits was also somewhat higher in these tests than at the following set points. The visual inspection showed that the deposits contained agglomerates formed by molten ash, similarly to the previous test series [8].

Table 5 AFB test runs with straw -95 carried out with different bed materials.

Set point	AFB/B24	AFB/B25	AFB/B26
Feedstock	Straw	Straw	Straw
Bed material	Limestone + sand	Dolomite+ sand	Limestone (Orsa)
T(bed, average), °C	800	800	800
T(freeboard), °C	800	800	800
C-conversion to dry gas, wt%	80.7	80.0	75.1
mg freeboard deposits/ g feedstock in the freeboard	1.7 some molten ash particles present	1.4 some molten ash particles present	1.9 some molten ash particles present
Total test time, min	125	170	252
Initiation of bed sintering, min	(115)	160	252

In order to compare the effect of limestone type, one test (AFB 26) was carried out with Orsa limestone, which is of somewhat harder grade than Parfil. This test resulted in a similar sintering behaviour as at set points AFB/24-25. The aim of the test series summarised in Table 6 was to study whether the ash sintering problems of straw gasification could be prevented by using special additives. Two additives were selected: kaolin and magnesium oxide (MgO). The reason for using these materials was that they are known to affect the ash melting behaviour favourably. Rather high

Table 6 AFB test runs with straw -95 carried out to study the effects of additives.

Set point	AFB/B28	AFB/B29	AFB/B30	AFB/B31
Feedstock	Straw + kaolin pelletised	Straw + MgO pelletised	Straw + kaolin	Straw + MgO
Bed material	Dolomite	Dolomite	Dolomite	Dolomite
T(bed, average), °C	830	830	830	830
T(freeboard), °C	830	830	830	830
C-conversion to dry gas, wt%	84.9	89.2	86.1	87.5
mg freeboard deposits/ g fed feedstock	0.7	< 0.5	0.6	0.6
Total amount of feedstock, g	3025	3055	3070	3215
used bed material, g	420	420	420	420
Total test time, min	240	240	240	240
Initiation of bed sintering, min	--	--	--	--

amounts of additives were used in these preliminary tests, which were not yet focused on optimising the use of additive.

The additives were added as fine powder to ensure good mixing with the fuel. They were mixed with the straw feedstock in two ways: First, they were added among the powder fuel and the mixture was pelletised. Another way was to add them directly into the feeding tank among the crushed feedstock. The particle sizes of the additives were < 20 μm for kaolin and < 70 μm for MgO. The amount of additive used was the same as the ash content in the straw (4.8 g in 100 g fuel). However, during the pelletising and crushing procedures, material losses took place to that extent that the final amount of kaolin was 55% of the amount added, and 70% of MgO, respectively. When the additives were mixed in the feeding tank, there were no losses.

In total four set points were carried out in AFB/28-31. The temperature in these tests was higher, i.e. 830 °C, than in the previous set points of straw gasification. Both additives (kaolin and MgO) proved to be effective: all tests were finalised without any signs of sintering in the bed or without deposits in the freeboard. Only small amounts of loose ash were collected from the reactor wall. The mixing procedure seemed to have no influence on sintering. A difference was observed, when the MgO additive was mixed during pelletising: the ash material collected from the freeboard contained significantly less carbon compared to addition into the tank. Probably, this additive catalysed the reactivity of carbon when mixed intimately with the biomass material.

The degree of agglomeration of the bed samples was determined by sieving the samples. The results are shown in Figure 3. Accordingly, when compared to the original bed material the intensity of agglomeration can be seen as an increase in the particle size. At the first two set-points B24 and B25 the original bed material was a mixture of sand with a particle size of 0.60 - 0.71 mm and dolomite or limestone of 0.71 -1.00 mm in size. At all other set points, only dolomite or limestone of 0.71 - 1.00 mm was used as the initial bed material. The bed agglomeration was clearly measurable at set points AFB/B25 and AFB/B26, while at AFB/B27 the amount of larger particles was only a few percents. At the other set points no measurable amounts of bed agglomerates of >1 mm in size were observed. In all tests, the bed particle size decreased significantly. This is due to the easy attrition of limestone and dolomite.

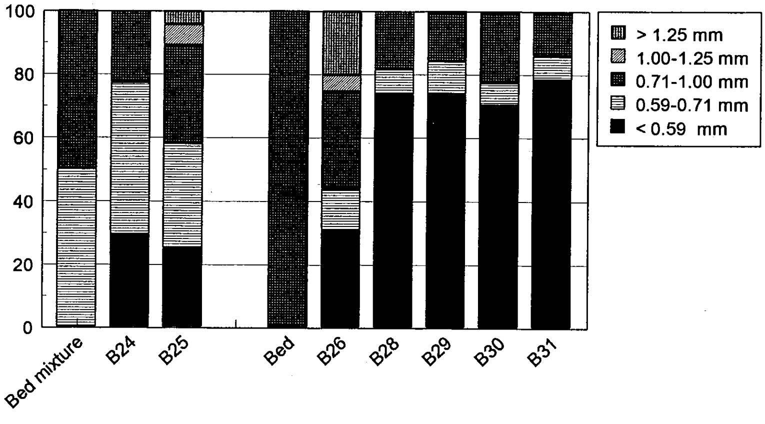

Fig. 3 Particle size distribution of bed materials and bed samples after the AFB set-points.

GASIFICATION OF DIFFERENT DANISH STRAWS

The gasification behaviour of different straws was also studied in AFB. The aim of these tests was: a) to confirm laboratory findings (thermobalance tests) concerning the ash sintering behaviour, which sets limits to the maximum gasification temperature) and b) to assess the gasification behaviour and ash sintering/deposition tendency in a full-scale fluidised-bed reactor.

Myanit dolomite was used as the bed material at all set points of this test series. Particle size of the bed material (0.71 - 1.00 mm) and the superficial velocity was selected so that good fluidisation was maintained.

The operation conditions and the main results of the gasification tests are presented in Table 7. The first set point AFB98/1 was carried out with wheat straw JB 2-3 at about 800 °C. The test run was successful and no signs of ash-related problems were met during the operation: bed temperature was constant and no signs of pressure drop fluctuation were seen. The bed material after the test contained only small agglomerates, and the freeboard and the gas outlet pipe were practically clean. Only some dust was deposited on the freeboard wall, which contained some small agglomerates consisting of fines from bed and ash glued by molten ash. Since there were no problems at the first set point, the second set point AFB98/2 was carried out with the same straw at higher temperature, at 830 °C. This test was as successful as the first one. No signs of ash-related problems were met during the operation. The same type of small size agglomeration was observed in the bed, as in the first set point. The freeboard deposit was also similar to the above.

Set point AFB98/3 was carried out with straw #7 (Barley JB6) at 800 °C. This test run was not as successful, as the pressure of the reactor started to rise after one hour operation and consequently, the operation had to be stopped earlier than planned. The removed bed material was fairly clean, as were also the freeboard and the gas outlet pipe. The blockage that caused the increase in reactor pressure was detected in the gas line after the cyclone.

Table 7 summary of operation conditions in the AFB tests with different straws

Set point	98/1	98/2	98/3	98/4	98/5
Feedstock	#4, JB 2-3, Wheat	#4, JB 2-3, Wheat	#7, JB6 Barley	Danish Wheat s.-97	Danish Wheat s.-97
T(bed), °C	800	830	800	800	770
T(freeboard), °C	805	830	805	805	770
Tars, g/m^3n	5.5	5.7	4.6	7.5	9.4
amount of freeboard deposits, mg/g of fed feed-stock	0.7	1.0	5.8	1.3	< 0.5
outlook of deposits	small porous agglomerates[3]	small porous agglomerates[3]	small porous agglomerates[3]	agglomerates, char particles	char particles
Total test time, min	240	240	93[2]	252	240
Initiation sign of bed sintering, min	-	-	-	252	-
Bed sinters after the test	no large agglo.merates[3], small agglomerates of the same size as bed particles*	no large agglomerates, small agglomerates of the same size as bed particles	no large agglomerates, small agglomerates of the same size as bed particles	very large agglomerates ***	larger char agglomerates and small molten ash particles (only a few small agglomerates)

[2] Test run was stopped as the pressure of the reactor was increasing due to a blockage in the gas outlet pipe. [3] Agglomerates comprise bed and ash particles glued by molten ash.

Set point AFB98/4 was carried out with Danish wheat straw-97 at 800 °C. No signs of fluidisation loss were met during the operation (bed temperatures and pressure drop remained stable). However, after the test there were very large agglomerates in the bed, but the freeboard and gas outlet pipe were practically clean. The freeboard dust contained small ash agglomerates. The bed agglomerates were quite porous and probably located at the enlargement section of the bed so that they did not affect fluidisation.

Because the temperature of 800 °C resulted in ash-related problems for Danish wheat straw -97, the next test run AFB98/5 was carried at a lower temperature of about 770 °C. This test was more successful. The freeboard and the gas outlet pipe were practically clean. The bed contained some large agglomerates consisting of char particles adhered together. In addition, in the bed sample there were some single glassy particles, which seemed to be formed solely by molten ash. A few agglomerates containing bed particles were also observed in the bed.

CFB GASIFICATION TESTS WITH STRAW

Gasification tests were carried out with the atmospheric-pressure Circulating Fluidised-Bed (CFB) gasification Process Development Unit (PDU) of VTT Energy [10]. Two wheat straw feedstocks were also used in the test runs, i.e., Danish wheat straws -95 and -97. The composition of these two straws were fairly close to each other, both having very high potassium and chlorine contents, which can be considered typical of dry harvesting seasons (Tables 1 and 2). Both straws had also a rather high reactivity, but the ash sintered strongly already at below 800 °C in the laboratory tests.

RESULTS

The straw gasification trials had two main goals: a) to find such gasification conditions, at which wheat straw could be gasified without ash-related problems, and b) to study the removal of potassium and chlorine derived from straw. According to the experiences from a CFB gasifier it is also possible to use such a biomass fuel that on the basis of laboratory characterisation seem to be very problematic. Under optimum conditions a carbon conversion efficiency of 95% was reached without any signs of ash-related problems. The tar content was also clearly lower in straw gasification than in wood gasification at the same temperatures. However, the achievement of the optimum conditions requires controlled operation of the gasifier, otherwise sintering and agglomeration problems are met, and moreover, carbon conversion is clearly lower [10, 12].

CHARACTERISATION OF ASH SAMPLES FROM THE CFB TESTS

Samples were collected from bottom ash, cyclone ash and hot filter dust in some of the CFB test runs carried out with straw. The samples were analysed by light microscopy and electron microscopy. With the first method, an overall inspection was carried out in order to monitor agglomerates and their form. Afterwards, cross-sections were prepared for the electron microscopic analysis (SEM), in which the CCSEM (computer controlled electron microscopy) technique was applied. These analyses were carried out at VTT Manufacturing Technology. In this analysis, sample particles were analysed for their size and chemical composition.

In almost all CFB gasification tests, some relatively small (1 - 3 mm) agglomerates were formed in the bed, comprising bed material particles glued by molten ash, the type and form being dependent on the process conditions. These agglomerates were removed from the gasifier together with bottom ash.

From the ash samples, cross-sections were prepared and analysed by SEM. In the analysis, particle sizes and their chemical composition were determined. In the analysis of chemical composition, the following elements were measured: Si, Al, Fe, Ca, Mg, K, Na, Ti, P, S, Cl, (Mn). The summary results of this SEM analysis are shown in Figure 4. The composition measured for particles was compared with the chemical composition of ash of the feedstock straw (also indicated in Figure 4). According to the results, the most abundant substance in bottom ash was silicon, the amount of which was locally much higher than that of straw ash. The potassium content was quite equal from particle to particle.

The dust particles collected from the 2nd cyclone contained less silicon than the bottom ash while the potassium and calcium contents were clearly higher. The chlorine content was also higher than in bottom ash. The particle sizes ranged 1.5 - 11 micrometers in the 2nd cyclone ash as measured in SEM. In the dust collected from the hot filter, the particle sizes ranged 0.2 - 4 micrometers, respectively (particle sizes were not measured for bottom ash due to their large sizes). In these particles, potassium, calcium and chlorine were clearly concentrated, and there seemed to be no dependence between particle size and composition. When potassium was plotted against chlorine, a linear correlation was found for potassium and chlorine, indicating the presence of potassium chloride in the particles (Figure 5). This observation was in accordance with bulk analysis carried out for potassium and chlorine in the 2nd cyclone and in the hot filter dust (Figure 6 [10]). The amount of water-insoluble alkaline metals also decreases from bottom ash to the 2nd cyclone ash and hot filter dust, as indicated in Figure 6. In bottom ash 100% is in form of insoluble alkaline metal, in 2nd cyclone ash about 50% and in hot filter dust 30%.

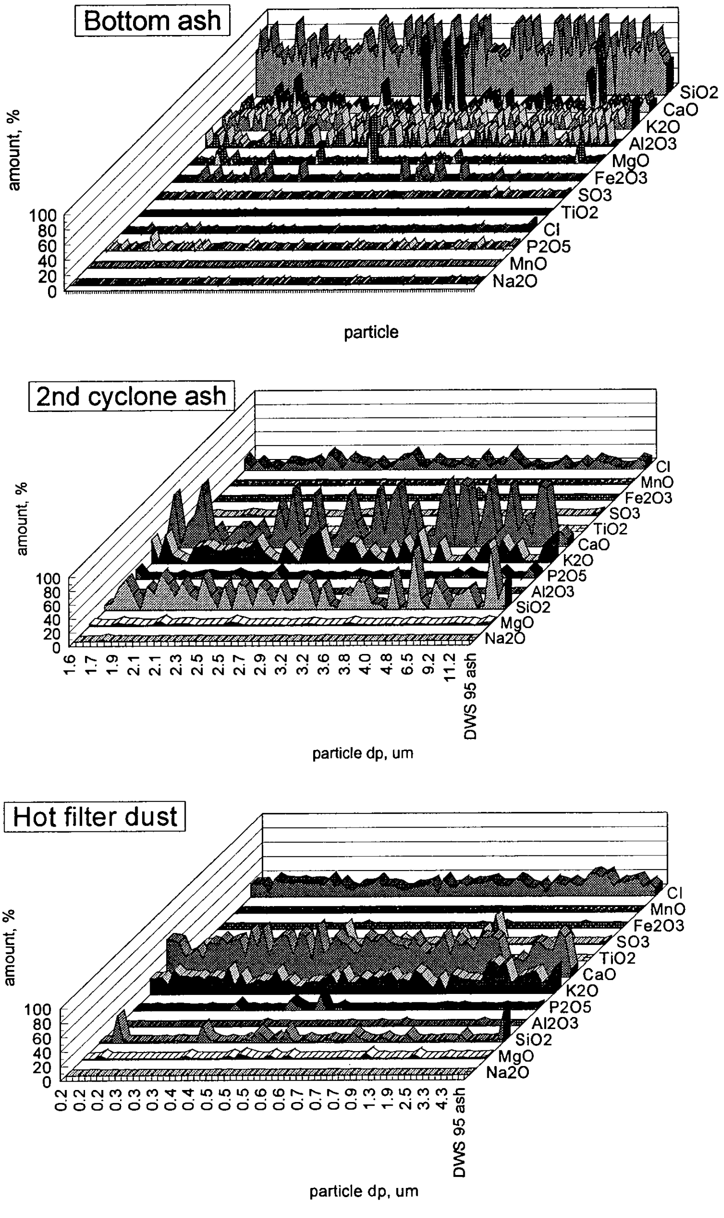

Fig. 4 The composition measured for particles of bottom, 2nd cyclone ash and hot filter dust samples taken from a CFB test run of wheat straw. For comparison, the chemical composition of ash of feedstock straw is shown as red bars at the right ends of the diagrams (note: for better visualisation, the array of the graphs in bottom ash diagram deviates from that of the other diagrams).

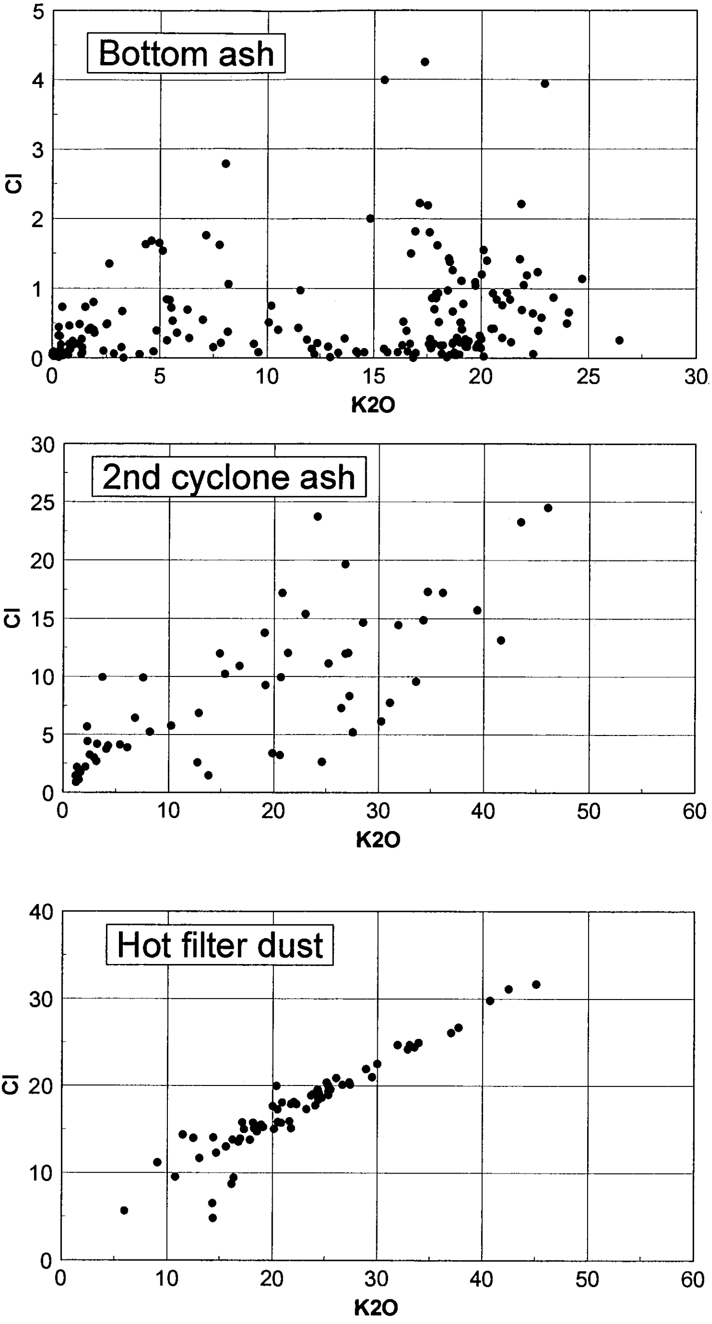

Fig. 5 Correlations between chlorine and potassium in the particles of bottom ash, 2nd cyclone ash and hot filter dust (CFB).

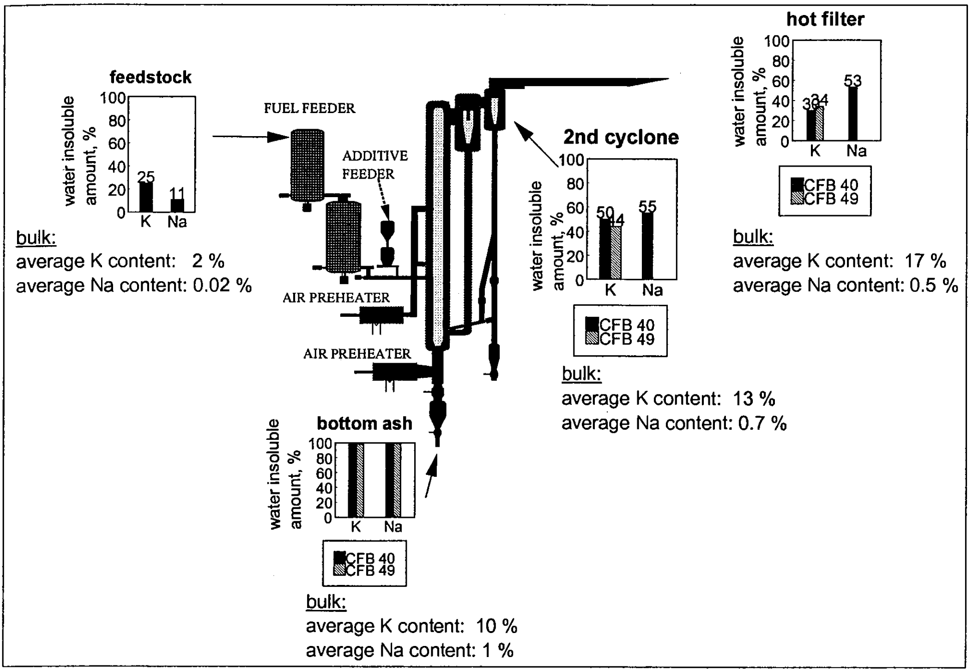

Fig. 6. Deviation of alkaline metals in CFB gasification of wheat straw (average K, Na content indicates the bulk analysis of ash samples); two CFB tests 40 & 49, the bars indicate the fraction of water insoluble K and Na (i.e. silicates).

CONCLUSIONS

The following conclusions were drawn from the results:

1. Characteristic data on ash behaviour can be obtained by laboratory tests and used for planning, e.g., run conditions for tests with pilot or PDU (process development unit) equipment.
2. With certain fuels (such as alfalfa and willow), ash sintering can be much stronger under pressurised conditions than under atmospheric pressure. This phenomenon seems to be related to the silicate content of ash: when the silicon content was low ash sintering was stronger under pressurised conditions than under atmospheric conditions.
3. The major part of potassium reacted to a water-insoluble form, i.e. potassium silicate, after the char conversion of 50%.
4. The use of kaolin or magnesium oxide additives had a great preventive effect on bed agglomeration and freeboard deposit formation in the bench-scale bubbling fluidised-bed gasification tests carried out with straw.
5. The differences between Danish wheat straw qualities were relatively small: almost all tested straws had a rather problematic ash sintering behaviour.
6. The Circulating Fluidised-Bed gasification process was not as sensitive to ash sintering as the small-scale bubbling fluidised-bed reactor. The amount of potassium chloride increased from bottom ash to hot filter dust.

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Title

Thermogravimetric characterisations of biomass and waste for gasification processes

Abstract

Gasification, among the several thermochemical conversion processes, possesses great potential in the advanced utilisation of biomass and wastes as a source for energy and material production. This work deals with the characterisation of reactivity and ash sintering in the gasification of biomass and wastes using thermogravimetry as a tool.

The gasification reactivity of biomass fuels depends on many factors; in particular the catalytic factors play a large role, and the behaviour is not easy to predict. On the basis of results obtained experimentally and information available in the literature, a method was developed for the characterisation of reactivity and ash sintering of fuels to be used in fluidised bed gasification processes, both atmospheric and pressurised. The purpose was to take into account the complexity of the phenomena rather than to find systematic correlations between the various fuel properties and reactivity and ash sintering, or to determine kinetic parameters. The observed complexity was the spur to develop a method, one that would be as simple as possible, to characterise biomass and solid recovered fuels or wastes intended as feedstocks for use in gasification while taking into account the conditions of the process. Thus, the temperature and pressure ranges, heating rates and gaseous environment for the thermobalance were selected so as to be relevant for the conditions existing in fluidised bed gasifiers, including pressurised conditions. The temperature maximum was thus 1000 °C, and the heating rate of the fuel sample was adjusted to that when feedstock enters the reactor. The gaseous environment was selected so that it would sufficiently describe that existing in a gasifier.

Solid recovered fuels were selected to represent waste-based fuels rather than waste as a whole. The gasification reactivity of solid recovered fuels was found to be similar to that of paper and higher than that of wood. Test results showed broad scattering before the samples were extracted by sample division.

The method also provides information about ash sintering. The ash is the residue remaining in the thermobalance after the gasification reactions, which thus represents the conditions of gasification, even pressurised gasification. A separate ash does not need to be prepared in the laboratory. The ash residue can be classified into three categories: non-sintered ash, partly sintered ash and totally sintered or fused ash. For some of the biomasses, ash sintering was much stronger under pressurised conditions than at atmospheric pressure. The laboratory findings for ash sintering appeared in various ways in real scale since several factors affect the ash depositing in the reactor. Each time sintering (even weak) was detected in the ash residue of the TG tests, agglomerates or deposits were found in the reactor.

The results of thermobalance tests on different fuels were in good correspondence with the behaviour of the fuels in fluidised bed gasifiers.

Keywords
thermogravimetric characterisation, thermobalance, biomass, wastes, gasification, fluidized bed gasifiers, fuel properties, reactivity, ash sintering, solid recovered fuel

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VTT PUBLICATIONS 607 Thermogravimetric characterisations of biomass and waste for gasification processes Antero Moilanen

Gasification, among the several thermochemical conversion processes, possesses great potential in the advanced utilisation of biomass and wastes as a source for energy and material production. The publication deals with a characterisation method that provides specific information about biomass and waste-based fuels intended for use as feedstock in atmospheric and pressurised gasification processes. The method, which is based on thermogravimetry, produces information about the gasification reactivity related to the achievable conversion of carbon in the process and about the ash sintering and deposition that may hamper the process operation.

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