VTT PUBLICATIONS 769

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ISBN 978-951-38-7748-4 (soft back ed.)
ISSN 1235-0621 (soft back ed.)

ISBN 978-951-38-7749-1 (URL: http://www.vtt.fi/publications/index.jsp)
ISSN 1455-0849 (URL: http://www.vtt.fi/publications/index.jsp)

JULKAISIJA – UTGIVARE – PUBLISHER

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Kopijyvä Oy, Kuopio 2011

Antero Moilanen & Muhammad Nasrullah. Gasification reactivity and ash sintering behaviour of biomass feedstocks. Espoo 2011. VTT Publications 769. 39 p. + app. 96 p.

Keywords biomass, fuel, gasification, reactivity, ash, sintering, pressure, bio diesel

Abstract

Char gasification reactivity and ash sintering properties of forestry biomass feedstocks selected for large-scale gasification process was characterised. The study was divided into two parts: 1) Internal variation of the reactivity and the ash sintering of feedstocks. 2) Measurement of kinetic parameters of char gasification reactions to be used in the modelling of a gasifier. The tests were carried out in gases relevant to pressurized oxygen gasification, i.e. steam and carbon dioxide, as well as their mixtures with the product gases H_2 and CO. The work was based on experimental measurements using pressurized thermobalance. In the tests, the temperatures were below 1000 ˚C, and the pressure range was between 1 and 20 bar. In the first part, it was tested the effect of growing location, storage, plant parts and debarking method. The following biomass types were tested: spruce bark, pine bark, aspen bark, birch bark, forestry residue, bark feedstock mixture, stump chips and hemp. Thick pine bark had the lowest reactivity (instantaneous reaction rate 14%/min) and hemp the highest (250%/min); all other biomasses laid between these values. There was practically no difference in the reactivities among the spruce barks collected from the different locations. For pine bark, the differences were greater, but they were probably due to the thickness of the bark rather than to the growth location. For the spruce barks, the instantaneous reaction rate measured at 90% fuel conversion was 100%/min, for pine barks it varied between 14 and 75%/min. During storage, quite large local differences in reactivity seem to develop. Stump had significantly lower reactivity compared with the others. No clear difference in the reactivity was observed between barks obtained with the wet and dry debarking, but, the sintering of the ash was more enhanced for the bark from dry debarking. Char gasification rate could not be modelled in the gas mixture of $H_2O + CO_2 + H_2 + CO$, similarly as it can be done for coal. The reasons were assumed to be that in the carbon dioxide gasification, the gasification rate was negatively dependent on the CO_2 pressure, the opposite of what is observed in steam gasification and the dependence of the

gasification reaction rate on the conversion had three patterns. Normally it increases with the conversion, but it may also decrease or go through a minimum. According to the sintering tests, the ash residues were not totally sintered but they consisted of molten particles (spheres), unreacted char particles and powdery ash. The strongest sintering was observed for hemp, spruce bark obtained by dry debarking, and aspen bark. Increased pressure and CO_2 resulted in intensified sintering, as has been observed in earlier studies.

Preface

This publication presents the results of the work carried out in the task of the project UCGFunda (titled Fundamental studies of synthesis-gas production based on the fluidized bed gasification of biomass). The project was directed towards methods of producing transportation biofuels via the synthesis-gas route, with emphasis on the synthesis-gas production and gas cleaning steps; it was realised during the years 2007–2011 in VTT, Aalto University and Åbo Akademi. The topic of the task was the characterisation of gasification reactivity and ash sintering behaviour of biomass feedstocks for the gasification step. During the project time, results were published in two papers and in a master thesis. The present publication consist of the summary part and the papers as well as the thesis are as appendices.

The project was financed by BioRefine programme of Tekes (The Finnish Funding Agency for Technology and Innovation) as well as companies Carbona/Andritz, Foster Wheeler Energia, Metso, Neste Oil, Stora Enso, UPM, Vapo and Gasum, which are gratefully acknowledged.

Espoo October, 2011

Authors

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Appendices

1. Introduction

The option for the production of liquid biofuel in Finland is based on the fluidized bed gasification of biomass and the Fischer-Tropsch synthesis. This large-scale process, which may reach up to 400 MW in capacity, needs large quantities of feedstock from various sources. For this reason, the main objective of this work was to study how the quality of biomass feedstocks selected for the gasification process varies. Here, the focus was on forestry biomass, and quality was represented by gasification reactivity and ash sintering properties. It is known that the general fuel characteristics of biomass may be affected by harvesting time, biomass growth locations, transportation, storage [1], debarking processes, etc., but it is not known how the characteristics relevant to gasification (reactivity and ash sintering) are affected. An important factor here is that during these steps, biomass is in contact with water, which may cause changes in the inorganic material present in biomass, such as leaching out, recrystallization, etc. This material is of special importance since it catalyses the gasification reactions of char and affects the ash sintering behaviour. In this respect, potassium compounds play a large role.

The total carbon conversion achieved in the gasifier, operating at temperatures below 1000 °C, depends mainly on the reactivity of the solid char residue remaining after the devolatilisation phase of the fuel feedstock. The reactivity of the char residue is affected by the temperature, the partial pressures of the reactants H_2O and CO_2 and the product gas components (CO and H_2), which inhibit reactivity. Alkaline and alkaline earth metal compounds play a significant role in reactivity, since they catalyse gasification reactions. Other elements, such as silicon, reacting with these metals and forming silicates (glasses) lead to losses in catalytic activity. These elements occur naturally in biomass, and their individual behaviours are dependent on the biomass type. The carbon conversion can be improved by increasing the temperature, but if it is too high, ash sintering can become significant and create problems in the operation of the gasifier. Increasing the total pressure of the process, is expected to increase reactivity, as in coal gasification, but for biomasses it has been observed that pressure may have no effect, or that reactivity is even reduced. This kind of behaviour is not well understood, but it can be regarded as a result of the behaviour of the inorganic material catalysing the gasification reactions.

The work was divided into two parts: 1) Study of the internal variation of the reactivity and the ash sintering of selected forestry biomass feedstocks relevant to a large-scale gasification process, and 2) Measurement of the kinetic parameters of char gasification reactions to be used in the modelling of a gasifier. The results of this work have been published in [3–5]. These publications are attached as Appendices II, III and IV.

2. Experimental

The work was based on experimental measurements using VTT's pressurized thermobalance. The method is the same as that presented in [2]. The sample material consisted of various forestry biomasses collected mainly from different parts of Finland. The sample material consisted mainly barks and forest residues grouped by biomass type, growth site, plant parts, storage and debarking. The tests were carried out using gases relevant to pressurized oxygen gasification, i.e. steam and carbon dioxide, as well as their mixtures with the product gases H_2 and CO. The temperature was below 1000 °C, and the pressure range was between 1 and 20 bar. The measurement procedure is presented in detail in [2].

The reactivity was expressed in the form of the instantaneous reaction rate, i.e. it was calculated by dividing the rate of mass change of the sample by the residual ash-free mass (explained in detail in [2]) plotted against fuel conversion; the conversion, expressed as percent, was the reacted part of the total ash-free sample. These parameters were derived from the weight-time curve obtained from the thermobalance. The plot shows the dependence of the rate on the conversion, i.e. reactivity profile, as shown Figure 18. The reactivity of a char having already reacted to a certain conversion value can thus be read on this plot. The char was produced from the sample to be tested *in situ* as described in [2]. The samples and the char amounts of each test, as well as the quantities of residues, are listed in Appendix 1.

After the reactivity test, the residual ash was inspected under a stereomicroscope to detect any sintering of ash particles or molten phases. The sintering was detected as either molten ash particles, which had a distinct spherical or shiny, glasslike form, or as larger agglomerates compared with the powdery ash particles, as shown in Figure 1. The following classification symbols were used for the degree of sintering (presented and illustrated in [2]):

- Non-sintered ash residue, classification: O (no stars)
- Partly sintered, i.e., signs of melting were found in the ash sample (two different classification degrees in this group), classification: *, ** (1–2 stars).
- Totally sintered ash, i.e., the ash sample was completely or nearly completely molten, classification: *** (3 stars).

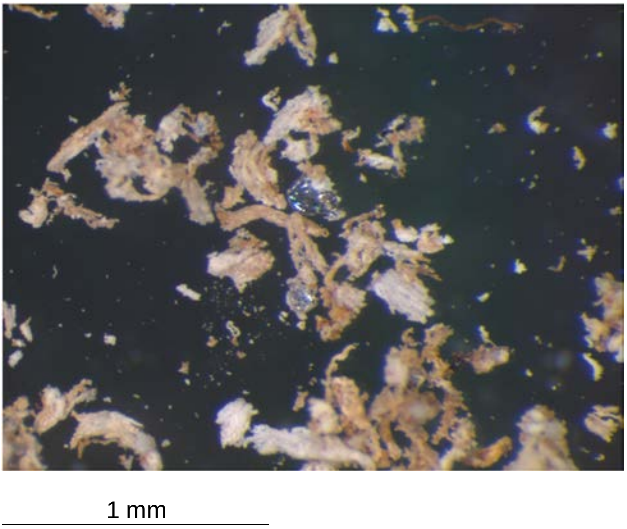

Figure 1. An example of the ash residue seen under the microscope. Molten transparent glassy particles can be seen at the centre.

3. Gasification reactivity

The gasification reactivities among biomasses were compared on the basis of the test results obtained at 850 °C and in 5 bar steam. The rate values for the comparisons were read at the point at which the fuel achieved 90% conversion (Figure 15).

3.1 Biomass type

The following biomass types were included in the tests: spruce bark, pine bark, aspen bark, birch bark, forestry residue, bark feedstock mixture, stump chips and hemp. The reactivities are compared in Figure 2. From the results, it can be seen that thick pine bark had the lowest reactivity (instantaneous reaction rate 14%/min) and hemp the highest (250%/min); all other biomasses laid between these values.

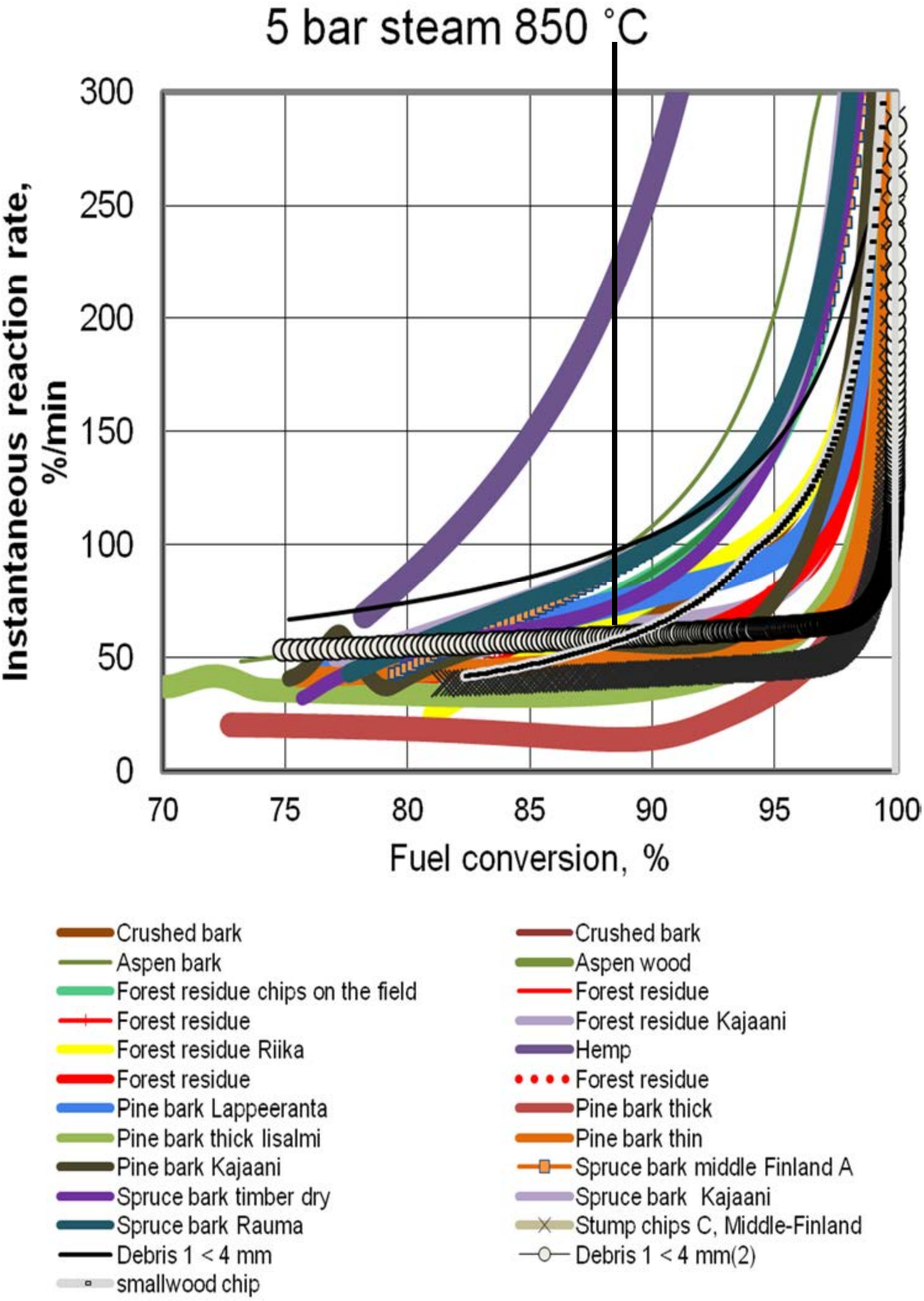

Figure 2. Comparison of the reactivities of various biomasses, determined at 850 °C in 5 bar steam. (The vertical line indicates the fuel conversion of 90%, at which the rate values were read for the comparisons).

3.2 Growth site

One objective of this work was to test how individual biomasses, such as spruce, differs from each other growing in different locations. For this testing, spruce and pine bark samples from different locations as shown in Figure 3 were selected (App. II). Also forest residue samples collected from different locations were included in the study. One of them was from Riga Latvia.

According to the results, there was practically no difference in the reactivities among the spruce barks collected from the different locations (see Figure 4). For pine bark, the differences were greater, but the differences observed were probably due to the thickness of the bark rather than to the growth location (see Ch. 3.4). For the spruce barks, the instantaneous reaction rate measured at 90% fuel conversion was 100%/min (Figure 4), while for pine barks it varied between 14 and 75%/min (Figure 5). The reactivities of the forest residues from different location can be seen in Figure 6, and according to them they are quite close to each other and the sample originating outside Finland (Riga) does not deviate significantly.

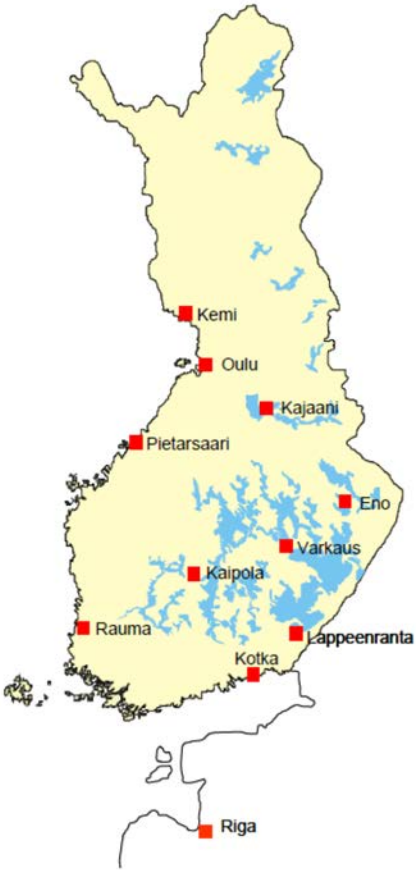

Figure 3. Biomass growth sites.

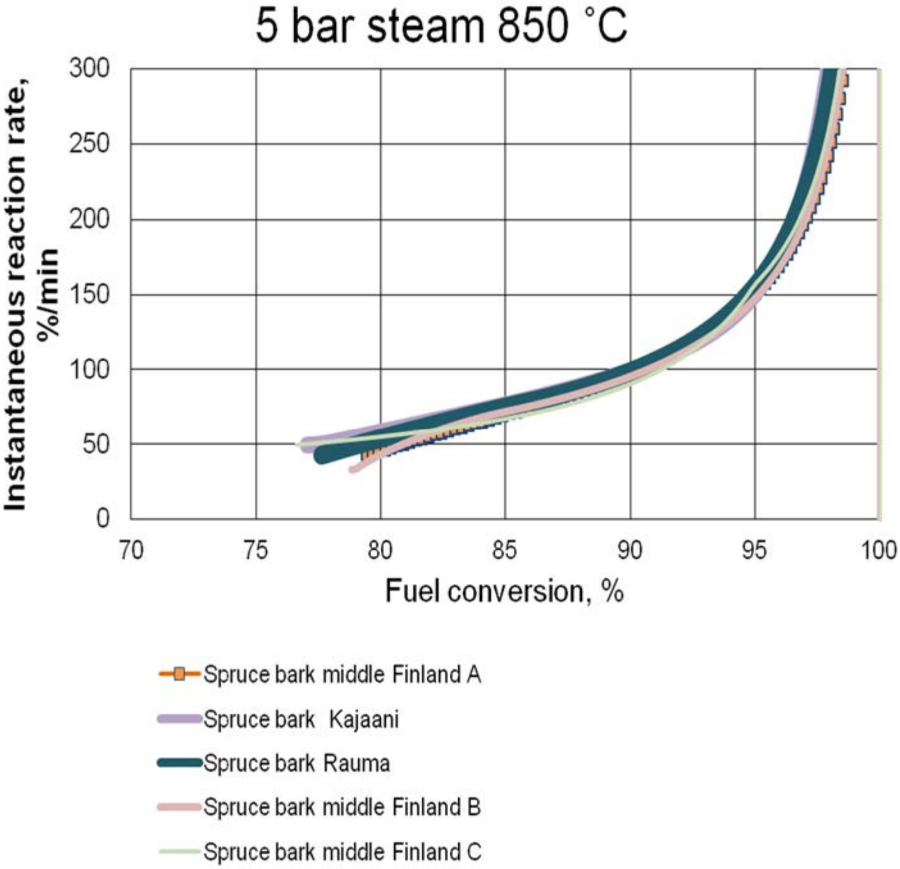

Figure 4. Comparison of the reactivities (determined at 850 °C in 5 bar steam) of spruce barks collected from different locations in Finland.

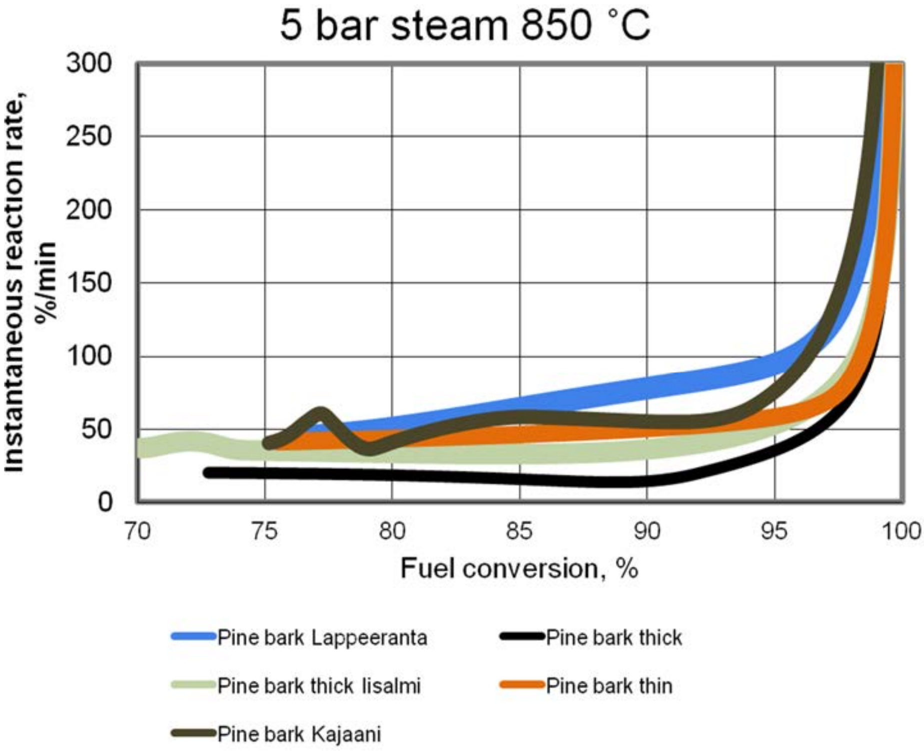

Figure 5. Comparison of the reactivities (determined at 850 °C in 5 bar steam) of pine barks collected from different locations in Finland.

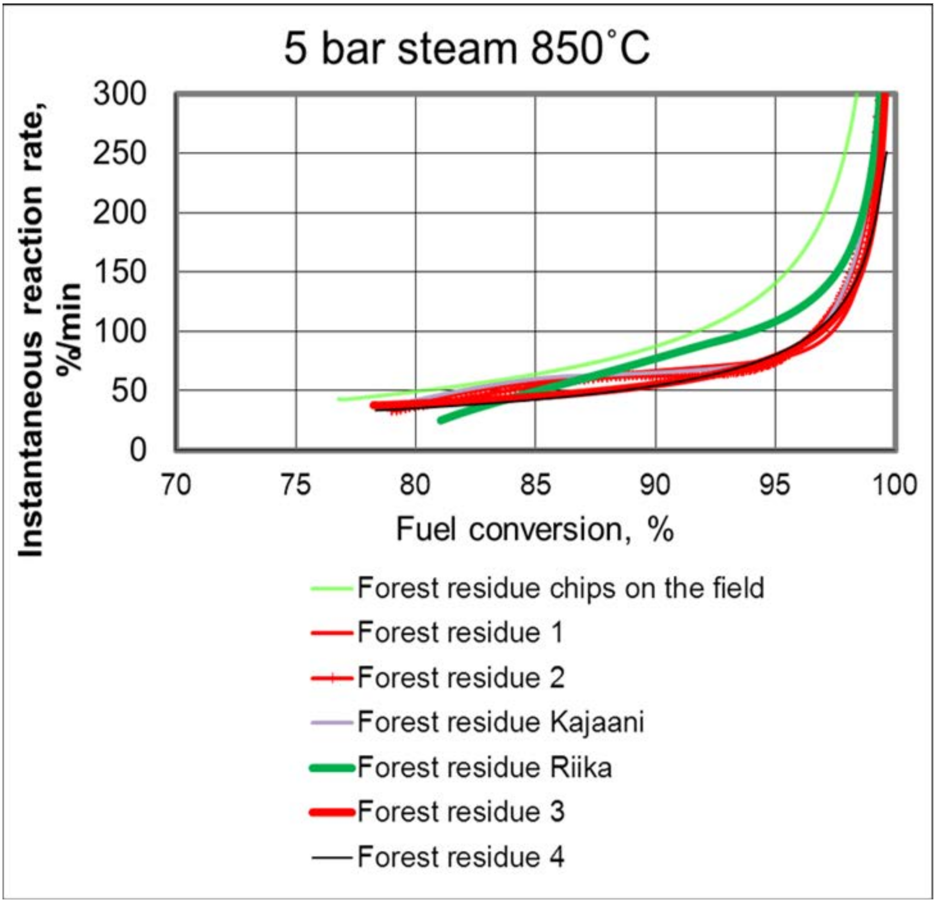

Figure 6. Comparison of the reactivities of forest residues from different sources (the source of the numbered samples was not known).

3.3 Storage

The conventional fuel characteristics (heating value, ash content, etc.) of forestry biomasses have been observed to change during storage [6]. During storage, the biomass is under the influence of rainwater, and it also decays, which may result in changes to the characteristics. In this work, a forest residue sample was selected that had been stored so that it was partly decomposed. To see this storage effect in particular, the tests were carried out on the decomposed part of the sample. The decomposed part was separated by sieving the fines from the samples with a 4 mm sieve (Figure 7). From the same batch of the forest residue, two samples were taken. They were indicated here as Debris 1 and Debris 2. The reactivity results are presented in Figure 8, which shows a large difference between the two samples. The result indicates that during storage, quite large local differences in reactivity seem to develop. To understand the reason for this, further studies are needed.

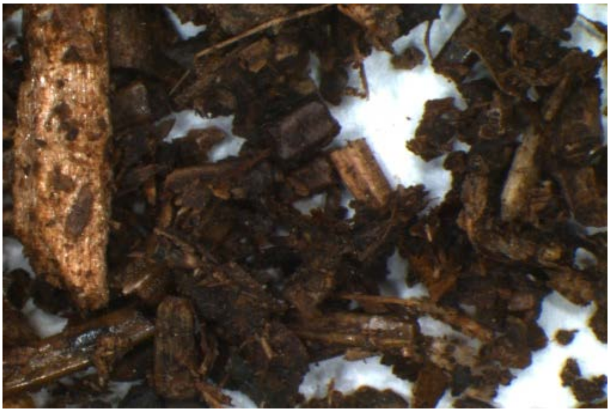

Figure 7. The structure of the decomposed forest residue (dark brown debris).

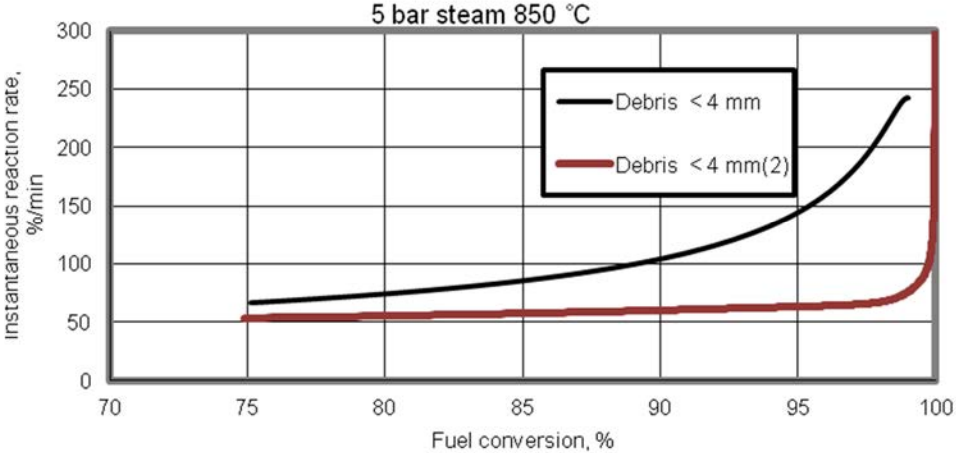

Figure 8. Reactivities of the decomposed part (debris, sieve fraction < 4 mm) of the two stored forest residue samples.

The effect of short-term storage was tested with a forest residue feedstock stored in a silo, from which samples were collected during its discharge from the bottom, middle and top. The forest residue appeared fractionated to some extent when inspected visually, with the result that the lighter part of the biomass was located at the top of the silo and was discharged last. The reactivity of this part was only slightly higher than that of the others (Figure 9).

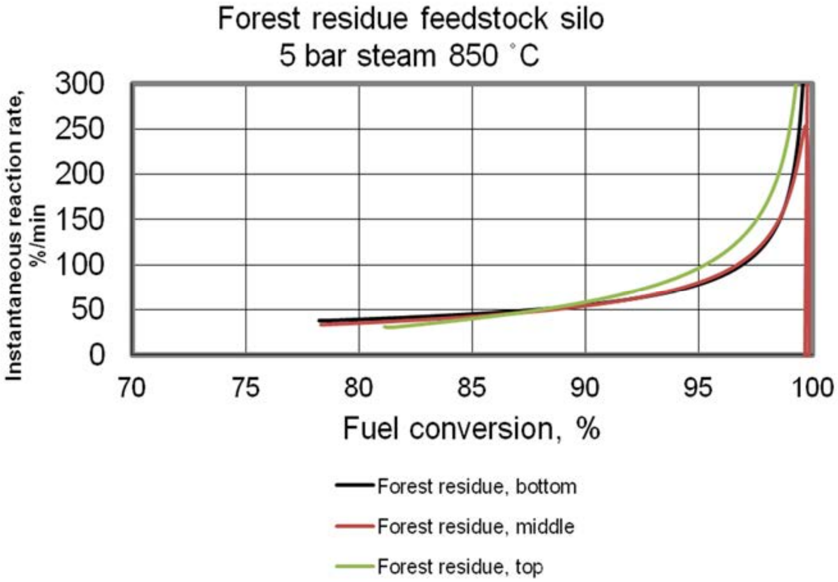

Figure 9. Reactivities of forest residue in short-term storage (silo).

The results from the similar test for bark in short-term storage are shown in Figure 10. The scattering of the reactivities was small. However, the species of the bark was not known. The rates are less than 100%/min, indicating the inclusion of bark other than spruce and/or heartwood. The bark here was a technical term and could include miscellaneous types of barks.

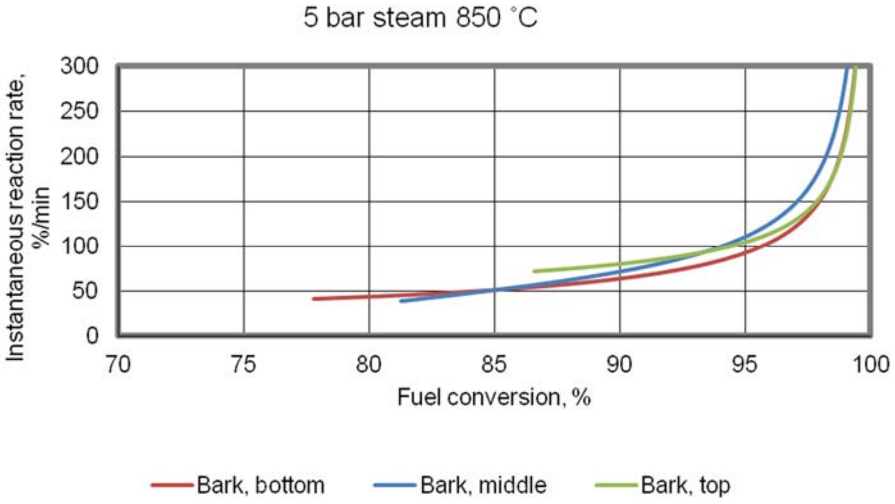

Figure 10. Reactivities of bark in short-term storage.

3.4 Plant parts

In earlier studies, it was observed that different parts of a tree, such as needles, bark and heartwood (i.e. wood without bark), have different reactivities and ash sintering behaviours [2]. Since pine bark has the most distinct differences in thickness compared with that of spruce, thin and thick pine barks were selected for the comparison. The thickness of pine bark varies so that the lower part of a pine tree has a thick rind, while upper parts and twigs have thinner bark. The results showed a clear difference in reactivities (Figure 11, for the tests, samples were milled to the same particle size): thin bark was 3–4 times more reactive than the thick bark. The reason for this might be that the thick bark from the low part of a pine tree was old and has been under the influence of rainwater, with the result that the catalytically active inorganic components may have leached out.

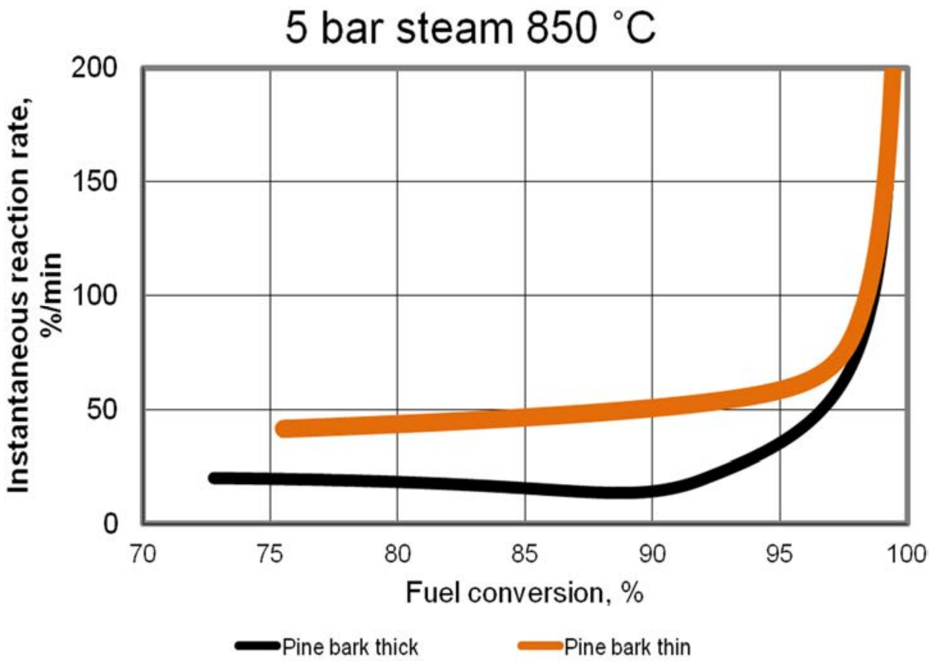

Figure 11. Comparison of the reactivities of thin and thick pine barks.

In Figure 12, other plant parts such as bark, and stump are compared. The bark and heartwood were from aspen, but the species of the stump was unknown. According to the results, stump had significantly lower reactivity compared with the others. The wood without bark has usually lower reactivity, as observed in earlier studies [2].

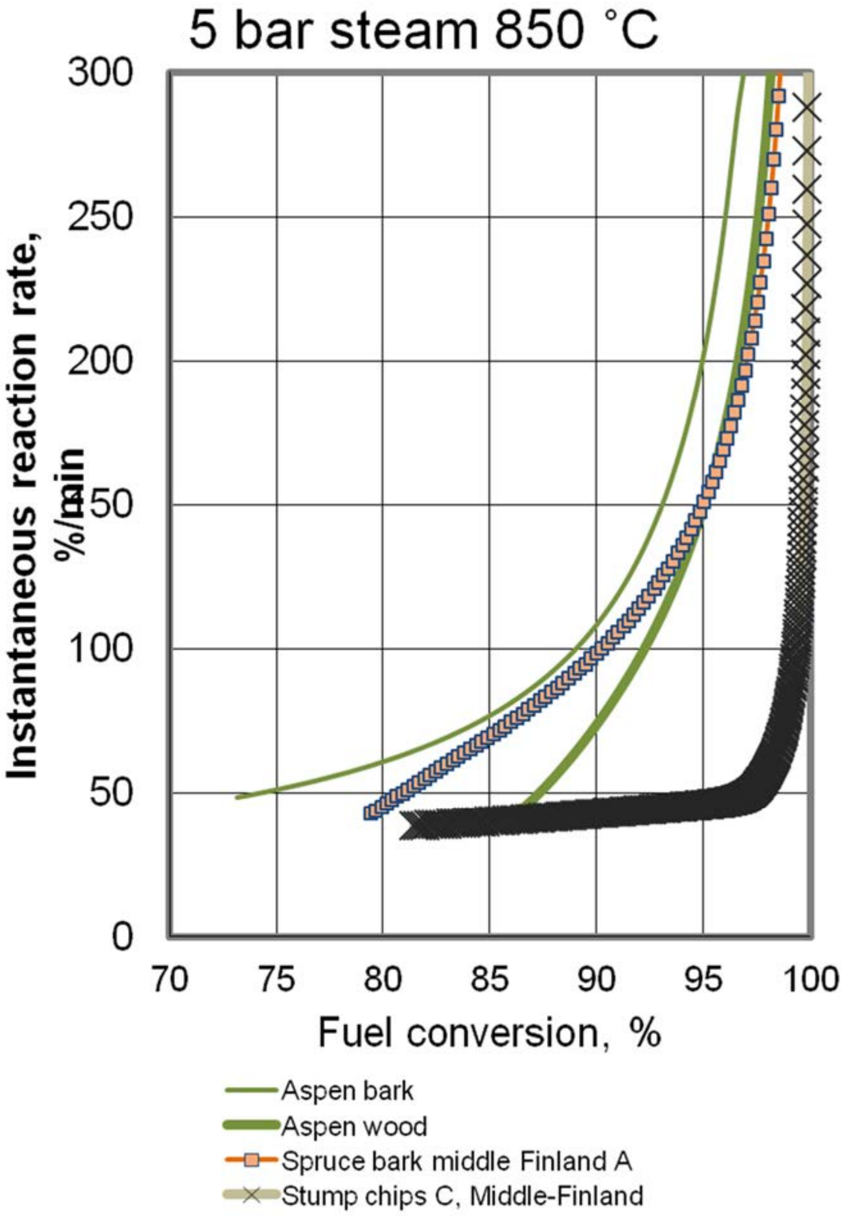

Figure 12. Comparison of the reactivities of various plant parts.

Forest residue is usually logging residue consisting of branches, leaves/needles, lops and tops Scattering of the results is therefore expected due to the inhomogeneity of the material. The reactivity results are presented in Figure 6, which shows that the rate varied between approximately 50 and 70%/min measured at

90% fuel conversion. This variation may be also due to the fact that the species of the forest residues was not identified, and the samples here could consist of miscellaneous species.

3.5 Debarking

In pulp making, bark is removed from the tree trunks in a separate debarking unit in the process, where warm water is used to ease the removal of the bark. For timber, the debarking is usually carried out using dry methods with no contact with water. Contact with water has an influence on the water-soluble salts (nutrients) occurring naturally in the bark. The salts are removed during the water treatment, then partially precipitate back into the bark structure when water evaporates from the bark during thermal drying. During this precipitation, the salt particles' (crystals') structures and sizes are changed from those of the original. Their chemical nature may also be changed, depending on the compound formed from the dissolved ions during the crystallization that takes place when water evaporates during drying. These factors may have an influence on the catalysis as well on the sintering properties. In this respect, it is known that potassium compounds play the most important role.

In Figure 13, the reactivities of the spruce barks removed using dry and wet debarking methods are compared. There was no clear difference in the reactivity, however, the sintering of the ash was more enhanced for the timber bark (see Ch. 5.2)

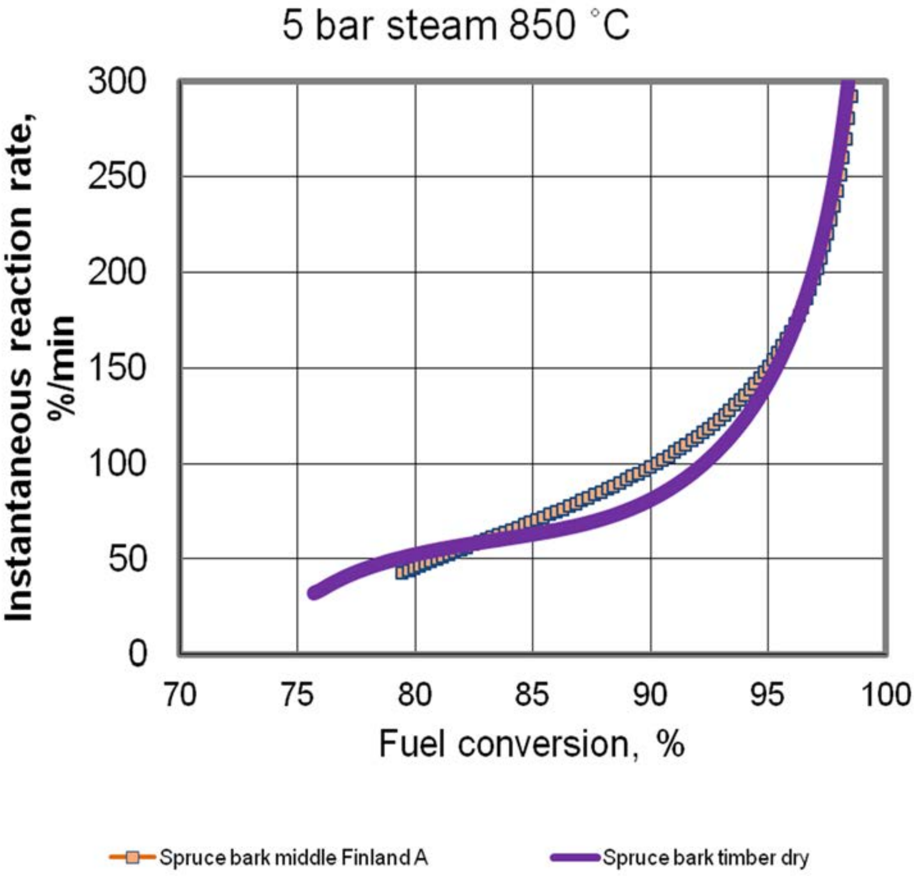

Figure 13. Comparison of the reactivities of the barks debarked wet (Spruce bark A) and dry (timber).

4. Kinetic parameters of biomass gasification

The gasification reactivity in the presence of product gases was characterized by TG measurements. The results were presented in [5], Appendix III. The kinetic parameters of the char gasification reactions were measured to enable the calculation of the gasification rate at different temperatures and the gas compositions needed in modelling. The parameters were determined from the measurements, which were carried out in the pure reactant gases, steam and CO_2 as well as in binary gas mixtures, in which the product gas component was mixed with the reactant gases. Hydrogen was mixed with steam, and CO with CO_2. This way of mixing enables gas phase reactions to be avoided. The procedure was the same as used for coal [6, 7]. In the determination of the kinetic parameters, the Langmuir-Hinshelwood mechanism was applied. The details of this work are presented by Nasrullah [3], Appendix IV. The char gasification in a gasifier takes place mainly in the gas mixture containing all the gas components, H_2O, CO_2, H_2 and CO. In principle, this mixture exists in two places: in the reactor, and inside char particles where the product gas is formed in the pore structure when the carbon is gasified (Figure 14).

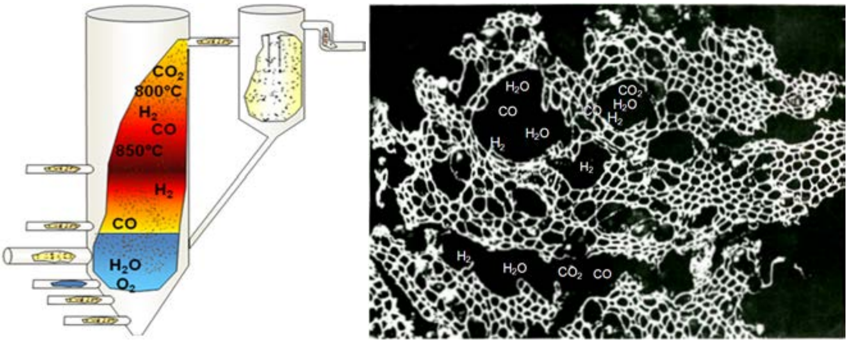

Figure 14. The existence of the gas mixture in the gasifier reactor and inside char particles (wood char).

The gasification reaction rate R as a function of the steam and CO_2 pressure was calculated using the Langmuir-Hinshelwood equations, (1) for steam gasification $C+H_2O \rightarrow CO+H_2$ and (2) for CO_2 gasification $C+CO_2 \rightarrow 2CO$.

$$R = \frac{r_1 P_{H_2O}}{1+r_2 P_{H_2O}} \tag{1}$$

$$R = \frac{r_4 P_{CO_2}}{1+r_5 P_{CO_2}} \tag{2}$$

In the formulas, r_i represents the rate constant, which depends on the partial pressure of the respective gas component, and P_{gas} (i.e. P_{H2O} and P_{CO2}) is the partial pressure of the gas. The rate constant r_i depends on the temperature according to the Arrhenius equation (3).

$$r_i = k_i \, e^{-E_i/RT} \tag{3}$$

Here k_i is the frequency factor, E_i the activation energy, R the gas constant and T the temperature.

In the binary gas mixtures, where hydrogen is added to steam and CO to CO_2, the reaction rate as a function of pressure can be calculated using the formulas (4) and (5), respectively:

$$R = \frac{r_1 P_{H_2O}}{1+r_2 P_{H_2O}+r_3 P_{H_2}} \tag{4}$$

$$R = \frac{r_4 P_{CO_2}}{1+r_5 P_{CO_2}+r_6 P_{CO}} \tag{5}$$

The kinetic parameters were determined using spruce bark (spruce bark A) as the sample material. The sample was pyrolysed *in situ*, as described in [2]. For the calculations of the kinetic parameters, the instantaneous reaction rate was selected at the point where fuel conversion was 90% (Figure 15). This value corresponds to approximately 50% char conversion. Using the formulas (1)–(5), the parameters were obtained by finding the best fit using the Microsoft Excel Solver Add-in tool. The parameters obtained are shown in Table 1.

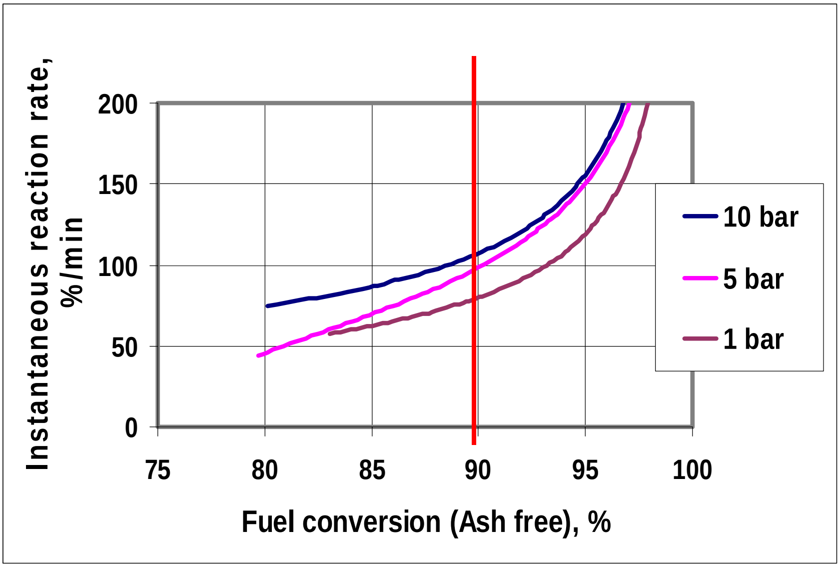

Figure 15. For the calculations, the reaction rate at 90% fuel conversion was selected.

The kinetic parameters obtained were used to calculate the gasification rate in the gas mixture containing all the gas components. Here the formula (6) was applied:

$$R = \frac{r_1 P_{H_2O} + r_4 P_{CO2}}{1 + r_2 P_{H_2O} + r_3 P_{H_2} + r_5 P_{CO_2} + r_6 P_{CO}} = \tag{6}$$

$$R = \frac{k_1 e^{-E_1/RT} * P_{H_2O} + k_4 e^{-E_4/RT} * P_{CO2}}{1 + k_2 e^{-E_2/RT} * P_{H_2O} + k_3 e^{-E_3/RT} * P_{H_2} + k_5 e^{-E_5/RT} * P_{CO_2} + k_6 e^{-E_6/RT} * P_{CO}}$$

The calculated rate values were verified with TG measurements carried out in the respective gas composition. Comparisons of the measured and calculated values are plotted in Figure 16. The fit shows a large scatter. This procedure has been applied successfully in coal gasification [6, 7]. The reason for the bad fit compared with that for coal may be that coal gasification is not controlled by the catalytically active inorganic material (in coal it is mainly in form of inactive silicates), while in biomass the inorganic material is catalytically active and also very reactive, leading to unpredictable changes in the catalyst's behaviour. This behaviour is not currently known in detail. A notable phenomenon observed in this study was that in the carbon dioxide gasification, the gasification rate was negatively dependent on the CO_2 pressure, the opposite of what is observed in steam gasification (Figure 17). This phenomenon may be the reason for the bad fit obtained in this work, and it requires further investigation before it can be understood and incorporated in the kinetic model.

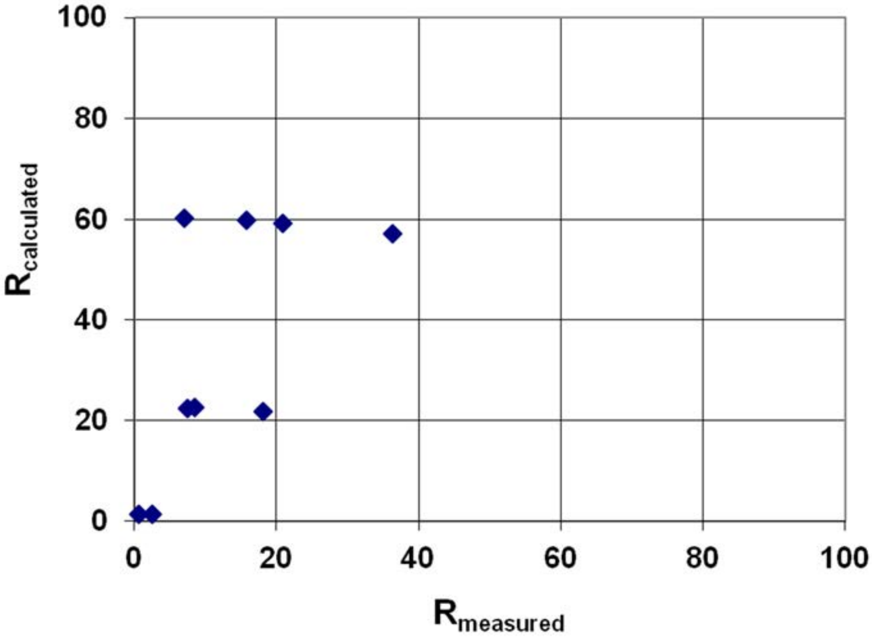

Figure 16. Plot of measured and calculated rate values obtained from the measurements carried out on the gas mixtures of $H_2O+CO_2+H_2+CO$.

Table 1. Values of frequency factors and activation energies presented in [3].

Frequency factor		**Activation Energy (kJ/mol)**	
k_1	7.48E+12	E_1	306.285
k_2	5.12E+09	E_2	201.812
k_3	1.22E-09	E_3	-214.046
k_4	-1053.633557	E_4	115.512
k_5	-0.000136566	E_5	-80.198
k_6	-3.22803E-22	E_6	-474.986

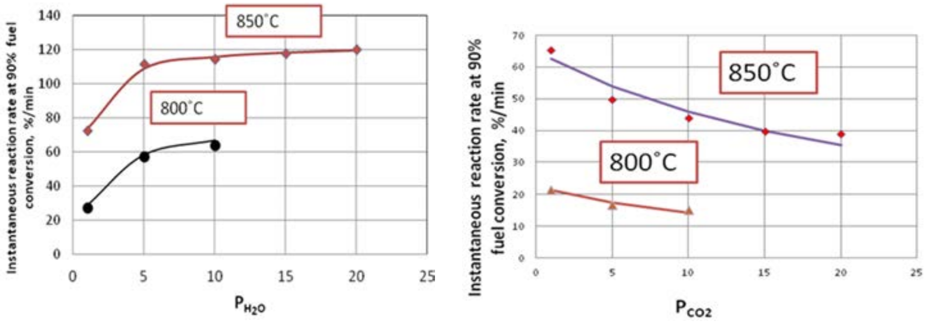

Figure 17. The dependence of the char gasification rate on a) steam and b) CO_2 pressure. The rate values were taken at 90% fuel conversion.

4.1 Reactivity profile

The dependence of the instantaneous reaction rate on the conversion has three patterns. Normally it increases with the conversion, but it may also decrease or go through a minimum (Figure 18).

The reaction rate as a function of conversion *x* can be described with the equation (7) presented by Zhang et al. [8]. The formula is based on a random pore model modified by parameters relating to the behaviour of the catalytically active material.

$$\frac{dx}{dt} = K\,(1-x)\sqrt{1-\psi \ln(1-x)}\,\left(1+\left(c[x)\right]^{p}\right) \tag{7}$$

In the present study, it was observed that the model (7) works for cases where the instantaneous reaction increases or decreases with the conversion, but not for the case where it goes through a minimum, as shown in Figure 18. Further investigation is therefore also needed here.

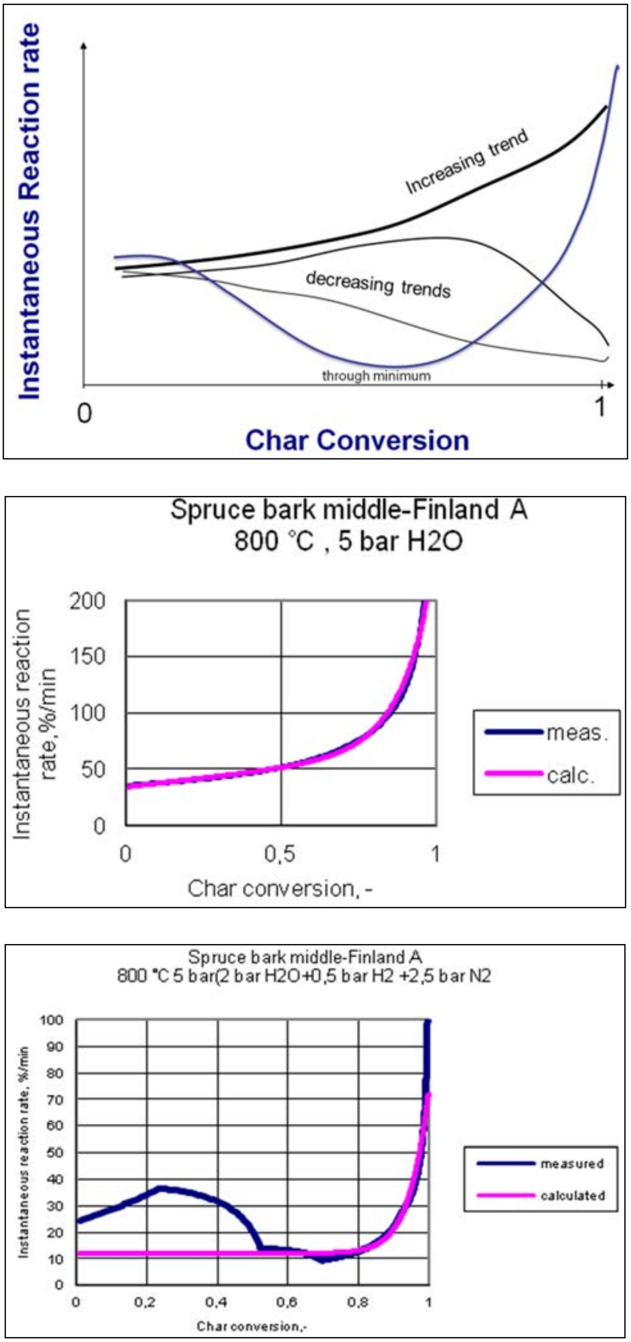

Figure 18. The dependence patterns of the reaction rate on conversion (top), examples: normal pattern (middle), the pattern with the rate minimum (bottom).

5. Ash sintering

The ash sintering results for all the tests are presented in the table of Appendix I. Often, the ash residues were not totally sintered, consisting rather of molten particles (spheres), unreacted char particles and powdery ash. The comparison tests for ash sintering were carried out in 5 bar steam at 850 °C. The results are presented in Table 2.

The strongest sintering (indicated as ***) was observed for hemp, which was an agro-biomass cultivated for energy purposes on an MTT/Jokioinen test field. The spruce bark, obtained from the timber trunks using dry debarking, and aspen bark also exhibited strong sintering.

5.1 Effect of pressure

The effect of pressure on sintering was tested under conditions where biomass was gasified at the same temperature at atmospheric pressure and at elevated pressures. The gasification was carried out in steam, carbon dioxide or in the gas mixture also containing the product gas components. The general observation in these tests was that increased pressure resulted in intensified sintering, as has been observed in earlier studies [2].

In particular, sintering was intensified when the gasification medium was CO_2, which created sintering even at atmospheric pressure (100% CO_2 gas), which did not happen with steam (spruce bark). This observation indicates that sintering is caused by low eutectic melting point of calcium and potassium carbonates, as has been observed previously [2]. Calcium carbonate is stabile when the partial pressure of CO_2 is high enough at the gasification temperature.

Gasification in the gas mixtures under pressure usually exhibited insufficient reactivity, due to the strong inhibition caused by the product gas components having a higher partial pressure. The low reactivity meant that it took a long time to reach total char conversion, so the residues inspected were still carbonaceous and ash was not totally revealed. The carbon material may prevent ash from sintering.

In some cases, such as for spruce bark (the sample Spruce bark A), the effect of high pressure on ash sintering was observed when tested in 10 bar steam and already at 700 °C. In this sample there were molten parts in the ash although it was not 100% reacted; the fuel conversion was 97% and the char conversion 87%. However, in 5 bar steam and at the same temperature no ash sintering was detected, although the achieved conversion was on the same level. In 10 bar steam at 750 °C, signs of sintering were detected for this spruce bark and similarly at 800 °C in 5 bar steam. In CO_2, ash sintering was again stronger: sintering was detected in 1 bar CO_2 at 800 °C. Spruce bark C from central Finland exhibited medium sintering (**) after testing at 800 °C in 10 bar steam. Aspen bark also exhibited clear sintering when tested in the H_2O+H_2+CO_2+CO gas mixture at 875 °C and 5 bar total pressure This aspen bark exhibited only weak sintering when measured in the same gas and at the same temperature, but at 1 bar. It therefore seems that sintering behaviour varies with pressure and temperature and, to some extent, even among the barks of the same species. To understand this, more research is needed.

5.2 Biomass type

The major biomass tested in this work was spruce bark, since spruce is common forestry biomass in Finland for the pulp industry. It is typical of spruce bark that its ash has an increasing tendency to sinter with pressure, as has been observed in earlier studies [2]. Another common forestry biomass is pine, whose bark produces ash with less sintering, in general, than does spruce bark. However, there was a clear difference in the sintering behaviour for different types of pine barks. Thin bark taken from the top part of pine or branches exhibited weak sintering when measured in 1 bar steam at 850 °C. Thick pine bark exhibited no sintering under the same conditions, but there were some signs of sintering in 10 bar steam at 850 °C. Pine bark measured in the gas mixture of H2O+H2+CO2+CO at 875 °C exhibited no sintering. However, 100% conversion could not be achieved in this test due to very low reactivity.

The feedstock called crushed bark here is in practice a mixture containing barks from different tree species (usually pine, spruce and birch). Regarding the sintering behaviour of this type of mixture, it can be seen that the ash was partly molten, indicating that the mixture contained biomass components with low-melting ash. In this work, the biomass composition of the bark mixture was not determined. On the basis of the results obtained for individual barks, the main sources for ash sintering are spruce, aspen and birch[1].

The results obtained for barks indicate great variation in the ash sintering behaviour, although the variation in reactivity was not very significant.

Since forest residues are inhomogeneous materials, variation in the ash sintering behaviour was expected, as it can be seen in tests 370, 467, 468, 470, 628 and 627. The fact that forest residues consist of bark, thin twigs, needles and logging residues is evident in ash residues having both unsintered parts and totally molten parts.

The effect of *storage* can be seen in tests 449, 454, 451, 493, 496 and 500. No significant effect could be seen, and the ash sintering was similar taking into account the above. Debris (59, 60) had weak sintering that could be the result of the alkaline metals being leached out by water.

Furthermore, no clear effect on ash sintering due to the *growth site* could be observed. For pine bark, the thickness had the dominant effect.

The *debarking* method seemed to have an effect on sintering. Using water in the debarking process seems to remove water soluble alkaline metal compounds (such as potassium compounds), resulting in less sintering than when bark was removed dry. However, the ash sintering of this dry bark was strong in 10 bar steam gasification (***), and to a smaller extent in 5 bar (*).

Table 2. Comparison of ash sintering. Steam gasification in 5 bar at 850 °C. The residue (%) indicates the residue after a test, which may contain unreacted char. (The indication 'O, molten particles' means that the major part of the ash was not sintered but some separate molten particles were visible.)

Run #	Biomass samples	Residue, %	Sintering degree
366	Crushed bark Varkaus time 1	2.2	O - *
365	Crushed bark Varkaus time 2	2.7	*
369	Crushed bark Varkaus time 3	2	O
370	Forest residue chips Varkaus	3.3	*
467	Forest residue chips UCG0823C	0.9	O some particles unreacted
468	Forest residue chips	2.6	O unreacted, ash coming out,

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[1] tested only in 1 bar steam.

	UCG0823C		molten particles
470	Forest residue chips UCG0823C	2.7	O, molten particles
479	Aspen heartwood	0.4	*
481	Aspen bark	1.7	**
628	Forest residue Kajaani	2.3	O unreacted char, ash coming out
627	Forest residue Riga	3.3	O molten particles
607	Hemp, Jokioinen	4.4	O - ***
618	Pine bark Lappeenranta	4.1	O molten particles
457	Pine bark thick	1.6	O
531	Pine bark thick, Iisalmi	0.8	O
460	Pine bark thin	2.8	O
619	Pine bark Kajaani	2	O
409	Spruce bark A	3.2	O - *
435	Spruce bark B	2.2	O molten particles
422	Spruce bark C	3.4	*, molten particles
524	Spruce bark timber (dry) Porvoo timber	1.9	*
617	Spruce bark Kajaani	2.4	O molten particles
616	Spruce bark Rauma	2.8	*
486	Stump chips C, Middle-Finland	1.9	*
75	Pine bark Kajaani	1.5	O, molten particles
79	Small wood chip, Varkaus	0.6	*
59	Debris 1, < 4 mm	4.8	*
60	Debris 2, < 4 mm	4.4	*
449	Feedstock silo test, bark top	3.1	O
454	Feedstock silo test, bark middle	5	O
451	Feedstock silo test, bark bottom	4.4	O, molten particles
493	Feedstock silo test, Forest residue bottom	1.7	O, molten particles
496	Feedstock silo test, Forest residue middle	1.5	*
500	Feedstock silo test, Forest residue top	0.7	*

Time 1 = 5.03.08 15:00
Time 2 = 19.03.08 16:00
Time 3 = 20.03.08 16:00

6. Conclusions

The objective of the work was to study the variation in quality of biomass feedstocks selected for large-scale gasification processes aimed at biodiesel manufacture. The focus was on forestry biomass, and quality was represented by gasification reactivity and ash sintering properties. The following biomass types were included in the tests: spruce bark, pine bark, aspen bark, birch bark, forestry residue, bark feedstock mixture, stump chips and hemp. The work was divided in two parts: 1) Study of the internal variation of the reactivity and the ash sintering of selected forestry biomass feedstocks relevant to a large-scale gasification process, and 2) Measurement of the kinetic parameters of char gasification reactions to be used in the modelling of a gasifier. The study was based on thermogravimetric measurements using a pressurized thermobalance.

The sample material consisted of various forestry biomasses collected mainly from different parts of Finland. The tests were carried out using gases relevant to pressurized fluidized bed oxygen gasification; the temperature was up to 1000 °C, and the pressure range was between 1 and 20 bar.

The reactivity was expressed as the instantaneous reaction rate plotted against fuel conversion. After the reactivity test, the residual ash was inspected under a stereomicroscope to detect any sintering of ash. For the reactivity comparisons the instantaneous reaction rate was measured at 90% fuel conversion.

The effects of biomass type, location, storage, debarking method and different plant parts were tested. The largest differences in the reactivity was observed between various biomass types and it varied between 14%/min (thick pine bark) and 250%/min (hemp). It was observed that growth location had no effect on the gasification reactivity and ash sintering of spruce bark. For pine bark, differences were observed, but they were most probably due to the thickness of the bark rather than to the location. For spruce barks, the reaction rate measured at 90% fuel conversion was 100%/min, while for pine barks it varied between 14 and 75%/min. The effect of storage was tested using the decomposed part of a stored forest residue sample. The results indicated that during storage, quite large local differences in the reactivity seem to develop, but the ash sintering was weak and no difference was observed. The thickness of pine bark varies, with the lower part of a pine tree having a thick rind, while upper parts and twigs have thinner bark. There was a clear difference in reactivity : the thin bark was 3–4 times reactive than thick bark. Stump had significantly lower reactivity compared with the others. The reaction rate of forest residue varied between 50 and 70%/min measured at 90% fuel conversion. The variation may be due to the fact the samples consisted of miscellaneous species. In pulp making, bark is removed from the tree trunks in a separate wet debarking unit using water to ease the removal of the bark. For timber, debarking is usually carried out using dry methods with no contact with water. The contact with water has an influence on the water-soluble salts (nutrients) occurring naturally in the bark. There was no significant difference in reactivity between the dry and wet debarking methods, but the sintering of the timber bark ash was stronger.

The kinetic parameters of the char gasification reactions were measured for the modelling purposes. The parameters were determined from the measurements, which were carried out in the pure reactant gases, steam and CO_2 as well as in the binary gas mixtures in which the product gas component was mixed with the reactant gases. Char gasification in a gasifier takes place mainly in the gas mixture containing all the gas components H2O, CO2, H2 and CO. According to the results, there was a poor fit between the measured and calculated values. The reason for this is related to the fact that biomass char gasification is controlled by the catalytically active inorganic material occurring in biomass, and there are unpredictable changes in catalytic behaviour, which is not currently known in detail. A notable phenomenon observed in this study was that in the carbon dioxide gasification, the gasification rate was negatively dependent on the CO_2 pressure, the opposite of what is observed in steam gasification. These phenomena require further investigation to enable the kinetic model for char gasification to be developed.

The results showed that the dependence of the instantaneous reaction rate on the conversion had three patterns. Normally it increases with the conversion, but it may also decrease or go through a minimum.

The main comparison of ash sintering was carried out using the tests carried out in 5 bar steam at 850 °C. Often, the ash residues were not homogeneously sintered, consisting rather of molten particles (spheres), unreacted char particles and powdery ash. The strongest sintering (indicated by ***) was observed for hemp. The spruce bark obtained from dry debarking and aspen bark exhibited similarly strong sintering. In general, the increase in pressure resulted in intensified sintering, as has been observed in earlier studies. Gasification in the gas mixtures under pressure usually exhibited insufficient reactivity due to the stronger inhibition of the product gas component. The low reactivity meant it took a long time to reach total char conversion, with the result that the residues inspected were still carbonaceous, and the carbon material may have prevented the ash from sintering.

For forest residues, there were variations in the ash sintering behaviour in the same sample due to the forest residue’s composition. No significant effect on sintering attributable to storage, as well as to growth site could be observed.

7. Future work

Biomass char gasification is controlled by the catalysis of the inorganic material occurring in biomass, and there are unpredictable changes in catalytic behaviour, which is not currently known in detail. This behaviour is assumed to be the reason for the phenomena observed in this work. In the future, these issues will be studied in two projects NORDSYNGAS (Biomass gasification fundamentals to support the development of BTL in forest industry) and GASIFREAC (Biofuel gasifier feedstock reactivity – explaining the conflicting results).

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APPENDIX I

Table of results

Table. Samples and conditions used in the TGtests. **Fuel conversion after pyrolysis** indicates the amount reacted (% sample) at the beginning of char gasification, **Residue** indicates the residual amount (ash) left after the test and **Sintering degree** describes how the ash in the residue was sintered.

Marking ‘O, molten particles’ means that the major part of the ash was not sintered but some separate molten particles were visible.

Run #	Biomass samples	Medium	Temperature, ˚C	Pressure, bar	Fuel conversion after pyrolysis,%	Residue, %	Sintering degree
478	Aspen bark	Steam	850	1	76,3	2,3	O
481	Aspen bark	Steam	850	5	73,2	1,7	**
593	Aspen bark Iisalmi	$H_2O+H_2+CO_2+CO$	875	1	76,3	2,8	*
594	Aspen bark Iisalmi	$H_2O+H_2+CO_2+CO$	875	5	74,9	3,7	* + *** plenty of molten particles
620	Aspen bark Iisalmi	$H_2O+H_2+CO_2+CO$	875	1	74,2	3	(*)
477	Aspen bark-free wood	Steam	850	1	88,4	0,6	O
479	Aspen heartwood	Steam	850	5	86,2	0,4	*
622	Birch bark Iisalmi	$H_2O+H_2+CO_2+CO$	875	1	84,2	1	(*) unreacted particles
590	Crushed bark Varkaus, time 1	$H_2O+H_2+CO_2+CO$	850	1	82,3	7,3	O unreacted, no ash
591	Crushed bark Varkaus time 1	$H_2O+H_2+CO_2+CO$	875	1	81,8	2,4	O unreacted, ash coming out
592	Crushed bark Varkaus time 1	$H_2O+H_2+CO_2+CO$	875	5	81,7	2,3	O unreacted, ash coming out
373	Crushed bark Varkaus time 1	$H_2O+ H_2$	850	1	84,9	3,2	O some unreacted particles
376	Crushed bark Varkaus time 1	$H_2O+ H_2$	850	10	82,6	4,2	O some unreacted particles
364	Crushed bark Varkaus time 2	Steam	850	10	76,9	1,7	*
365	Crushed bark Varkaus time 2	Steam	850	5	81,3	2,7	*
511	Crushed bark Varkaus time 2	H_2O+H_2	850	5	77,3	2	O some unreacted particles
369	Crushed bark Varkaus time 3	Steam	850	5	77,8	2	O
368	Crushed bark Varkaus time 3	Steam	850	10	75,2	3,4	***
359	Crushed bark Varkaus time 3	Steam	852	1	78,5	2,3	O
506	Crushed bark Varkaus time 3	H_2O+H_2	850	1	79,7	1,6	O + molten particles
507	Crushed bark Varkaus time 3	CO_2	850	1	77,1	2,5	*
357	Crushed bark Varkaus time 1	Steam	854	1	89,9	1,3	* +molten particles
503	Crushed bark Varkaus time 1	CO_2	850	1	82,6	1,7	*
505	Crushed bark Varkaus time 1	H_2O+H_2	850	1	83,8	0,9	O
361	Crushed bark Varkaus time 1	Steam	850	10	79,8	2,8	*+ molten particles

366	Crushed bark Varkaus time 1	Steam	850	5	79,4	2,2	O - *
375	Crushed bark Varkaus time 1	$H_2O + H_2$	850	5	81,0	3,9	O some unreacted particles
508	Crushed bark Varkaus time 1	CO2	850	5	80,3	1,4	O
509	Crushed bark Varkaus time 1	H_2O+H_2	850	5	82,2	1,3	O some unreacted particles
512	Crushed bark Varkaus time 1	CO_2	850	10	77,8	1,5	*
513	Crushed bark Varkaus time 1	H_2O+H_2	850	10	81,4	1,9	O unreacted particles, ash coming out
358	Crushed bark Varkaus time 2	Steam	852	1	80,7	2,1	O + molten particles
342	Birch bark	Steam	853	1	90,7	1	O
339	Birch bark	Steam	853	1	79,1	2	O
501	Birch bark	CO_2	850	1	81,1	2,9	**
502	Birch bark	H_2O+H_2	850	1	81,2	1,6	O-*
538	Forest residue A middle Finland Kaipola	Steam	850	1	86,2	5,7	O unreacted, ash coming out
539	Forest residue B middle Finland Kaipola	Steam	850	1	84,9	6,1	O unreacted, ash on char surface
540	Forest residue C middle Finland Kaipola	Steam	850	1	82,7	3,2	O partly unreacted, molten particles
360	Forest residue chips Varkaus	Steam	854	1	80,6	2,5	O, molten particles
370	Forest residue chips Varkaus	Steam	850	5	76,8	3,3	*
467	Forest residue chips UCG0823C	Steam	850	5	77,7	0,9	O some particles unreacted
468	Forest residue chips UCG0823C	Steam	850	5	79,1	2,6	O unreacted, ash coming out, molten particles
469	Forest residue chips UCG0823C	Steam	850	1	81,6	2,2	O small number of molten particles and some unreacted particles
470	Forest residue chips UCG0823C	Steam	850	5	77,9	2,7	O, molten particles
367	Forest residue chips Varkaus 20.03.08	Steam	850	10	76,1	4,8	*
628	Forest residue Kajaani	Steam	850	5	78,7	2,3	O unreacted char, ash coming out
639	Forest residue middle Finland B Kaipola	Steam	850	1	84,9	6,1	**
627	Forest residue Riika	Steam	850	5	81,0	3,3	O molten particles
606	Hemp Jokioinen	Steam	850	1	78,8	3,8	Very little ash
607	Hemp Jokioinen	Steam	850	5	78,2	4,4	O-***, very little ash
449	Bark 9:35 280708 Biomass feedstock silo test	Steam	850	5	86,6	3,1	O
452	Bark (12: 05 12 :20) 280708 Biomass feedstock silo test	Steam	850	1	82,5	3,6	O
454	Bark (12: 05-12:20) 280708 Biomass feedstock silo test	Steam	850	5	81,3	5	O
450	Bark (9:35-9:50) 280708 Biomass feedstock silo test	Steam	850	1	83,0	4,2	O

451	Bark (9:35-9:50) 280708 Biomass feedstock silo test	Steam	850	5	77,8	4,4	O, molten particles
448	Bark 9:35 280708 Biomass feedstock silo test	Steam	850	1	90,5	3,1	O
492	Forest residue (0–15 min) Biomass feedstock silo test	Steam	850	1	81,0	2	O
493	Forest residue (0–15 min) Biomass feedstock silo test	Steam	850	5	78,2	1,7	O, molten particles
494	Forest residue (0–15 min) Biomass feedstock silo test	CO_2	850	5	76,2	2,1	(*), molten particles
495	Forest residue (135–150 min) Biomass feedstock silo test	Steam	850	1	80,8	1,7	O, contained unreacted particles
496	Forest residue (135–150 min) Biomass feedstock silo test	Steam	850	5	78,3	1,5	*
498	Forest residue (last) Biomass feedstock silo test	Steam	850	1	83,9	0,4	O - *
500	Forest residue (last) Biomass feedstock silo test	Steam	850	5	81,3	0,7	*
535	Mixed Stump chips and Spruce bark abut 50 : 50	Steam	850	5	77,1	1,9	O, molten particles
621	Pine bark Iisalmi	$H_2O+H_2+CO_2+CO$	875	1	78,7	4,4	O unreacted
618	Pine bark Lappeenranta	Steam	850	5	76,4	4,1	O molten particles
456	Pine bark thick	Steam	850	1	77,8	2,2	O
457	Pine bark thick	Steam	850	5	72,8	1,6	O
531	Pine bark thick, Iisalmi	Steam	850	5	70,1	0,8	O
532	Pine bark thick, Iisalmi	Steam	850	10	73,3	1,2	*
458	Pine bark thin	Steam	850	1	77,7	2,3	*
460	Pine bark thin	Steam	850	5	75,5	2,8	O
619	Pine bark Kajaani	Steam	850	5	75,2	2	O
338	Wood chip, no bark	Steam	855	1	88,1	0,8	O
343	Wood chip	Steam	853	1	89,1	0,58	O
528	Spruce bark 0.5 mm	Steam	850	1	80,2	2,2	*
529	Spruce bark 1 mm	Steam	850	1	79,8	2	O
530	Spruce bark 2 mm	Steam	850	1	78,4	2,1	O - (*)
407	Spruce bark A	Steam	800	1	78,9	3,2	O
405	Spruce bark A	Steam	850	1	79,9	5,6	O
406	Spruce bark A	Steam	900	1	79,1	4	O
409	Spruce bark A	Steam	850	5	79,5	3,2	O - *
411	Spruce bark A	Steam	850	10	75,2	4,3	*
412	Spruce bark A	Steam	800	10	79,5	3,1	O- (*) some unreacted particles
428	Spruce bark A	Steam	800	5	76,5	3,9	molten particles
429	Spruce bark A	Steam	900	5	76,9	3,5	some molten particles
430	Spruce bark A	Steam	900	10	80,7	3,7	*
515	Spruce bark A	CO_2	850	5	77,0	3	*
516	Spruce bark A	H_2O+H_2	850	5	78,6	3,1	*
526	Spruce bark A	$H_2O+CO_2+O_2+N_2$	850	1	76,1	2,9	O
414	Spruce bark B	Steam	850	1	77,3	2,4	molten particles

431	Spruce bark B	Steam	800	1	79,4	2,6	O
432	Spruce bark B	Steam	900	1	82,6	3,3	O
435	Spruce bark B	Steam	850	5	78,8	2,2	molten particles
436	Spruce bark B	Steam	900	5	77,3	3,2	O
437	Spruce bark B	Steam	800	10	77,6	3,3	*
438	Spruce bark B	Steam	850	10	76,9	3,1	*
439	Spruce bark B	Steam	900	10	75,9	3,8	*
440	Spruce bark B	Steam	800	5	76,6	2,7	O
517	Spruce bark B	CO_2	850	1	77,4	2,4	*, molten particles
518	Spruce bark B	H_2O+H_2	850	1	79,9	2,2	molten particles
418	Spruce bark C	Steam	850	1	79,9	3	O
419	Spruce bark C	Steam	900	1	80,7	3,1	molten particles
422	Spruce bark C	Steam	850	5	76,6	3,4	*, molten particles
425	Spruce bark C	Steam	850	10	77,4	3,4	**
441	Spruce bark C	Steam	800	1	77,8	2,9	O
442	Spruce bark C	Steam	800	5	76,3	2,9	O
444	Spruce bark C	Steam	900	5	76,9	3,4	molten particles
446	Spruce bark C	Steam	900	10	79,9	3,4	*
447	Spruce bark C	Steam	800	10	79,8	3,8	**
490	Spruce bark C	H_2O+H_2	850	1	79,1	2,1	O
491	Spruce bark C	CO_2	850	1	77,6	3,3	*, molten particles
519	Spruce bark C	CO_2	850	10	73,7	3,2	*
520	Spruce bark C	H_2O+H_2	850	10	77,5	2	O
541	Spruce bark A	Steam+CO_2	850	5	77,7	3,6	*
542	Spruce bark A	Steam+CO_2	850	10	76,4	3,5	**
543	Spruce bark A	Steam+CO_2	850	10	76,4	3,7	* - **
554	Spruce bark A	Steam	725	1	77,9	9,8	O unreacted
555	Spruce bark A	Steam	750	1	80,2	3,2	O unreacted
556	Spruce bark A	Steam	800	1	79,6	2,8	O
558	Spruce bark A	Steam	825	1	80,2	2,8	O, molten particles
557	Spruce bark A	Steam	850	1	78,3	2,8	O
559	Spruce bark A	Steam	900	1	78,9	2,8	O
560	Spruce bark A	Steam	950	1	80,9	2,8	O, molten particles
561	Spruce bark A	Steam	725	5	79,2	4,5	O - *
562	Spruce bark A	Steam	750	5	77,8	2,4	O
563	Spruce bark A	Steam	775	5	76,6	3	O
564	Spruce bark A	Steam	800	5	75,7	2,6	O, molten particles
566	Spruce bark A	Steam	900	5	78,1	3,1	O, molten particles
567	Spruce bark A	Steam	700	1	80,5	7,8	O unreacted, no ash
568	Spruce bark A	Steam	700	5	76,7	6,7	O unreacted
569	Spruce bark A	Steam	700	10	77,1	5,7	unreacted, molten particles
570	Spruce bark A	Steam	750	10	76,1	2,8	**
571	Spruce bark A	Steam	800	10	76,4	3	**
572	Spruce bark A	Steam	775	10	75,6	2,8	*-**
574	Spruce bark A	H_2O+H_2	800	5	76,2	7,4	O unreacted, no ash
575	Spruce bark A	H_2O+H_2	850	5	77,7	2,7	O some particles unreacted
576	Spruce bark A	CO_2+CO	850	5	74,8	3,2	o-*, (*** molten particles)
577	Spruce bark A	H_2O+H_2	850	5	78,1	2,5	O
578	Spruce bark A	H_2O+H_2	850	5	76,8	2,7	O
579	Spruce bark A	H_2O+H_2	850	5	77,4	2,6	O
580	Spruce bark A	$H_2O+H_2+CO_2+CO$	800	5	75,7	11	O unreacted
581	Spruce bark A	$H_2O+H_2+CO_2+CO$	850	5	76,7	4,2	unreacted, ash coming out
582	Spruce bark A	$H_2O+H_2+CO_2+CO$	875	5	76,9	3,1	***, unreacted (molten particles)
583	Spruce bark A	$H_2O+H_2+CO_2+CO$	900	5	75,2	2,7	* - **
584	Spruce bark A	$H_2O+H_2+CO_2+CO$	900	5	77,1	2,9	* - ***
585	Spruce bark A	$H_2O+H_2+CO_2+CO$	875	10	76,1	4	O unreacted, ash coming out, molten particles

586	Spruce bark A	$H_2O+H_2+CO_2+CO$	875	1	77,1	2,6	O - *
596	Spruce bark A	Steam	850	10	75,2	1,9	*, molten particles
597	Spruce bark A	Steam	900	10	79,8	2,8	*, molten particles
598	Spruce bark A	Steam	850	10	75,9	2,7	O, molten particles
599	Spruce bark A	H_2O+H_2	850	1	75,9	2,2	O, molten particles
600	Spruce bark A	H_2O+H_2	850	5	77,7	2,8	O, molten particles
601	Spruce bark A	H_2O+H_2	850	10	77,9	2,9	O, molten particles
602	Spruce bark A	CO_2	800	1	76,9	3,6	*
603	Spruce bark A	CO_2	800	5	75,2	3,8	*, molten particles
604	Spruce bark A	CO_2	800	10	72,4	4,5	* - **, molten particles
605	Spruce bark A	CO_2	850	1	77,1	3,2	**, molten particles
608	Spruce bark A	Steam	850	2	78,4	2,8	*
609	Spruce bark A	Steam	850	2	77,3	3,1	O
610	Spruce bark A	CO_2	850	1	79,8	2,4	*
611	Spruce bark A	CO_2	850	5	77,9	3,2	*
612	Spruce bark A	CO_2	850	10	75,0	3,6	* - **
613	Spruce bark A	CO_2	850	1	78,8	2,9	*
614	Spruce bark A	CO_2+CO	850	7,2	71,5	7,6	O and unreacted
615	Spruce bark A	H_2O+H_2	850	7,2	79,7	2,6	*
629	Spruce bark A	CO_2+CO	850	6,3	73,7	4,4	O - (*), unreacted
630	Spruce bark A	CO_2+CO	850	5,6	75,0	2,8	*, molten particles
631	Spruce bark A	CO_2+CO	850	5,6	74,2	3,1	*, molten particles
632	Spruce bark A	CO_2+CO	850	6,3	74,1	3	*
635	Spruce bark A	H_2O+H_2	800	5	77,8	2,7	O - (*) and a little unreacted and molten particles
636	Spruce bark A	H_2O+H_2	800	5	76,1	4,3	O and unreacted
638	Spruce bark A	H_2O+H_2	800	5	77,1	7,7	unreacted, no ash
640	Spruce bark A	Steam	850	20	79,4	2,8	***
641	Spruce bark A	CO_2	850	15	72,9	3,8	***(very little ash)
642	Spruce bark A	CO_2	850	20	75,5	4	***(very little ash)
643	Spruce bark A	CO_2	900	1	80,2	2,9	***(very little ash)
644	Spruce bark A	CO_2	800	1	76,9	3,3	O molten particles
645	Spruce bark A	CO_2	750	1	73,4	10	O unreacted ash coming out
646	Spruce bark A	CO_2	725	1	74,9	14	O unreacted, no ash
647	Spruce bark A	$H_2O+H_2+CO_2+CO$	875	15	70,8	6,3	O unreacted, glossy char (tar char)
648	Spruce bark A	$H_2O+H_2+CO_2+CO$	875	20	75,8	8,7	O unreacted no ash
649	Spruce bark A	H_2O	950	1	83,8	2,8	O
650	Spruce bark A	H_2O	1000	1	82,2	2,8	O
654	Spruce bark A	CO_2+CO	850	5	76,6	4,1	O molten particles
655	Spruce bark A	H_2O+H_2	850	5	78,4	2,9	
656	Spruce bark A	CO_2+CO	850	5	78,1	3,3	*+molten or crystals
657	Spruce bark A	CO_2+CO	850	5	74,7	3,1	*
658	Spruce bark A	$H_2O+H_2+CO_2+CO$	850	1	78,2	2,7	O molten particles
659	Spruce bark A	$H_2O+H_2+CO_2+CO$	850	10	76,6	7,8	O unreacted, no ash
664	Spruce bark A	CO_2+CO	800	5	74,4	9,3	O and unreacted and molten particles
665	Spruce bark A	CO_2+CO	800	5	74,1	13	O unreacted and coming out
666	Spruce bark A	CO_2+CO	800	5	74,1	16	O unreacted no ash
668	Spruce bark A	$H_2O+H_2+CO_2+CO$	850	15	77,0	5,8	O unreacted no ash
669	Spruce bark A	$H_2O+H_2+CO_2+CO$	800	1	78,9	4,8	O unreacted ash covered char
670	Spruce bark A	$H_2O+H_2+CO_2+CO$	800	10	78,5	15	O unreacted, no ash
565	Spruce bark A	Steam	850	5	77,0	2,8	O
521	Spruce bark timber (dry) Porvoo timber	Steam	850	1	79,3	2	O

524	Spruce bark timber (dry) Porvoo timber	Steam	850	5	75,7	1,9	*
525	Spruce bark timber (dry) Porvoo timber	Steam	850	10	74,9	2,4	***
617	Spruce bark Kajaani	Steam	850	5	77,1	2,4	O molten particles
616	Spruce bark Rauma	Steam	850	5	77,6	2,8	*
536	Stump chips and spruce bark 50 : 50 by weight	Steam	850	1	80,7	1,9	O
534	Stump chips and Spruce bark about 50 : 50	Steam	850	1	81,1	1,7	O molten particles
537	Stump chips and spruce bark mixed 50 : 50 by weight	Steam	850	5	80,2	2,7	* molten particles
484	Stump chips C, Middle-Finland	Steam	850	1	86,9	1,7	O and unreacted and molten particles
486	Stump chips C, Middle-Finland	Steam	850	5	81,4	1,9	*
487	Stump chips C, Middle-Finland	CO_2	850	5	82,3	1,5	*
489	Stump chips C, Middle-Finland	H_2O+H_2	850	5	82,3	7,9	O unreacted, no ash, glossy char
623	Stump chips Middle Finland A	$H_2O+H_2+CO_2+CO$	875	1	80,8	4,8	O unreacted ash on surfaces
347	Birch bark	Steam	750	1	80,7	1,9	O - *
382	Bark mixture Varkaus UCG 08 23C	Steam	850	5		3,2	**
62	Aspen bark Iisalmi	CO_2+CO	850	5		3,1	**
61	Aspen bark Iisalmi	CO_2	850	5		3,6	**
63	Aspen bark Iisalmi	CO_2+CO	850	5		2,9	**
65	Pine bark Kajaani	CO_2	850	5		1,9	*
59	Debris 1 < 4mm	Steam	850	5		4,8	*
60	Debris 2 < 4mm	Steam	850	5		4,4	*
64	Pine bark, Kajaani	CO_2+CO	850	5		1,9	*
66	Aspen bark Iisalmi	Steam	850	10		2,6	***
67	Aspen bark Iisalmi	Steam	800	5		2,9	**
68	Aspen bark Iisalmi	Steam	875	5		2,4	**
69	Pine bark Kajaani	$H_2O+H_2+CO_2+CO$	875	5		2,2	* unreacted
70	Birch bark Iisalmi	$H_2O+H_2+CO_2+CO$	875	5		1,5	O unreacted, ash coming up
71	Spruce bark Kajaani	$H_2O+H_2+CO_2+CO$	850	5		3,8	O unreacted, ash coming up
72	Pine bark Kajaani	$H_2O+H_2+CO_2+CO$	875	5		2,8	O unreacted, ash coming up
73	Pine bark Kajaani	Steam	800	5		1,5	O-(*)
74	Pine bark Kajaani	Steam	750	5		1,6	O-*
75	Pine bark Kajaani	Steam	850	5		1,5	O, molten particles
76	Birch bark	Steam	800	5		1	*
77	Spruce bark A	$H_2O+H_2+CO_2+CO$	850	5		4,1	O unreacted, ash coming up
79	Small wood chip, Varkaus	Steam	850	5		0,6	*
80	Small wood chip, Varkaus	Steam	850	10		0,7	**

Time 1 = 5.03.08 klo15:00
Time 2 = 19.03.08 klo16:00
Time 3 = 20.03.08 klo16:00

APPENDIX II

Variation in fuel reactivity and ash characteristics of biomass feedstocks for large scale gasification

Proc. 17th European Biomass Conference and
Exhibition. 29 June – 3 July 2009, Hamburg,
Germany, VP2.2.19. Florence: ETA-Renewable
Energies. Pp. 952–955.
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VARIATION IN FUEL REACTIVITY AND ASH CHARACTERISTICS OF BIOMASS FEEDSTOCKS FOR LARGE-SCALE GASIFICATION

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ABSTRACT:

Reactivity and ash sintering of biomass fuel are important parameters to be considered for large-scale biomass gasification process. The reactivity affects the extent and time required for the completion of fuel conversion, and ash sintering can lead towards the blockage problems in the gasifier. This task was about studying the effect of temperature, pressure and gasifying medium on the variation of fuel reactivity and ash sintering for different types of biomass feedstock relevant to large-scale biomass gasification. The variables in selecting the same and different types of sample material (biomass feedstock) were the location (e.g. various parts of Finland), contact with water (transportation, storage time, debarking etc.). The samples were different barks (spruce, pine, birch and aspen), forest residue and stump chips. The tests were performed in the thermogravimetric apparatus. The conditions were selected mainly to aim at oxygen gasification. The tests were carried out in the temperature and pressure ranges of 800°C - 900°C and 1 bar-10 bar, respectively. The range of particle size was 0.5 - 1.5mm. Gasifying mediums were steam and carbon dioxide. The inhibition effect was characterised by adding H_2 to steam, carbon monoxide to CO_2 and a gas mixture containing all the gas components. It was observed that there was a significant variation of reactivities and ash sintering among different types of biomass in the presence and the absence of the product gases. Inside one biomass type the variation in the reactivity was small, and no clear differences in the ash sintering was found. The contact with water was observed to have a weakening effect on ash sintering, most probably due to the leaching of low melting alkaline compounds, and no difference in reactivity was found.

Keywords: gasification, biomass, feedstock, reactivity, ashes, sintering

1 INTRODUCTION

Gasification reactivity and ash sintering of biomass fuels are two important characteristics which can delimit the operational conditions in a biomass gasification process. The extent of the carbon conversion and the time taken for the complete conversion is based on the reactivity of the char residue after the pyrolysis stage. Ash sintering can cause blockages and agglomerates in the gasifier. In earlier research, it was observed that these gasification characteristics can vary to a great extent between various biomass species [1, 2, 3, 4]. For them, the variation of the reactivity determined as the instantaneous reaction rate was measured to be in the range of 7 to 400 %/min at 95% ash-free fuel conversion (equivalent approximately 75 % ash-free char conversion) [5]. The sintering intensity of ashes varied from zero to complete melting. The ash sintering was intensified in the pressurised gasification compared to the gasification in the normal pressure; the conditions were the same otherwise [6].

For large scale gasification processes based on fluidised bed technology, as planned to build in Finland [7, 8], information is needed about the above-mentioned characteristics also, how they can vary inside a large amount of a feedstock. The conventional fuel characteristics of a biomass fuel (heating value, ash content etc.) are affected by transportation and storage [9]. During these operations biomass can be in contact with water which may cause leaching or extraction of chemical substances present in biomass.

The purpose of this work was to create information on the characteristics needed for designing the operational control of the process, taking also into account that in practice the feedstock is often a mixture of various biomasses. The basic data is also helpful in modelling of a gasification process. The optimum conditions for a fluidised bed gasification process are those on which feedstock have relatively high reactivity and no ash sintering tendency in the gasifier.

2 EXPERIMENTAL

Sample of biomass fuels (types) were collected from various locations in Finland as shown in Fig. 1. There was also a sample from Latvia. The tested biomass fuel samples were different barks (spruce, aspen, birch and pine), forest residue and stump chips.

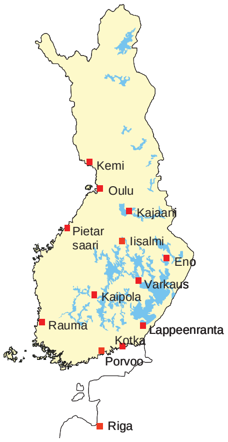

Figure 1: The sample collecting locations.

The tests for the reactivity (char) and ash sintering were performed in the pressurised thermogravimetric apparatus, as described earlier [5].

- Temperature: 800°C - 900°C
- Pressure: 1 bar, 5 bar and 10 bar
- Gasifying mediums: 100 vol-% steam; 70 vol-% steam with 30 vol-% H_2; 100 vol-% CO_2; 70 vol-% CO_2 with 30 vol-% CO and a gas mixture containing all the gas components.

The results of the reactivity measurements are given in the form of the instantaneous rate of reaction. The instantaneous rate was derived from the weight-time curve by dividing the rate of mass change of the sample by the residual ash-free mass (%/min). Thus, it describes the reactivity of the char reacted to a certain conversion degree.

After the reactivity measurement, the residual ash was inspected under a 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 and because of the larger size compared with the powdery ash particles since they are fused together.

3 RESULTS

The effect of the temperature on the reactivity and ash sintering of biomass fuel is so that by increasing temperature, reactivity also increases but it should not be too high to avoid the ash sintering. If the reactivity of the fuel is high, comparatively it takes lesser time for the completion of the char carbon conversion. The effect of the temperature on the fuel reactivity is shown in Fig 2. It was observed that at atmospheric pressure, no ash sintering was found till 900°C. But the effect of the pressure on the fuel reactivity was not very clear (Fig. 2 lower graph). Generally, the reactivity increases by increasing pressure but in some cases the reactivity at higher pressure can be lesser than that of at lower pressure. This is related with the behaviour of the ash forming material which also catalyses the char gasification reactions. Earlier it has been noticed that the probability of ash sintering/melting becomes more with the increase in pressure even at the same temperature [5].

The gasifying medium also affects on reactivity and ash sintering. For example, the presence of carbon dioxide in the process can cause formation of carbonates leading to a carbonate melt [4]. Similarly, it was observed that with steam as a gasifying medium, fuel reactivity was usually higher than compared to that of with carbon dioxide (CO_2).

The reactivities of different barks were in the decreasing order as follows: aspen > birch with the white part > spruce > pine bark. Measured at 850°C and in 1 bar steam, the instantaneous reaction rates were for aspen 115 %/min, birch bark with white part 84 %/min, spruce bark 72 %/min and pine bark 37 %/min at 90% conversion (Fig. 3).

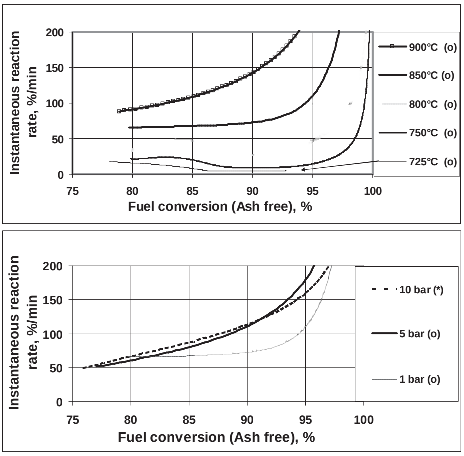

Figure 2: Steam gasification reactivity of spruce bark at different temperatures in 1 bar steam and (upper graph), and in different pressures (lower graph) at 850°C; (o): no ash sintering.

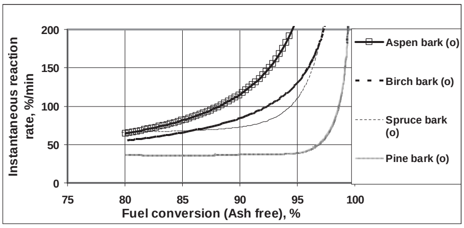

Figure 3: Steam gasification reactivity of different barks at 850°C and in 1 bar steam

The difference between the reactivities of bark mixture, forest residue and stump chips can be seen from Fig. 4 measured at 850°C and in 5 bar steam. The reactivities of crushed bark mixture, forest residue and stump chips are of the rates of 77, 65 %/min and 43 %/min, respectively.

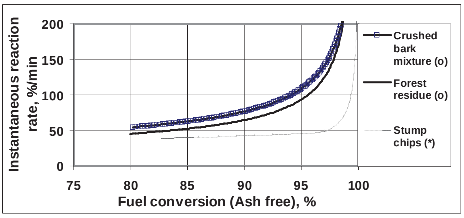

Figure 4: Steam gasification reactivity of different biomass types at 850°C and in 5 bar steam, (o) : no ash sintering, (*) weak sintering.

The reactivity and ash sintering of the same biomass collected from different locations in Finland is seen in Fig. 5 showing spruce barks collected from various locations in Finland. The instantaneous reactions rates were relatively close each other.

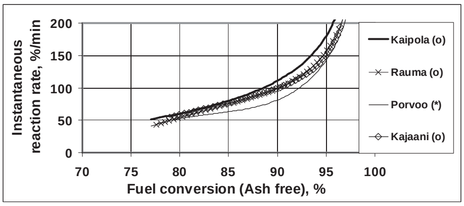

Figure 5: Steam gasification reactivity of spruce bark collected from different locations (see Fig. 1) at 850°C and in 5 bar steam, (o) : no ash sintering, (*) weak sintering.

Similarly, difference in reactivities for pine barks and forest residues can be seen from Figs 6 and 7, respectively. The scattering of the reactivities were somewhat higher in pine barks and forest residues as compared with spruce barks. Reasons for the scattering can be found in the observations that thick pine bark reacts significantly slower in steam than thin pine bark [10], and forest residues are not homogenous material consisting of barks, twigs and needles.

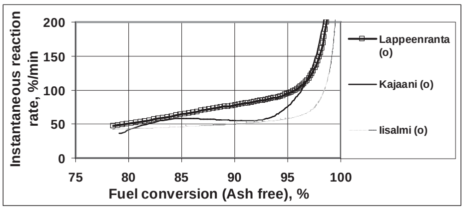

Figure 6: Steam gasification reactivity of pine bark collected from different locations in Finland (Fig. 1) at 850°C and in 5 bar steam, (o): no ash sintering

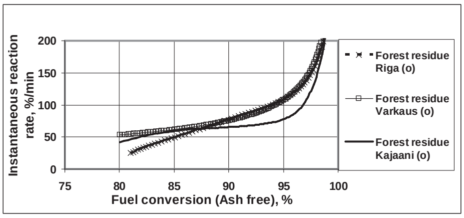

Figure 7: Steam gasification reactivity of forest residue collected from different locations in Finland (Fig. 1) and from Riga Latvia Pine bark at 850°C and 5 bar steam (o): no ash sintering

The reason for the higher reactivity of the thin part of pine bark compared to the thicker bark was probably that it contained more catalytic active alkaline metals, which in the thicker part (older) have been leached out.

The transportation, storage conditions and debarking method of wood/bark may also affect on ash sintering tendency. During these processes, it remains in contact with water for certain period of time which can cause leaching or extraction of ash forming material, especially water soluble alkaline metal compounds. These metals have direct effect on ash sintering. This is shown by tests performed with spruce barks (Fig. 8). The bark taken from wood by dry debarking showed higher ash sintering than the one by wet debarking. The sintering was weak or none if it was in contact with water.

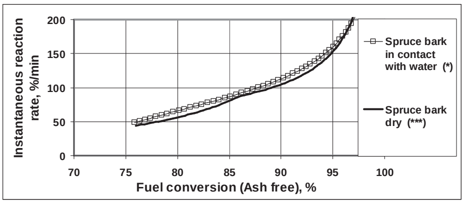

Figure 8: Spruce barks (treated differently) at 850°C and 10 bar steam

During the tests carried out on thermobalance, samples of three different particle sizes i.e. 0.5 mm, 1 mm and 1.5mm were used. But the reactivity of fuel remains almost same in this range of particle sizes. This particle size range was measured for comparative testing only. Large particles or pieces of biomass fuel have more effect on the reactivity as observed earlier [11].

Inhibition effect of product gases was studied here separately and then with a mixture of product gases. The tests performed by adding separately hydrogen to steam (Fig. 9) and and carbon monoxide to carbon dioxide (Fig. 10) showed clearly that the adding of these gases clearly decreased the reactivity. Similarly, it was also observed that the product gases in the mixture (CO +CO_2 + H_2O + H_2) inhibited the reactivity. The composition of product gas can be different in different sections of gasifier and therefore this inhibition effect of product gas varies within the gasifier, forexample at the bottom, in the middle and at the top.

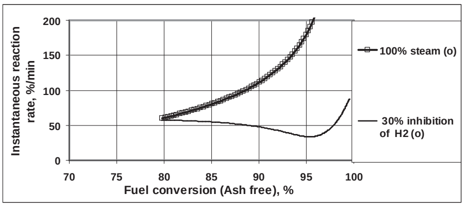

Figure 9: Inhibition effect of H_2 in steam gasification of spruce bark at 850°C. The steam pressure was 3.5 bar and the hydrogen pressure was 1.5 bar (5 bar total)

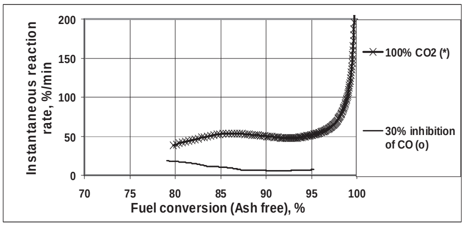

Figure 10: Inhibition effect of CO in CO_2 gasification of spruce bark at 850°C. The CO_2 pressure was 3.5 bar and the CO pressure was 1.5 bar (5 bar total).

Different barks were tested on same conditions of temperature and pressure in the presence of the product gases in the gas mixture of steam, CO_2, H_2, CO and N_2 (the nitrogen was used for dilution). Clear differences were found in reactivities but there was no difference in ash sintering as shown in Fig. 11.

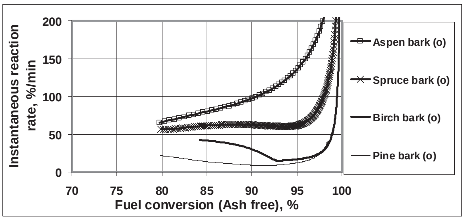

Figure 11: Gasification reactivity and ash sintering of various barks in the gas mixture of 0.3 bar steam, 0.2 bar H_2, 0.25 bar CO_2, 0.15 bar CO and 0.1 bar N_2 at 875°C.

4 CONCLUSIONS

For large scale gasification processes based on fluidised bed technology, information is needed about the gasification reactivity and ash sintering among biomass types, and also inside the same biomass type. From the results of this study following conlusions can be drawn:

- There was a significant variation of reactivities and ash sintering among different types of biomass in the presence and the absence of the product gases.
- Inside one biomass type the variation in the reactivity was small, and no clear differences in the ash sintering was found. The reason for the variation observed can be due to the differences in the reactivities in thin and thick barks (pine) and in the inhomogeneity of the feedstock (forest residue).
- The contact with water was observed to have a weakening effect on ash sintering, most probably due to the leaching of low melting alkaline compounds. No difference in reactivity was found.

5 ACKNOWLEDGEMENTS

Financial support provided by BioRefine programme of Tekes (The Finnish Funding Agency for Technology and Innovation) as well as companies Carbona/Andritz, Foster Wheeler Energia, Metso, Neste Oil, Stora Enso, UPM and Vapo are gratefully acknowledged.

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APPENDIX III

The effect of biomass feedstock type and process parameters on achieving the total carbon conversion in the large scale fluidized bed gasification of biomass

In: Environmental Progress & Sustainable Energy.
28(3), pp. 355–359. doi:10.1002/ep.10396

The Effect of Biomass Feedstock Type and Process Parameters on Achieving the Total Carbon Conversion in the Large Scale Fluidized Bed Gasification of Biomass

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One option for the production of liquid biofuel in Finland is based on fluidized bed gasification of biomass and Fischer-Tropsch synthesis process. The total carbon conversion achieved in the gasifier, operating at temperatures below 1000°C, depends mainly on the reactivity of solid char residue. The reactivity of the char residue is affected by temperature, partial pressures of the reactants H_2O *and* CO_2 *and product gas components (*H_2 *and CO), which are inhibiting the reactivity. In this reactivity, catalytic active substances, alkaline and earth-alkaline metal compounds play a significant role. Other elements like silicon can react with the metals, leading to losses in the catalytic activity. These elements are naturally occurring in the biomass, and their behavior is individually dependent on the biomass type. The carbon conversion can be improved by increasing temperature, but it should not be too high to avoid ash sintering. By increasing the pressure, the reactivity increases normally, but for biomass it sometimes has no effect or it is even reduced. It was also observed that during the process of debarking and storage of biomass, it remains in contact with water, which can reduce the amount of some alkaline and earth alkaline metals because of leaching that can further affect reactivity and ash sintering. We studied the effects of the above-mentioned factors on various barks, like spruce, pine, birch, aspen, which are the most potential biomass feedstock to be used in the large-scale gasification in Finland. The measurements were carried out in the pressurized thermobalance in the conditions relevant for the pressurized oxygen gasification. Thus, the total pressure range was up to 20 bar, and the partial pressures of the reactants and the product gas components varied respectively. The parameters measured will be used for the development of the gasifier model.* © 2009 American Institute of Chemical Engineers Environ Prog, 28: 355–359, 2009

Keywords: biomass, fluidized-bed gasification, ash, sintering, reactivity

INTRODUCTION

One option for the production of liquid biofuel in Finland is based on fluidized bed gasification of biomass and Fischer-Tropsch synthesis process [1, 2].

Figure 1. Classification of the ash residues with increasing sintering, as seen under microscope [14]. [Color figure can be viewed in the online issue, which is available at **www.interscience.wiley.com.**]

In this type of large scale process, information is needed about how the quality of the biomass feedstock selected for the gasification changes as a function of time. Here, the quality stands for gasification reactivity and ash behavior properties (sintering). In earlier research, it has been observed that these gasification characteristics can vary to a great extent between various biomass species [3–6]. There is no information available, however, about how these gasification characteristics vary inside a biomass selected as a feedstock to the large-scale biomass gasification process. According to the published studies [7], general fuel characteristics of biomass feedstock can be affected by harvesting time, biomass growth locations, transportation, storage, debarking processes, *etc*. During theses steps, biomass can remain in contact with water, which may cause leaching or extraction of the minerals present in biomass. These minerals consisting of mainly alkaline metals are of special importance in their catalytic properties in the gasification and their ash sintering behavior.

The total carbon conversion achieved in the gasifier, operating at temperatures below 1000°C, depends for the most part on the reactivity of solid char residue [8]. The reactivity of the char residue is affected by temperature, partial pressures of the reactants H_2O and CO_2 and product gas components (CO and H_2), which inhibit the reactivity. In this reactivity, catalytic active substances, alkaline and earth-alkaline metal compounds play a significant role [9–12]. Other elements like silicon can react with the metals, leading to losses in the catalytic activity [9]. These elements are naturally occurring in the biomass, and their behavior is individually dependent on the biomass type. The carbon conversion can be improved by increasing the temperature, but if it is too high ash, sintering can become significant and create problems in the gasifier operation. By increasing total pressure of the process, biomass reactivity increases normally, but sometimes it has no effect or it is even reduced, which can be a result of the behavior of the catalytic active material during the gasification.

In this work, the gasification reactivity and ash sintering was studied on laboratory level to reveal the effects of the above-mentioned factors on the gasification characteristics of various barks, which have the most potential as biomass feedstock to be used in the large-scale gasification in Finland. The characteristic differences in forest biomass harvested at different sites are reported earlier in [13]. The measurements were carried out in the pressurized thermobalance in the conditions relevant for the pressurized oxygen gasification. Thus, the total pressure range was up to 20 bar, and the partial pressures of the reactants and the product gas components varied respectively. The parameters measured will be used for the development of gasifier model in the continuation of this work.

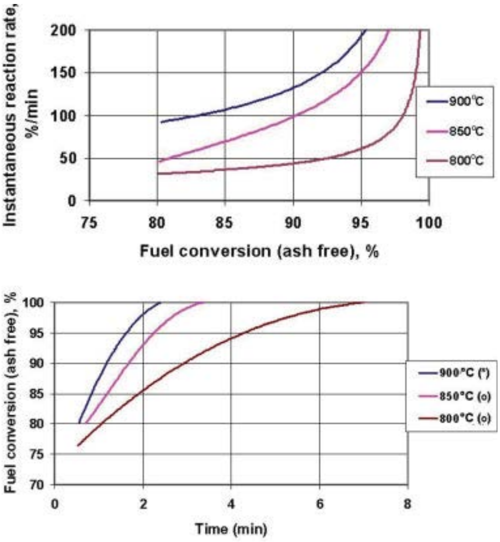


Figure 2. Steam gasification reactivity of spruce bark at various temperatures and in 5-bar pressure of steam: The instantaneous reaction rate as a function of fuel conversion (upper); the fuel conversion as a function of time (lower), respectively. The * and o indicate the ash sintering degree (see Figure 1). [Color figure can be viewed in the online issue, which is available at **www.interscience.wiley.com.**]

EXPERIMENTAL PROCEDURES

The measurements were carried out in the thermobalance method which is described in Moilanen [14]. The test conditions were selected to correspond to the pressurized oxygen gasification, so that especially the partial pressures varied respectively. Temperature level in the tests was below 1000°C. The partial pressures in steam gasification varied for hydrogen between 0.2 and 3 bar and for steam between 0.3 and 10 bar. In carbon dioxide gasification, the partial pressures varied for carbon monoxide and carbon dioxide, respectively. The biomass fuels tested were various barks like spruce, pine, birch and aspen.

The results of the reactivity measurements are given in form of the instantaneous rate of reaction *vs.*

fuel conversion. The instantaneous rate was derived from the weight-time curve by dividing the rate of mass change of the sample by the residual ash-free mass. Thus, it describes the reactivity of a char having already reacted to a certain conversion value. After the reactivity measured in thermobalance, the residual ash was inspected under a stereomicroscope to detect any sintering of ash particles or molten phases [14]. A molten phase is detected as distinct spherical particles of shiny or glassy appearance and, because of the larger size compared with the powdery ash particles, because they are fused together. The following classification symbols were used for the sintering degree (see Figure 1):

- Non-sintered ash residue, classification: o (no stars)
- Partly sintered, *i.e.*, signs of melting were found in the ash sample (two different classification degrees in this group), classification: *, ** (1–2 stars).
- Totally sintered ash, *i.e.*, the ash sample was completely or nearly completely molten, classification: *** (3 stars).

RESULTS

The most obvious parameter affecting the reactivity and thus the carbon conversion is the temperature. In Figure 2, the effect of temperature for the gasification reactivity of spruce bark is shown as a function of temperature. The gasification reactivity, *i.e.*, the instantaneous reaction rate measured in 5-bar steam varied for spruce bark from 45%/min at 800°C to 130%/min at 900°C. At 850°C, the rate was 100%/min. The values were taken at 90% fuel conversion, which corresponds the char conversion value of 45 to 50%. The times needed to achieve 100% conversion in the thermobalance were, respectively, 2.4, 3.4 and 7 min at each temperature, as shown in the lower graph of Figure 2. At 900°C, the ash residue of spruce bark had small signs of sintering. Figure 3 illustrates the effect of pressure on gasification reactivity determined at 850°C. The pressure varied between 1 and 10 bar of steam, and the rates were quite close to each other, varying (at 90% fuel conversion) from 80 and 108%/min. However, the conversion behavior (*i.e.*, the rate *vs.* conversion) showed no clear dependence on pressure.

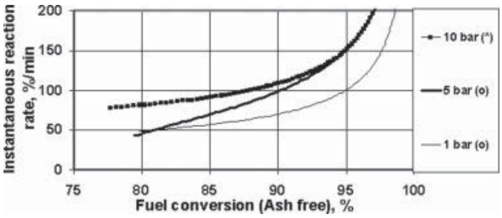
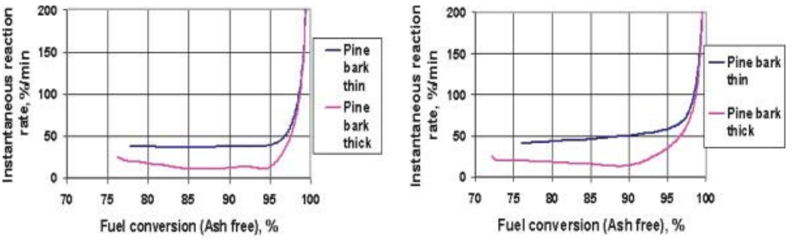


Figure 3. The steam gasification reactivity of spruce bark in various steam pressures at 850°C.

In general, the gasification reaction rates measured for the biomass fuels in this study at 90% fuel conversion and at 850°C and in the pressure range of 1 and 10 bar steam showed the lowest values for pine bark (15%/min) and the highest values for spruce bark (120%/min). In carbon dioxide gasification, the rates were the same or lower. Thus, the steam gasification may control the overall reactivity. This corresponds to the results measured earlier [14, 15]. In addition, different parts of the same biomass may have differences in the reactivity. For pine bark, the thicker bark parts were considerably less reactive than the thin parts (see Figure 4). This can be explained by noting that in the thick barks (representing older age of a pine tree), more leaching took place to remove the catalytic active substances. Another example of water contact was observed for the spruce bark, which had strong ash sintering (***) when it was debarked without water at 10 bar pressure compared with the spruce bark, which was debarked in a wet process resulting in only weak sintering.

The carbon conversion is also influenced by the product gas component because they inhibit the reactivity. In earlier research it has been observed that the product gas inhibits the gasification reactions in various ways for biomasses [16]. The product gas inhibition can be seen when hydrogen is added to steam and carbon monoxide to carbon dioxide gas (see Figure 5). Here, reactivity of spruce bark reduces considerably by adding hydrogen to steam and carbon monoxide to carbon dioxide. By increasing



1 bar

5 bar

Figure 4. Steam gasification reactivity of thin and thick pine bark in 1- and 5-bar steam pressures at 850°C. [Color figure can be viewed in the online issue, which is available at **www.interscience.wiley.com.**]

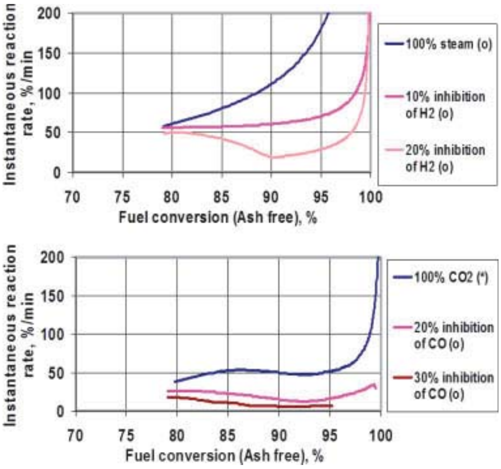


Figure 5. Inhibition effect on gasification spruce bark by adding H_2 into steam, and CO to CO_2 at 850°C and 5-bar pressure (total), with increasing concentrations of H_2 in steam and CO in CO_2 (lower). The * and o indicate ash sintering degree (see Figure 1). [Color figure can be viewed in the online issue, which is available at **www.interscience.wiley.com.**]

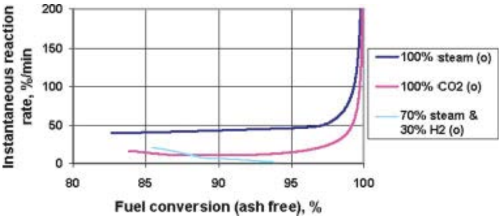


Figure 6. Effect of hydrogen inhibition on steam gasification of stump chips at 850°C and at 5-bar total pressure compared with steam and CO_2 gasification. The * and o indicate ash sintering degree (see Figure 1). [Color figure can be viewed in the online issue, which is available at **www.interscience.wiley.com.**]

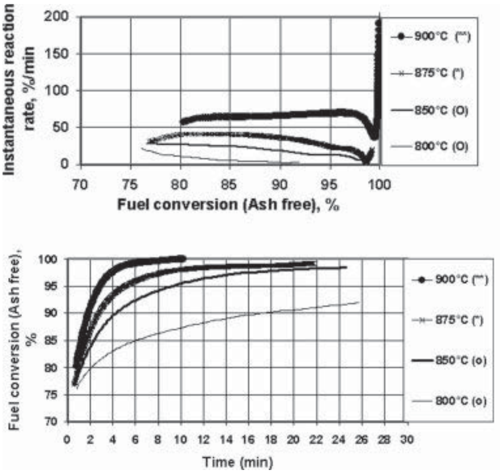


Figure 7. The gasification reactivity of spruce bark in the gas mixture containing 1.5 bar steam, 1 bar H_2, 1.25 bar CO_2, 0.75 bar CO and 0.5 bar N_2 (total pressure 5 bar) at various temperatures. The instantaneous reaction rate as a function of fuel conversion (upper); the fuel conversion as a function of time (lower), respectively. *, ** and o indicates the ash sintering degree (see Figure 1).

the concentration of hydrogen and carbon monoxide into steam and carbon dioxide, respectively, the inhibition effect increases and, as a result of that reactivity, decreases. Figure 6 illustrates the situation for stump chips, where it reduced the reactivity significantly. The reaction was almost stopped at relatively low conversion value.

The example of the reactivity in the gas mixture including all the gas components (except methane), which may exist in a gasification product gas is shown in Figure 7 for spruce bark. The rate is lower than in 100% steam (see Figure 2), but the raise in temperature increased the reactivity. At the lowest temperature measured (800°C), it took 25 min to reach 93% fuel conversion. Increase in temperature shortened the time significantly to less than 10 min. At the higher temperature signs of ash sintering were detected.

CONCLUSIONS

The carbon conversion in the biomass gasification is affected by the following factors related to the char gasification reactivity:

- The reactivity of biomass char increases with the temperature, which is obvious.
- The reactivity of biomass varies with the increase in pressure; pressure increase does not necessarily mean increase in reactivity. The lowest reaction rate, at 850°C, was 15%/min (for pine bark, thick part) and 120%/min for spruce bark.
- In general, ash sintering ranged from none to weak; in some cases the sintering was stronger at high pressure. Biomasses studied here were usually in contact with waters, leading to leaching of alkali metals, which is generally known to be the main reason for low ash melting.
- The reactivity of different parts of biomass may vary, because thin pine bark had more than five times higher reactivity than thick pine bark (lower than spruce bark)
- The reactivity in the gas mixture, including all the gas components, was lower than in 100% steam. Increase in temperature increased the reactivity significantly but in the higher temperatures, ash sintering was detected.

ACKNOWLEDGMENTS

Financial support provided by BioRefine Programme of Tekes (The Finnish Funding Agency for Technology and Innovation), Carbona, Foster Wheeler Energia, Metso Power, Neste Oil, Stora Enso, UPM-Kymmene and Vapo are gratefully acknowledged.

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APPENDIX IV

Modelling of char gasification reactivity for biomass in a fluidised bed gasifier

Master’s Thesis, Aalto University, 2009.
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HELSINKI UNIVERSITY OF TECHNOLOGY
Faculty of Chemistry and Materials Sciences
Degree Programme of Chemical Technology

Muhammad Nasrullah

MODELLING OF CHAR GASIFICATION REACTIVITY FOR BIOMASS IN A FLUIDIZED BED GASIFIER

Master's thesis for the degree of Master of Science in Technology submitted for inspection, Espoo, 14 December, 2009.

Supervisor	Professor Markku Hurme
Instructor	Dr. Antero Moilanen

HELSINKI UNIVERSITY OF TECHNOLOGY
Faculty of Chemistry and Materials Sciences
Degree Programme: Chemical Technology

ABSTRACT OF MASTER’S THESIS

Author

Muhammad Nasrullah

Title of Thesis

MODELLING OF CHAR GASIFICATION REACTIVITY FOR BIOMASS IN A FLUIDIZED BED GASIFIER

Abstract

The mathematical modelling of a gasifier for biomass gasification requires information and data from different aspects of process. The kinetics of char gasification plays a key role in developing a mathematical model for gasifier. This thesis work focuses on determining the kinetics data/parameters of char gasification and further use of this to develop a Langmuir-Hinshelwood equation based model to calculate the char gasification reactivity for biomass in a fluidized bed gasifier. The effects of process parameters on completion and improvement of char conversion in the gasifier are also studied. The ‘inhibition’ effect of product gas ($CO+H_2$) on biomass gasification process is determined by adding H_2 to steam gasification and CO to CO_2 gasification respectively and also in the presence of gas mixture (steam+CO_2+H_2+CO+N_2) in the thermobalance. The measured and calculated (modelled) values of char gasification reactivity for biomass (spruce bark) are compared at different conditions of temperature and pressure (higher than atmospheric pressure). This model of calculating char gasification reactivity for biomass will be used to make a block model for gasifier in future.

Supervisor Professor Markku Hurme	Instructor Dr. Antero Moilanen
Chair Plant Design	Chair code KE-107
Pages 72+4	Language English
Keywords Char gasification, inhibition effect, gas mixture, fluidized bed gasifier	Date 14.12.2009

Foreword

This thesis work has been done at VTT, Technical Research Centre of Finland from 1st of February 2009 till 31st of December 2009. It is my pleasure and a privilege for me that i got opportunity to work in such a nice and professional environment of VTT.

First of all I am greatly thankful to the Allah Almighty for His countless blessings on me and making me the follower of Hazrat Muhammad (PBUH) which is the biggest blessing on me.

I thank my supervisor Professor Markku Hurme for his nice guidelines and advices to make this thesis work even better.

Especially, i am really very thankful to my instructor Dr. Antero Moilanen, Senior Research Scientist at VTT, who helped and guided me in all the aspects related with my thesis work. He helped me for designing the tests, measuring and calculating data for modelling purpose and in report writing also. He has been very helpful, cooperative and patient throughout my work here at VTT. I also really appreciate the support provided by Esa Kurkela, Senior research Scientist and Development Manager of gasification team at VTT for the completion of my thesis work.

I am always very happy and thankful to my whole family, my teachers and friends for their unique and precious support and love for me.

Muhammad Nasrullah

14.12.2009, Espoo Finland

Table of Contents

Symbols

A	frequency factor i.e. an empirical relationship between temperature and rate coefficient
C (O)	Intermediate complex form during reaction
nC_i	Number of inactive carbon atoms or molecules
nC_f	Number of free active carbon atoms or molecules
d	Diameter of biomass particle
E_a	Energy of activation
k	Rate coefficient
P	Partial pressure
R	Gas constant
r	Rate constant
r_{calc}	Reaction rate (biomass gasification reactivity) calculated
r_{meas}	Reaction rate (biomass gasification reactivity)
r_s	Rate of reaction
T	Temperature
t_1	Time at point 1
t_2	Time at point 2
W_1	Mass of sample at point 1
W_2	Mass of sample at point 2
W_{ash}	Mass of ash remains at the end of test
X	Char conversion

Abbreviations

CFBG	Circulated fluidized bed gasifier
CFBC	Circulated fluidized bed combustor
HTW	High temperature Winkler

1. Introduction

In the recent time, use of biomass for the production of heat, power and biofuel is becoming very important to fulfil part of future energy demands and to limit carbon dioxide emissions in the atmosphere. Different technologies for biomass processing are available for example, thermochemical processing and biochemical processing of biomass. Thermochemical processing of biomass is one of the currently developed alternatives. Gasification is a thermochemical process which converts carbonaceous material into gaseous components with the application of heat. Biomass gasification is more efficient way of converting fuel into gaseous form than direct combustion of biomass. The gasification is also environmentally beneficent over combustion, because the fuel gas produced by a gasifier is lower in both volume and temperature than the fully combusted product from a combustor. Because of these characteristics, there is an opportunity to clean and condition the fuel gas prior to use.

Modelling of gasifier requires data of biomass gasification kinetics' parameters. These parameters include process temperature, partial pressures of gaseous components, char reactivity and char conversion. Char reactivity controls the biomass gasification process and plays an important role in designing and operation of fluidized bed gasifier. The completion of fuel conversion in the gasifier is affected by the char gasification reactivity of the biomass. For designing of a gasifier, char reactivity usually determines the volume required for the gasifier and it also has direct impact on parameters like dynamic bed height and biomass feeding point position and indirect influence on other design and operating parameters like freeboard diameter, insulation and distributor etc. [1].

1.1 Aim

The aim of this thesis is to develop a mathematical model to calculate the char gasification reactivity of biomass for a fluidized bed gasifier and to study the significance of process parameters on completion of char conversion which will be used to make a block model for gasifier in future. For this purpose, spruce bark is tested at different process conditions on thermogravimetric apparatus i.e. thermobalance.

2. Basic Features of Biomass

2.1 What is biomass?

Biomass can be defined as ‘all the matter that can be derived directly or indirectly from plant photosynthesis, vegetal and animal’ [2].

In the context of biomass for energy, normally it is plant based material but applicable to animal derived material also. On sustainable basis, biomass available for energy includes woody and herbaceous energy crops, agricultural material, wood wastes and residues, aquatic plants, and other waste material. Biomass is heterogeneous chemically complex carbon based material composed of organic molecules containing hydrogen, normally atoms of oxygen, nitrogen, sulphur, phosphorous and also other atoms including alkali, earth alkaline, chloride and heavy metals in small quantities. These alkali and earth alkaline metals can be in some compound form of calcium, potassium, magnesium, aluminium and silicon including small amount of nitrogen and phosphorus also. The amount of sulphur in most types of biomass is negligible and therefore reduces sulphur dioxide (SO_2) emissions in atmosphere. However, some biomass fuels like straw/agriculture residue contain relatively higher quantity of sulphur and can produce sulphur dioxide (SO_2), biomass also contains some nitrogen but much lower than coal resulting in very low NO_x emissions [2].

Biomass as a source of energy can be used for the production of biofuel and power generation on industrial scale. The important techniques or methods used to convert biomass into power/biofuel are thermochemical conversion and biochemical conversion. The use of biomass is beneficial environmentally as compared with fossil fuel.

2.2 Difference between biomass, peat and fossil fuel

One main difference among biomass, peat and fossil fuel is of time scale. Since, biomass is biological material derived directly or indirectly from recently living organisms, while fossil fuel is biological material produced by the decomposition of ancient living organisms. The fossil fuel (coal, crude oil and natural gas) can be millions of years old. Peat is also a biological material, time scale of which is considered in between biomass and fossil fuel.

2.3 Comparison of biomass with coal

Biomass differs from coal in certain properties. Forexample, energy contents for both are different depending on H/C and O/C ratio of fuel. Bituminous coal has 30.2MJ/Kg; hard woods have 19.8MJ/Kg (dry) and agricultural residue average about 18MJ/Kg energy contents [2, 5]. Normally, carbon content in fuel determines the energy contents. There is considerable amount of sulphur in coal, the removal of which at high temperature is a key obstacle. On the other hand biomass contains very little sulphur as compared to coal which is also beneficial environmentally [5]. After densification by processing and compactation bulk volume of some biomass types and that of coal is shown in table 1.

Table 1: Compressed bulk volume of different types of biomass and coal [2].

Type of fuel	Bulk volume (m^3/ton)
Wood chips	4.4–5.6
Wood pellets	1.6–1.8
Loose straw	24.7–49.5
Baled straw	4.9–9.0
Waste pellets	1.7–2.3
Coal	1.1–1.5

2.4 Composition of biomass

The composition (weight % age dry) of main components of soft and hard wood is shown in table 2.

Table 2: Main components of wood [3].

Wood type	Cellulose	Hemicellulose	Lignin
Hard wood	40–44%	15–35%	18–25%
Soft wood	40–44%	20–32%	25–35%

The prominent elements of wood are carbon, oxygen and hydrogen, although minor amount of extraneous material, normally in the form of organic extractives and inorganic ash forming constituents e.g. potassium, calcium, magnesium, aluminium, sodium and silicon etc. are present. Table 3 shows the elemental composition of wood.

Table 3: Elemental composition of wood [4].

Element	% age dry weight
Carbon	49–50
Oxygen	44
Hydrogen	6
Metal ions	Traces

The chemical composition of ash of solid fuel consists of different elements forexample, Si, Al, Fe, Ca, Mg, K, S, N and P [5, pp. 18–21]. In biomass these compounds are in the form of salts, organically bound compounds and material like soil and sand. Some of the fuel characteristics of biomass are given below in tables 4 and 5 based on dry basis and dry ash free basis respectively.

Table 4: Fuel characteristics for selected biomasses (Dry basis) [5, pp. 18–21].

	Moist	**Ash**	**Volat. Matter**	**Fix. C**	**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
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	19.7	52.5	5.7	0.4	39.7	0.03	29	2133	85

Table 5: Fuel characteristics for selected biomasses (Dry ash free basis) [5, pp. 18–21].

	C	**H**	**N**	**S**	**Volatile matter**	**Fixed carbon**	**HHV**	**LHV**
	%	%	%	%	%	%	MJ/kg	MJ/kg
Northern woody biomass								
Wood chips	52.1	6.1	0.3	0.01	80.5	19.5	21.0	19.7
Forest residue chips	52.0	6.2	0.4	0.02	80.4	19.6	20.9	19.6
Sawdust (pine)	51.0	6.0	0.1	0	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 biomass								
Barley straw	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 grasses	49.4	6.3	1.5	0.15	80.6	19.4	20.2	18.8

2.5 Types of biomass [6]

Biomass can be classified into different types.

- Wood
- Energy crops
- Agricultural residues
- Food waste
- Industrial waste and co-products
- Animal waste.

Wood consists of variety of products like, bark and arboriculture arising (cutting of branches etc.), logs, sawdust, wood chips and wood pellets and briquettes etc. Energy crops are grown for high output per hectare with low inputs. These include food crops forexample, corn and sugarcane and non-food crops like poplar trees and switch grasses. Short rotation woody crops and herbaceous woody crops are important for this category. In agricultural residue there is variety of different types of biomass. It can come from straw or husks, animal manures and slurries and organic material such as grass silage. In the food supply chain starting from production, processing, handling and distributing to customers, waste is remained at all these steps that is a food waste. At different stages, food materials are processed to remove some of its inedible components are removed e.g. peel or skin, shells, husks, cores, pulp from juice and oil extraction etc. Industrial waste and co-products have good potential as biomass fuel. It can be divided into woody and non-woody material. The woody material consists of untreated wood, treated wood wastes and residues and wood composites and laminates. While, non-woody material consists of wastes from paper and pulp mills, textiles wastes and sewage sludge. Although, industrial wastes can be further processed as biomass fuel and different conversion technologies can be applied on these, but there are regulatory and environmental constraints associated with the use of waste material from industries.

2.6 Biomass resources [7]

The resources of biomass can be classified as following.

1. Untapped natural resources

   Untapped natural resources can be further divided into two groups.

   a. Agriculture, livestock, forestry and fishery group
   - Agriculture: Such as rice husk, rice straw, wheat straw, vegetable residue, etc.
   - Livestock: For example animal waste, butchery waste, etc.
   - Forestry: Wood barks, forest residue, thinned wood, processing waste, sawdust etc.
   - Fishery: Processing waste, bowel, dead fish, etc.

   b. Other waste group
   - Industry: Sewage sludge, organic, processing waste, etc.
   - Household: Garbage, human waste, etc.

2. Plantation (production group)

   Continental area: Grain, plant, vegetable, fat and oil, etc.

   Water area: Algae, photosynthetic bacteria, etc.

3. Biomass Gasification and Gasification Process

3.1 Gasification in general

Gasification is a process of partial oxidation of carbonaceous materials (substances rich in carbon molecules with elevated carbon to hydrogen ratio) such as coal, petroleum or biomass which is converted into carbon monoxide and hydrogen plus carbon dioxide and some hydrocarbons such as methane on high process temperature with a controlled amount of oxygen and/or steam. 'The mixture of carbon monoxide and hydrogen produced during gasification process is itself a fuel and is called synthetic gas or syngas'. The gasification of carbonaceous material takes place at elevated temperatures > 700°C. The range of temperature is normally 700–1000°C [8]. The process of gasification takes place in the presence of gasifying medium such as, steam, oxygen, air or with combination of some of these.

Industrially, gasification is mostly used for the production of electricity from coal, where the resulting synthesis gas is burned in gas turbine. Integrated gasification combined cycles (IGCC) is also in use for the purpose of producing electricity from coal by using gasification process. Because of excess in availability and high energy contents, coal gasification has a lot of potential in the field of energy but on the other hand it has some serious issues with producing green house gases in the atmosphere. The second issue is continuous depletion of fossil fuel (crude oil, coal etc.) due to its huge consumption. Because of these issues, biomass gasification is becoming point of focus now days. The biomass based fuels are non-fossil, renewable and regarded as carbon dioxide (CO_2) neutral, because biomass takes CO_2 from atmosphere during its growth and is re-used by plants after burning of fuel. Therefore, carbon dioxide generated after the use of fuel produced from biomass does not add up as green house gases in atmosphere. The natural carbon cycle related with use of biomass is shown in figure 1.

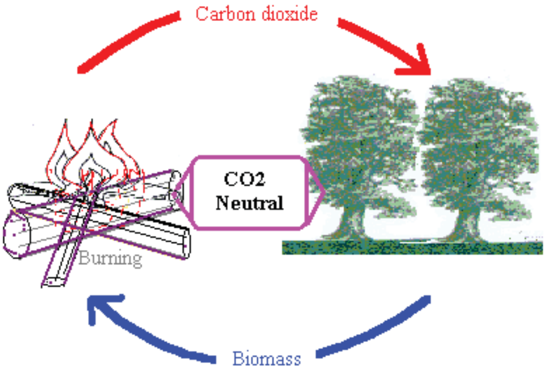


Figure 1: Natural carbon cycle related with use of biomass [9].

3.2 History

Originally, gasification process was developed in 1800s to produce town gas for lightening and cooking purposes, which then latterly replaced by electricity and natural gas. The gasification was also used to produce synthetic fuel during World War II in which engines of many vehicles were given synthetic fuel from gasification process. The evolution of gasification got boost after the first energy crisis in 1973. The world’s first Integrated Gasification combined cycle (IGCC) was also supported financially at that time and meanwhile some chemical plants were converted from petroleum to coal for producing syngas. Similarly, in 1990s medium sized (about 250 MWe) projects were funded for further demonstration for the feasibility of the IGCC process. In the present stage of gasification evolution, commercial developers started building IGCC power plants without government subsidies. Another important and visible change and development in the field of gasification is using non-fossil raw materials such as biomass for the production of energy [10].

3.3 Biomass gasification

Biomass gasification is a thermochemical process of partial oxidation which converts biomass materials into gaseous components. The resulting product gas or syngas can be used to run internal combustion engines and substitute of furnace oil in direct heat applications [11] and can be converted into electricity or biofuel after cleaning; from the same process useful chemicals can also be obtained. It is considered that biomass gasification is one of the promising routes for the production of syngas or combined heat and power generation because of the potential for higher efficiency cycles [12]. Due to high potential and efficiency, thermal processing of biomass can play a major role to meet the increasing demands of bio-energy and renewable energy sectors. Gasification of biomass is more efficient than just burning of biomass to get energy. Therefore, high efficient gasification is preferred over traditionally low efficient processes of simple burning. Energy from biomass based on short rotation forestry and other energy crops can contribute significantly towards the objectives of Kyoto Agreement in reducing the green house gases emissions and to the problems related to climate change [13].

3.4 Concept of integrating Fischer-Tropsch synthesis plant with pulp and paper mills

The raw material used in the pulp and paper mill is biomass in the form of wood or some other fibrous material. The composition of wood consists of both fibrous and non fibrous materials; fibrous material is convertible into pulp, which is then further processed into paper products. On the other hand, non fibrous material i.e. lignin is not converted into pulp; instead it forms black liquor which is then used in the boiler for burning and energy purposes. Similarly, there are some other biomass materials in pulp mill like, bark. Thus the concept of integrating Fischer-Tropsch synthesis plant with pulp mill is supported by these facts. The main raw material can be used for the production of pulp and paper which remains the main product. But other material like barks, forest residue and other waste biomass can be used for gasification purposes, which provide the energy to fulfill the requirement of pulp mill itself and also produces valuable transportation fuel and some other useful chemical products. This can also boost the struggling forest industry by fulfilling the energy requirement to some extent and also producing valuable products. Integration of biorefinery with pulp and paper mill reduces the overall cost of biorefinery plant, because the facilities like land requirement for plant, logistics needs and utilities etc. are already there in pulp and paper mill which requires some changes and modifications for integration. This concept is explained below in figure 2.

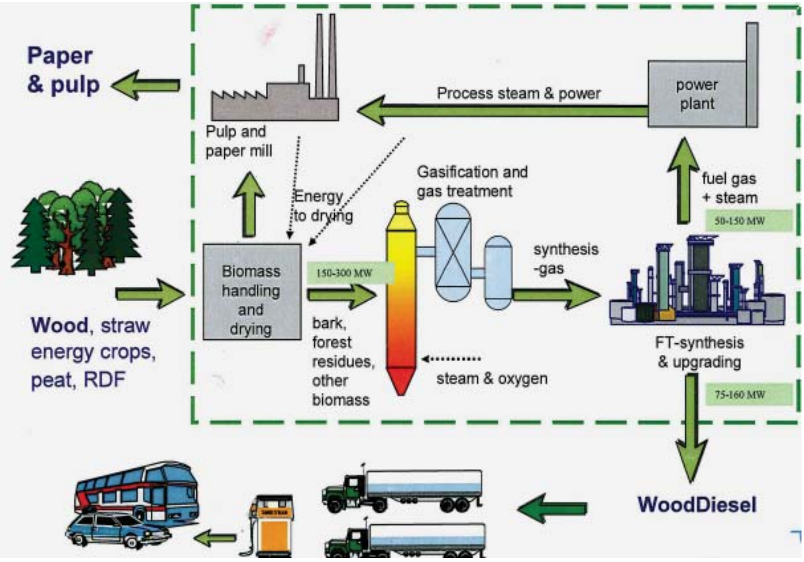


Figure 2: Integration of FT-synthesis plant to a pulp and paper mill [14].

3.5 Fischer-Tropsch process

In Fischer-Tropsch process, syngas mixture of carbon monoxide and hydrogen ($CO+H_2$) is converted into waxes in the presence of catalysts like Fe, Co and Ru and typical products of this process are waxes (can be refined), diesel, olefins and gasoline [14]. One option for the production of liquid biofuel in Finland is based on fluidized bed gasification of biomass and Fischer-Tropsch synthesis process [15, 16].

3.6 Biomass gasification process

There are different processes or steps take place after feeding biomass as raw material in the gasifier. In first step water and volatile matters are released very fast and char residue is left to react further and it mainly controls the conversion achieved during the process of gasification [5]. For biomass, pyrolysis starts at about above 300°C of temperature. As a result of this process, organic materials are transformed into gases, vapors, a small quantity of liquid and a solid residue consisting of carbon residue and ash.

The hottest part of the gasifier is combustion zone, where carbon and hydrogen are partially combusted with oxygen and provides heat for reactions take place there [17]. In this zone carbon and hydrogen reacts with oxygen to produce carbon dioxide and water vapors.

The solid residue of carbon left there is called char. The process of biomass gasification revolves around char gasification, being char is an important part of biomass and plays a key role in gasification process. Biomass gasification starts in the temperature range of 750–1000°C [18] and at atmospheric or pressurized conditions. Both oxygen and steam gasification produce nitrogen free product gas. The scheme of biomass gasification process is shown in figure 3.

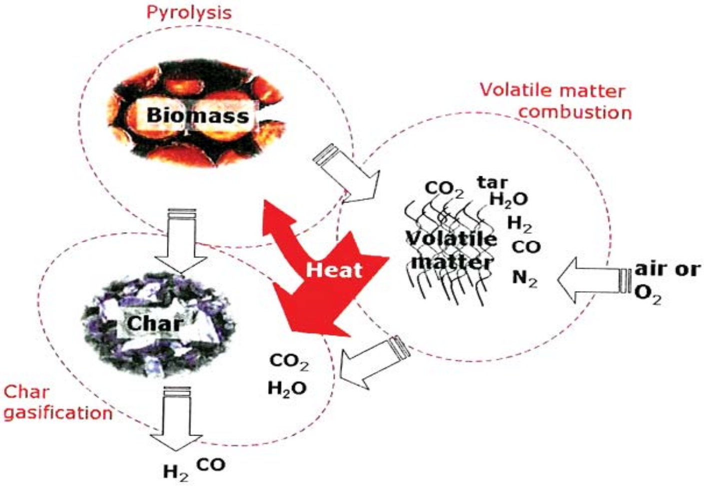


Figure 3: Scheme of the biomass gasification process [18].

Syngas ($CO+H_2$) produced in the result of gasification process can be used for the production of electricity or biofuel after further processing. It needs to be cleaned from some gases, char particles, tar, ash and other impurities before transforming into useful form of energy. The removal of impurities from syngas is a tedious and tricky task; especially compounds like H_2S and HCN are difficult to remove. These impurities (H_2S and HCN) can efficiently be removed to the level required by the guard beds with commercial absorption processes based on solvents [19].

3.7 Reaction mechanism of gasification process

Three steps or processes are involved in describing the biomass gasification mechanism in the gasifier; these are pyrolysis, combustion and char gasification.

A series of endothermic reactions take place in gasification process supported by heat which is produced by combustion reactions. There are four major gasification reactions take place during the process as given below [20].

1. Water-gas reaction
2. Boudouard reaction
3. Water-gas shift reaction
4. Methanation.

Brief description of these reactions is given below. In the following chemical equations, -ve and +ve signs are used for endothermic and exothermic reactions respectively.

Water-gas reaction

It is a partial oxidation of carbon with steam. This steam can come from different sources forexample, water vapors associated with the incoming air, vapors of evaporated water and during pyrolysis of fuel. In this heterogeneous reaction steam reacts with the hot carbon to produce hydrogen and carbon monoxide gases as given below in reaction 1.

$C + H_2O = H_2 + CO - 131.38$ kJ/kg mol carbon (1)

Boudouard reaction

It is an endothermic reaction in which carbon dioxide present in the gasifier (produced during pyrolysis of fuel) reacts with carbon to produce carbon monoxide according to Boudouard reaction shown in reaction 2.

$CO_2 + C = 2CO - 172.58$ kJ/kg mol carbon (2)

Shift conversion (Water-gas shift reaction)

The reduction of steam by carbon monoxide to produce hydrogen is highly desirable, because heating value of hydrogen is higher than that of carbon monoxide. This endothermic reaction increases the ratio of hydrogen to carbon monoxide in the gas and is employed during the manufacture of synthesis gas. This is described in reaction 3.

$CO + H_2O = CO_2 + H_2 - 41.98$ kJ/kg mol carbon (3)

Methanation

Carbon reacts with hydrogen gas to produce methane in the gasifier according to following exothermic reaction 4.

$C + H_2 = CH_4 + 74.90$ kJ/kg mol carbon (4)

Combustion

Most of the reactions take place during gasification is endothermic, so heat is required for them to occure. This heat is produced during combustion process, where oxygen supplied to the gasifier reacts with carbon and hydrogen gas to produce carbon dioxide and water vapors respectively according to following exothermic reactions 5 and 6.

$$C + O_2 = CO_2 + 393.77 \text{ kJ/mol carbon} \qquad (5)$$

$$H_2 + ½ O_2 = H_2O + 742 \text{ kJ/mol carbon} \qquad (6)$$

Heat produced from above reactions (5) and (6) is used for endothermic reactions take place during gasification process in the gasifier.

3.8 Effect of gasifying medium on gasification process [21]

Following are given some gasifying mediums/agents which can be used in gasification process.

3.8.1 Air gasification

Air gasification is less expensive but produces syngas (there is nitrogen also in the gas mixture) having lower heating value of 4–7 MJ/Nm^3. For gasification, values of air excess ratio are usually between 0.2 and 0.4 and the optimum value being about 0.25. If the air excess ratio is lower, the char will not be gasified and some energy will retain in the wood as a charcoal; on the other hand for higher air excess ratio some of the gas will be burned and temperature will rise rapidly.

3.8.2 Steam gasification

The term steam gasification can consist of only steam, a mixture of air/steam and a mixture of oxygen/steam as a gasifying medium in biomass gasification process. The higher steam content in gasifying medium provides hydrogen (H_2) rich product gas.

3.8.3 Oxygen gasification

Using only oxygen as a gasifying medium means that nitrogen free gasifying agent; in the result of this the product gas obtained is also nitrogen free having higher heating value.

These above described gasification processes based on gasifying medium are summarized in following given table 6.

Table 6: Comparison of gasification agents [21].

Gasification agent	**Advantages**	**Disadvantages**	**Heating value of product gas (MJ/Nm^3)**
Air	Inexpensive	Low heating value	4–7
Oxygen	N_2 free product gas Medium heating value	Expensive	10–18
Steam	N_2 free product gas Medium heating value Enhanced H_2 content	Very endothermic process	10–18

3.9 Types of gasification technologies [22]

Gasification technologies can be categorized into three types:

1. Fixed bed gasification
2. Fluidized bed gasification
3. Novel designs for gasification.

Fixed bed gasification can be further classified into different types:

- Down draft co-current fixed bed
- Updraft co-current fixed bed
- Updraft counter current fixed bed
- Cross-draft fixed bed
- Open core fixed bed [22].

Similarly, fluidized bed gasification is of following further types:

- Atmospheric circulating fluidized bed
- Pressurized circulating fluidized bed.

And novel designs for gasification are: [22]

- Supercritical water gasification
- Plasma Arc gasification
- 2-stage gasifier
- Open-Top
- Aqueous phase reforming.

4. Types of Gasifiers

There are various types of gasifiers, but main of them can be divided into three groups, which can be further sub-divided as following.

1. Fixed/moving bed gasifiers
    a. Updraft gasifier (counter-current)
    b. Downdraft gasifier (co-current)
    c. Cross-current moving bed
2. Fluidized bed gasifiers
    a. Circulated fluidized bed gasifier (CFB)
    b. Bubbling fluidized bed gasifier (BFB)
3. Entrained flow gasifier.

Each type of gasifier operates satisfactorily with respect to stability, gas quality, and efficiency only within the certain ranges of the fuel properties of which the most important are [23]:

- Energy content
- Moisture content
- Volatile matter
- Ash content and ash chemical composition
- Reactivity
- Size and size distribution
- Bulk density
- Charring properties.

Following are given the different types of gasifiers with some description and detail.

4.1 Fixed/moving bed gasifiers

In fixed/moving bed gasifiers, the gasification medium flows through and thus comes in contact with a fixed bed of solid fuel particles. Depending upon the flow direction of gasifying medium through the bed of fuel these gasifiers are of three types.

4.1.1 Updraft gasifier (Counter-current)

In an updraft gasifier, feed is introduced from the top and air / gasifying medium from the bottom which makes the flow of feed and gasifying medium in counter-current direction. The product gas produced as a result of gasification process is drawn out from somewhere top of the gasifier. The updraft gasifier achieves the highest efficiency as hot gas passes through fuel bed and leaves the gasifier at low temperature. The raw gas produced in an updraft gasifier has an excessive amount of tar and poor loading capability [24]. Different zones related with drying, pyrolysis, reduction and oxidation of fuel in updraft gasifier are shown below in figure 4.

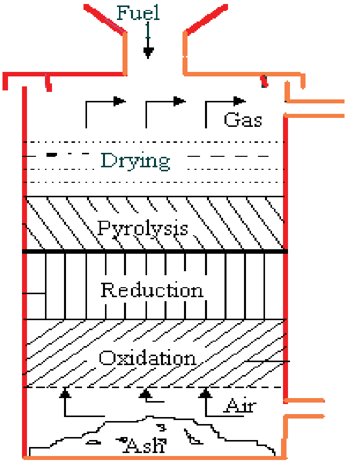


Figure 4: Updraft gasifier [24].

Some important features of updraft gasifier are, [25]

Output	< 10 $\mathrm{MW}_{\mathrm{thermal}}$
Feedstock size	10–100 mm
Moist feedstock	< 50 p-%
Gas temperature	< 300°C
Dirty gas	

4.1.2 Downdraft gasifier (Co-current)

In the downdraft gasifier, fuel is introduced from top while air/gasifying medium is introduced from somewhere in the middle section. In this case, product gas is drawn out from the lower (bottom) section of gasifier as shown in figure 5.

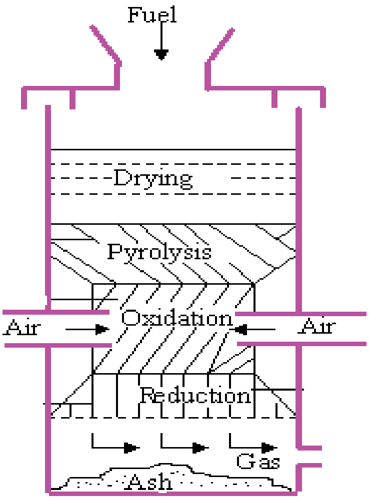


Figure 5: Downdraft gasifier [24].

It has lower overall efficiency and difficulties in handling higher moisture feedstock.

The amount of residue ash is also higher [24]. Some important features of downdraft gasifier are [25],

Output	< 2MW$_{\text{thermal}}$
Feedstock size	10–100 mm
Dry feedstock	<20 p-%
Gas temperature	< 800°C
Clean gas	

4.1.3 Cross-current moving bed (Cross-draft gasifier)

Although, this type of gasifier has some advantages over updraft and downdraft gasifiers, but still they are not very common and ideal. There are also some disadvantages with this type of gasifier such as high exit gas temperature and high gas velocity are the consequence of design [24]. Figure 6 shows different section of cross-current moving bed.

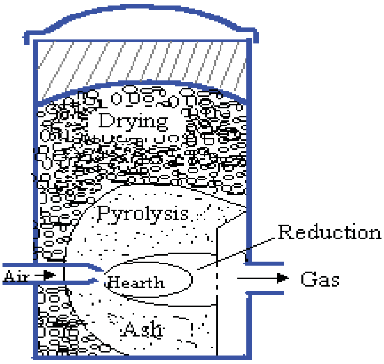


Figure 6: Cross-current moving bed [24].

4.2 Fluidized bed gasifiers

Fluidized bed gasifiers have advantages over fixed bed gasifiers, especially regarding mixing, reaction kinetics, gas solid contact and their ability to achieve uniform temperature distribution inside the gasifier zone [26]. The uniformity of temperature is achieved by the use of fine-grained bed material into whish the gasifying material is introduced. Fluidizing the bed material ensures the intimate mixing of the hot bed material with gas and biomass feed [27].

Air (gasifying medium) and fuel are mixed in a hot bed of granular solid such as sand in a fluidized bed gasifier. In fluidized bed gasifier different zones such as drying, pyrolysis, oxidation and reduction can not be distinguished because of intense gas-solid mixing there (bubbling and circulated fluidized beds). But due to this intense gas-solid mixing the temperature remains uniform throughout the bed. In fluidized beds, air-to-fuel ratio can be changed or adjusted as a result of that bed temperature can be controlled. The product gas however contains tar which can be cleaned in further steps or processes [28]. Following are some important features of fluidized bed gasifiers [25],

Output	> 20 $MW_{thermal}$
Feedstock size	< 10 mm
Gas temperature	< 800°C.

There are two main types of fluidized bed gasifiers.

4.2.1 Circulated fluidized bed gasifier

In a typical circulated fluidized bed gasifier, solid fuel particles are brought into contact with controlled amount of gasifying medium such as oxygen, air and steam or with some combination. The solid fuel passes through different stages such as drying, pyrolysis, oxidation and reduction in the gasifier. In circulated fluidized bed gasifier these stages are hard to distinguish separately, because the bed is moving, circulating and fluidizing throughout. Different sections of CFBG are shown below in figure 7.

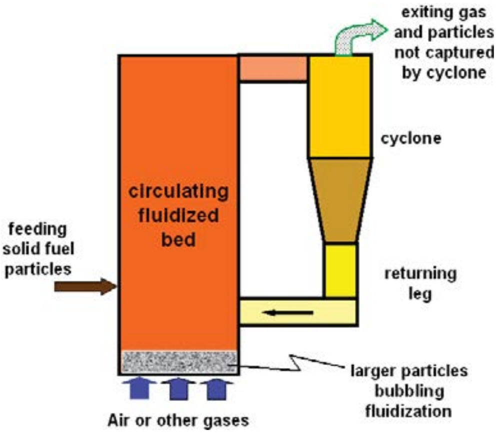


Figure 7: Circulating fluidized bed gasifier [29].

Some important features of CFBG are [25],

- Fluidizing velocity 5–10 m/sec
- Higher output/diameter
- Reactive feedstock.

Fluidized bed gasifiers have [28],

1. Higher throughput than fixed gasifier
2. Improved heat and mass transfer from fuel
3. High heating value
4. Reduced char.

A circulating fluidized bed gasifier is known for its excellent heat and mass transfer and longer residence time, can achieve better conversion [28].

4.2.2 Bubbling fluidized bed gasifier

There is a moving bed of fine-grained material into which biomass or fuel is introduced. and air is introduced from the bottom. Typically, the bed temperature is in the range of 800–950°C [30]. The biomass in the presence of gasifying medium is gasified in the hot bed producing char with gaseous components. The contact of hot bed material causes the cracking of high molecular weight compounds to form product gas containing some tar content also. Figure 8 gives some comparison of bubbling fluidized bed gasifier and circulated fluidized bed gasifier.

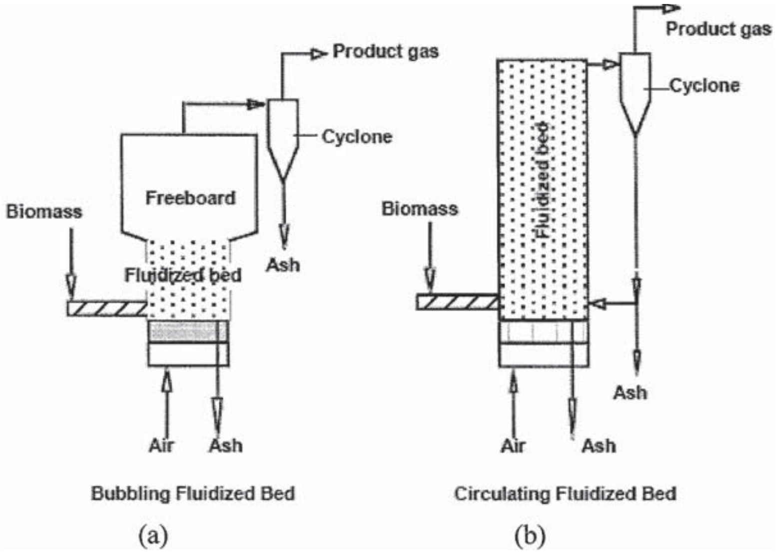


Figure 8: Bubbling fluidized bed gasifier and circulated fluidized bed gasifier [30].

Following are some important features of BFBG [25],

- Fluidizing velocity 1–3 m/sec
- Long residence time.

4.2.3 Entrained flow gasifier

In entrained flow gasifier, fuel and gasifying medium i.e. air/oxygen along with steam are introduced from the top as shown below in figure 9. These have higher capacities than other types of gasifiers. Entrained bed gasifiers are generally used for fossil fuels like coal and refinery wastes etc. but can be used for biomass gasification also. It requires a very fine particle size which makes its use limited for biomass gasification.

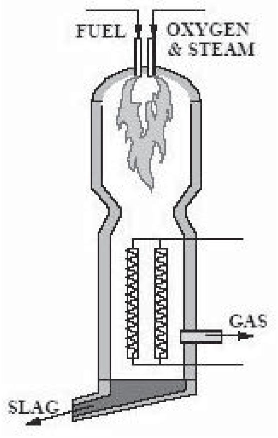


Figure 9: Entrained flow gasifier [30].

The main features of entrained flow gasifiers are [25],

• Output	> 100 $\mathrm{MW}_{\mathrm{thermal}}$
• Feedstock size	< 0.1mm
• Coal oxygen gasification	
• Gasification temperature	1300–1700°C.

5. Kinetics of Biomass/Char Gasification

The kinetics of biomass/char gasification plays an important role in the design of gasification reactors or gasifiers, because gasification is a relatively slower process than that of initial pyrolysis. Hence the achievable burnout degree is set by gasification kinetics and not by the pyrolysis kinetics [31]. The change in gasification rate occurs due to the change of mass of char with respect to time. The rate of the reaction is the change of the mass of carbon as function of time expressed by the degree of gasification also called “burn-off” [32]. High or low gasification reactivity depends on how fast the change (decrease) in mass of char takes place with respect to time. The gasification reactivity also affects on fuel conversion in the gasifier. Often first order kinetics (surface- or mass-based) hold for only part of the conversion interval [31].

In combustors and gasifiers, biomass conversion takes place as a result of a strong interaction between chemical and physical processes [33].

5.1 Biomass gasification kinetics on thermogravimetric apparatus

Since the amount of biomass sample used in thermogravimetric apparatus (thermobalance) is very small i.e. about 100–120 mg, therefore the effect of product gas produced during gasification of this sample is almost negligible. It is quite reasonable with the thermogravimetric apparatus to study the effect of different gasifying mediums on char gasification such as steam gasification, air/oxygen gasification, carbon dioxide gasification and inhibition effect of H_2 and CO to steam and CO_2 gasification respectively.

5.2 Kinetics of steam gasification

Because of the variability (composition, structure, reactivity, physical properties etc.) of biomass raw material and severe conditions (temperature, residence time, heating rate, etc.), the modeling of biomass steam gasification to synthesis gas is challenging [34]. Process temperature and partial pressure of steam affects the rate of gasification. During steam gasification generally following reaction (7) takes place,

$$C + H_2O \leftrightarrow CO + H_2 \qquad (7)$$

The mechanism for this steam gasification reaction can be as given in reactions (8) and (9).

$$C + H_2O \leftrightarrow H_2 + C(O) \qquad (8)$$

$$nC_i + C(O) \rightarrow CO + nC_f \qquad (9)$$

Where,

nC_i are the inactive carbon atoms or molecules
nC_f are the free active carbon atoms or molecules
C (O) is intermediate complex form during reaction.

At certain temperature, the gasification rate of char carbon can be expressed in mathematical form as shown in relation (10) below [35]. This equation is derived from Langmuir-Hinshelwood equation for gas-solid reactions.

$$r_s = \frac{r_1 P_{H2O}}{1 + r_2 P_{H2O}} \tag{10}$$

Where,

r_s is the rate of reaction
r_1 and r2 are the rate constants
P_{H2O} expresses the partial pressure of steam.

Since, the amount of sample used in thermobalance is very small, therefore the amounts of hydrogen (H_2), carbon monoxide (CO) and some other gas produced during gasification are also very small which can be neglected in relation (10).

5.3 Kinetics for adding hydrogen to steam gasification

To study the effect of hydrogen in steam gasification of biomass/char, hydrogen (H_2) can be added along with steam as a gasifying medium. The following relation (11) expresses this effect [35].

$$r_s = \frac{r_1 P_{H2O}}{1 + r_2 P_{H2O} + r_3 P_{H2}} \tag{11}$$

Where,

r_s is the rate of reaction
r_2 and r3 are rate constants
P_{H2O} expresses the partial pressure of steam.
P_{H2} expresses the partial pressure of hydrogen gas.

5.4 Kinetics of carbon dioxide gasification

Like steam, carbon dioxide (CO_2) is also used as a gasifying medium in gasification processes. The chemical reaction (12) is also called Boudouard reaction [35].

$$CO_2 + C \leftrightarrow 2CO \tag{12}$$

The mechanism of Boudouard reaction is given in reactions (13) and (14) below [35].

$$CO_2 + nC_f \leftrightarrow C(O) + CO \tag{13}$$

$$C(O) + nCi \rightarrow CO + nCf \tag{14}$$

Where,

nC_i are the number of inactive atoms or molecules of carbon
nC_f are the number of free active atoms or molecules of carbon
C(O) is the complex or intermediate form during the reaction.

So, at specific temperature, the gasification rate can be calculated according to relation (15) when carbon dioxide is used as gasifying medium.

$$r_s = \frac{r_4 P_{CO2}}{1 + r_5 P_{CO2}} \tag{15}$$

Where,

r_s is reaction rate
r_4 and r_5 are rate constants
P_{CO2} is the partial pressure of CO_2.

5.5 Kinetics for adding CO to CO_2 gasification

Carbon monoxide is one of the components of product gas produced in biomass gasification process. How the production of carbon monoxide affects on the biomass gasification, can be studied by adding CO into CO_2 as a gasifying medium. This effect of carbon monoxide is expressed in following relation (16) mathematically [35].

$$r_s = \frac{r_4 P_{CO2}}{1 + r_5 P_{CO2} + r_6 P_{CO}} \tag{16}$$

PCO and r_6 are partial pressure of carbon monoxide and rate constant respectively.

5.6 Kinetics of gasification process in the presence of gas mixture (steam+CO_2+H_2+CO)

The combined inhibition effect of product gas on biomass gasification process is given in following relation (17) [35]. This can be studied by adding the gas mixture of steam, CO_2, H_2 and CO in thermobalance for char gasification.

$$r_s = \frac{r_1 P_{H2O} + r_4 P_{CO2}}{1 + r_2 P_{H2O} + r_3 P_{H2+} r_5 P_{CO2} + r_6 P_{CO}} \tag{17}$$

Where, r_s is the reaction rate, r_1 to r_6 are rate constants and P denotes the partial pressure of relevant components (H_2O, CO_2, H_2 and CO).

6. Experimental Part

The results of this thesis work are based on tests performed on thermogravimetric apparatus (thermobalance) [5]. The application part is divided into three main sections.

- Thermogravimetric characteristics of biomass
- Effect of product gas inhibition on biomass gasification process and making a Langmuir-Hinshelwood equation based model to determine the biomass gasification reaction rate (char reactivity)
- Block Model approach of char conversion in circulated fluidized bed Gasifier and significance of process parameters to improve char conversion.

6.1 Biomass samples used for experiments

Different types of biomass samples are collected from different locations of Finland such as, Kaipola, Iisalmi, Porvoo, Lappeenranta, Varkaus, Rauma, Kajaani, Kemi, Oulu and Riga (outside Finland) as shown in figure 10.

The biomass samples used for experiments are different barks along with some other types, these biomass are,

- Spruce bark
- Pine bark
- Aspen bark
- Birch bark
- Mixture of different barks
- Forest residue
- Stump chips.

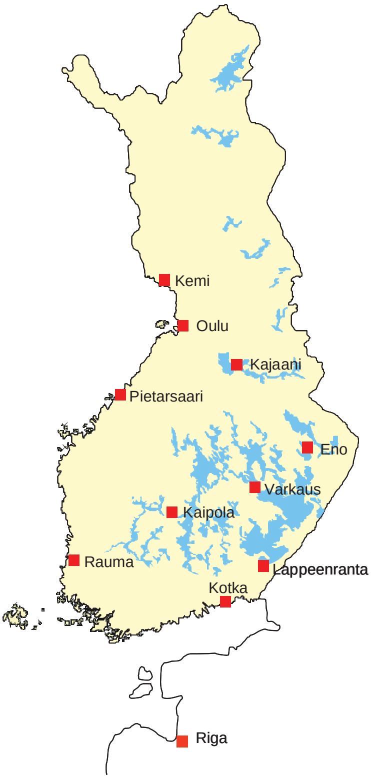


Figure 10: Various samples collecting locations of Finland.

6.2 Thermogravimetric apparatus (thermobalance)

Thermobalance is proven to be very useful apparatus to study the thermogravimetric characteristics of biomass and also inhibition effect of product gas on biomass gasification process. Different parts of thermobalance are shown in figure 11 and 12 respectively. In figure 13, sample holders used for thermobalance tests are shown along with sample lock.

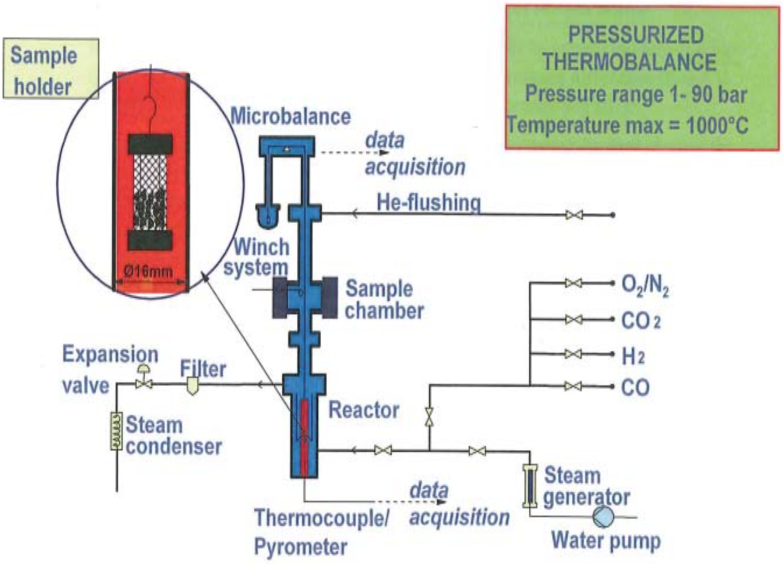
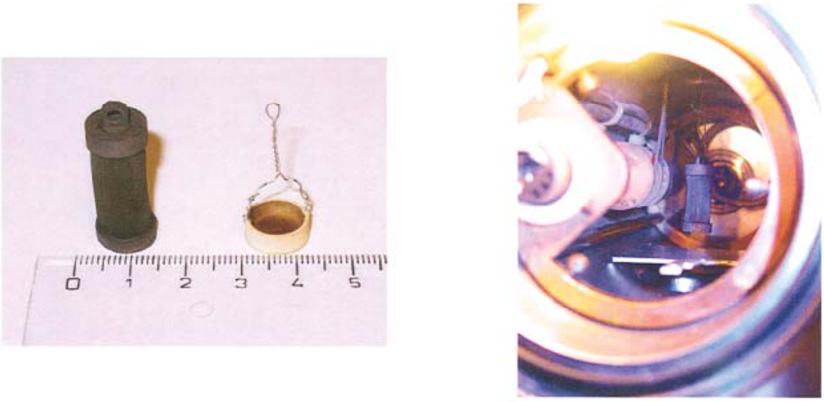


Figure 11: Pressurized thermobalance [5].

Figure 12: Thermobalance and reactor.



(a) (b)

Figure 13: a) Two different types of sample holders b) The sample holder in the sample lock.

7. Thermogravimetric Characteristics of Biomass

The gasification reactivity of char, char conversion and ash sintering/melting are characteristics of biomass, studied here under the influence of different parameters such as,

- Effect of temperature
- Effect of pressure
- Effect of gasifying medium
- Different types of feedstock (biomass)
- Same biomasses collected from different locations of Finland
- Effect of storage, debarking and transportation methods of biomass.

This leads towards finding the optimum process conditions for biomass gasification process.

7.1 Fuel gasification reactivity (Instantaneous rate of reaction)

The total carbon conversion achieved in the gasifier, operating at temperature below 1 000°C, depends for the most part on the reactivity of solid char residue [36]. In thermobalance, gasification reactivity or instantaneous rate of reaction is determined by monitoring the weight of biomass sample as a function of time. The low or high biomass reactivity depends on how fast or slow the change (decrease) of biomass fuel takes place with respect to time on the given process conditions. This decrease in weight starts from devolatilization step and continues till the completion of gasification unless fuel residue or ash remains finally. The behavior of weight as a function of time is shown in figure 14 below.

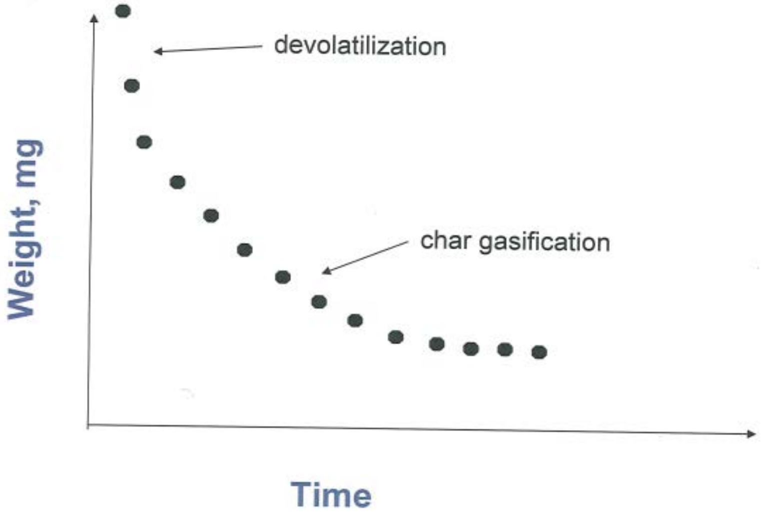


Figure 14: Weight as a function of time [5].

The rate of reaction is calculated according to following equation (18) [5].

$$r_{(\%/\min)} = \frac{W_1 - W_2}{(W_2 - W_{ash}) * (t_2 - t_1)} * 60 * 100 \qquad (18)$$

Where,

r is the instantaneous reaction rate in %/min
W_1 and W_2 show masses (mg) of sample at points 1 and 2
W_{ash} (mg) is the mass of ash remains at the end of test
t_1 and t_2 (sec) express time at two points.

The relation (1) is multiplied by 60 and 100 to convert it into %/min.

The points W_1, W2, W_{ash}, t_1 and t_2 are explained in figure 16.

Depending on reaction rate or fuel reactivity, different reactivity profiles i.e. rate vs. conversion are observed. The reactivity profile behavior for biomass gasification is shown below in figure 15.

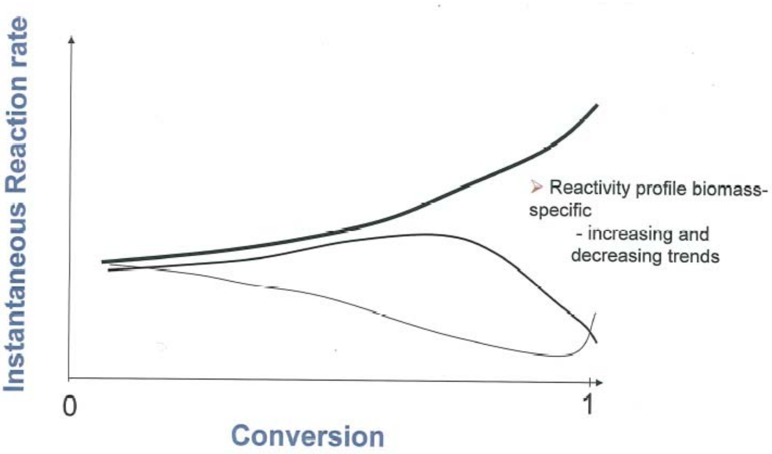


Figure 15: Reaction rate vs. conversion – Reactivity profile [1].

7.2 Biomass fuel/char conversion

Achieving high biomass char conversion is very important parameter in gasification process. Maximum conversion of biomass is desired from gasification process. The char conversion is calculated according to equation (19) as explained in figure 16.

$$X_{(in\%)} = 100 * \frac{W_{sample} - W_2}{(W_{sample} - W_{ash})} \qquad (19)$$

Where,

X represents conversion (ash free) in %

W_{sample} shows mass of original sample in mg
W_2 is mass of gasified sample in mg. at point 2
W_{ash} expresses the mass of ash or residue remains at the end of process.

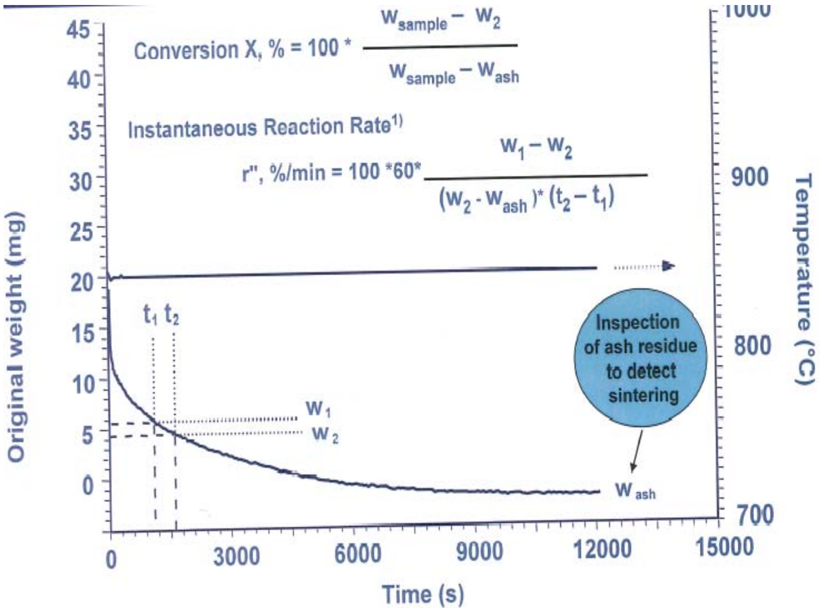


Figure 16: Change in original weight with respect to time [1].

7.3 Ash sintering/Melting

Ash sintering can be critical for gasification process and can lead towards blockage problems in the gasifier [37]. The sintering of ash or residue in the gasifier depends mainly on process conditions of temperature and pressure. The intensity or degree of ash sintering is observed visually by a microscope [5]. The intensity of ash sintering is described as shown in figure 17.

- O means ash is in powder form so no ash sintering
- *-** means weekly sintered (*) and more sintered (**)
- *** means ash is in molten state i.e. completely sintered.

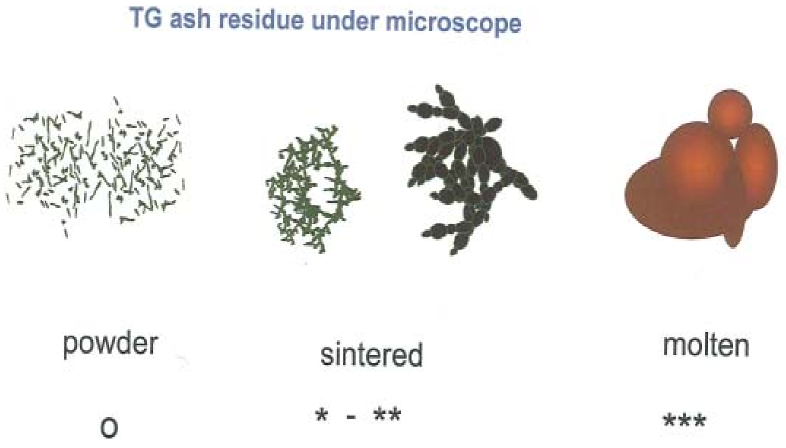


Figure 17: Classification of ash sintering/melting [5].

7.4 Results of thermogravimetric characteristics of biomass

The results of thermogravimetric characteristics of biomass are explained in terms of effects of different parameters on biomass gasification process.

7.4.1 Effect of temperature

With steam as a gasifying medium

The effect of temperature on fuel reactivity, char conversion and ash sintering of biomass is studied by keeping the pressure and gasifying medium constant but varying temperature for same type of biomass. The effect of temperature on biomass characteristics is observed to be so that,

- Fuel reactivity increases by increasing temperature
- Char conversion is better on higher temperature as compared to that of at lower
- The chances of ash sintering becomes more at higher temperature.

The figure 18 describes the effect of temperature on spruce bark during gasification process at constant pressure of 1 bar and same gasifying medium i.e. steam with varying process temperature.

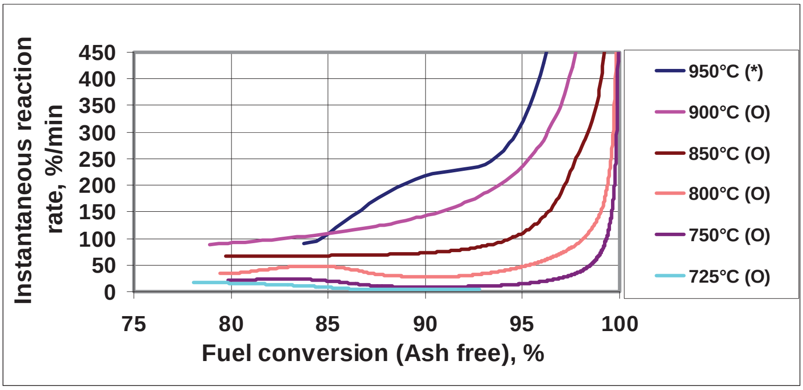


Figure 18: Effect of temperature on fuel reactivity and ash sintering of spruce bark at atmospheric pressure with steam (100%) as gasifying medium.

- At atmospheric pressure, no ash sintering is observed till 900°C but weak ash sintering is observed at 950°C as shown by figure 18.

Higher the reactivity or instantaneous rate of reaction of fuel means the fuel conversion completes in less time and vice versa. This can be seen from figure 19.

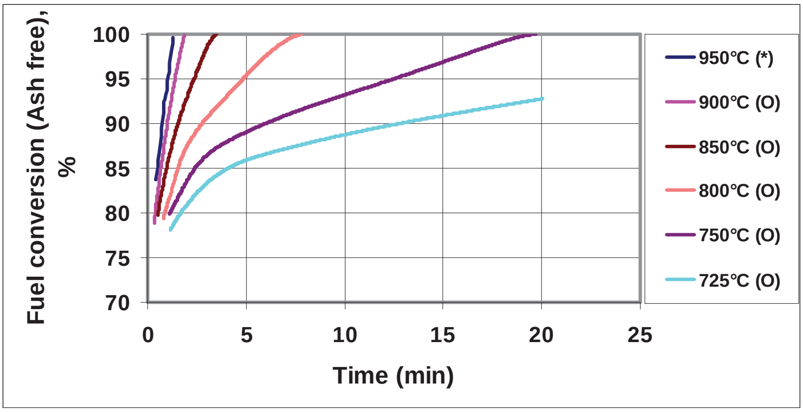


Figure 19: Effect of temperature on time taken for the completion of char conversion of spruce bark at atmospheric pressure with steam (100%) as a gasifying medium.

With CO_2 as gasifying medium

The effect of temperature on fuel reactivity, char conversion with respect to time and ash sintering of spruce bark using CO_2 as a gasifying medium is shown in figures 20 and 21 respectively.

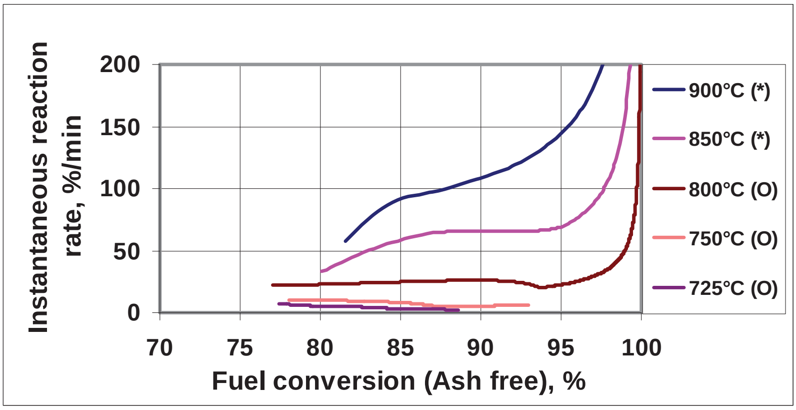


Figure 20: Effect of temperature on fuel reactivity and ash sintering of spruce bark at atmospheric pressure with CO_2 (100%) as gasifying medium.

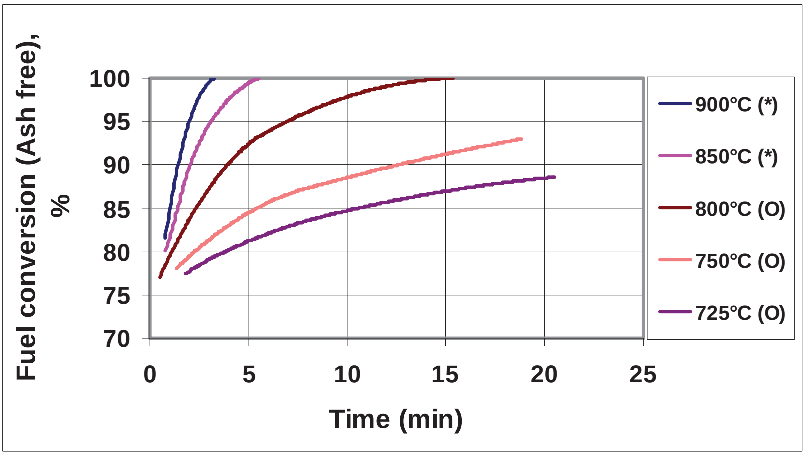


Figure 21: Effect of temperature on time taken for completion of char conversion of spruce bark at atmospheric pressure with CO_2 (100%) as a gasifying medium.

7.4.2 Effect of pressure

With steam as a gasifying medium

The effect of pressure on biomass gasification is studied by keeping the temperature and gasifying medium same but varying pressure.

- The effect of pressure on fuel reactivity is not as straight forward as in case of temperature, because by increasing pressure normally reactivity increases but at some stage or points it starts decreasing also.
- By increasing pressure, the probability of ash sintering also increases.

The behavior of fuel reactivity with the pressure is yet to be studied in detail, but there can be two reasons for this.

- The reactivity behavior of biomass under the application of pressure, alkaline and earth-alkaline metal (Na, K, Ca, Mg etc) compounds play a significant role [38, 39, 40, 41], and some other elements like silicon can react with the metals leading to losses in the catalytic activity [38].
- The second reason can be, since the product gas inhibits the reactivity of biomass gasification process, the small amount of product gas produces in the thermobalance on higher pressure inhibits the reactivity on some points to decrease it. Since, the product gas here is in very small amount therefore the inhibition effect is not very significant but still there is some.

The effect of pressure on fuel reactivity and ash sintering of spruce bark is explained by figure 22 and table 6 at 850°C and varying pressure with steam (100%) as a gasifying medium. This shows that at some points (95% fuel conversion shown in table 6) of curves the fuel reactivity at higher pressure is lower than that at lower pressure. On the other hand the effect of pressure on ash sintering is so that at higher pressure ash sintering becomes severer. The ash sintering behavior shown in table 6 is described in figure 17.

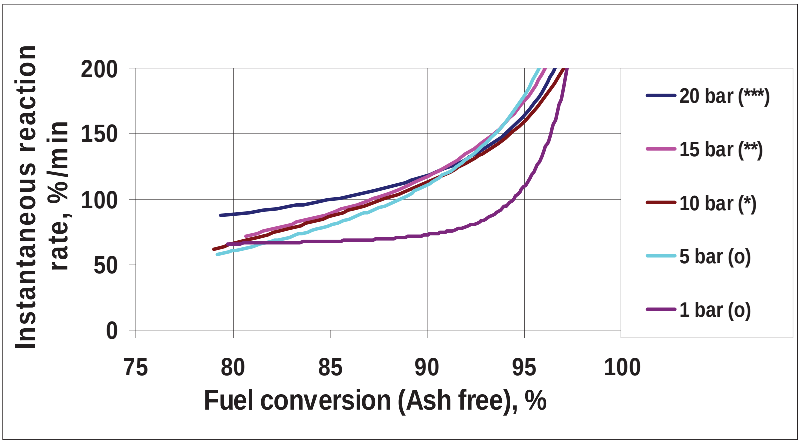


Figure 22: Effect of pressure on fuel reactivity and ash sintering of spruce bark at 850°C with steam (100%) as gasifying medium.

Table 6: Effect of pressure on instantaneous rate of reaction and ash sintering of spruce bark at 850°C with steam (100%) as gasifying medium.

Pressure (bar)	**Instantaneous reaction rate at 90% fuel conversion (%/min)**	**Instantaneous reaction rate at 95% fuel conversion (%/min)**	**Ash sintering**
1	72.8	110	O
5	111.6	180.5	O
10	114.4	160.2	*
15	117.2	176.8	**
20	118.8	165.8	***

The effect of pressure on the time taken for the completion of char conversion is explained by figure 23.

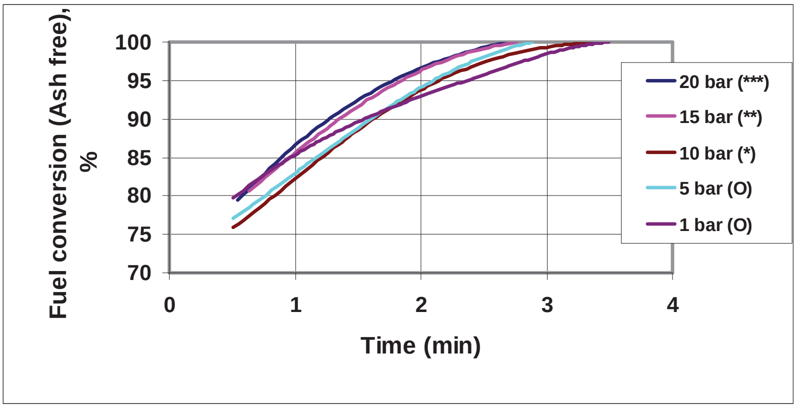


Figure 23: Effect of pressure on time taken for completion of char conversion of spruce bark at 850°C with steam (100%) as a gasifying medium.

With CO_2 as a gasifying medium

The effect of pressure on fuel reactivity, char conversion and ash sintering of spruce bark in the presence of CO_2 as a gasifying medium is so that, by increasing pressure of CO_2 the fuel reactivity is observed to be decreasing. Because reactivity decreases therefore, the char conversion also becomes slower at higher pressure than that at lower one. This is shown in figure 24 and table 7 respectively.

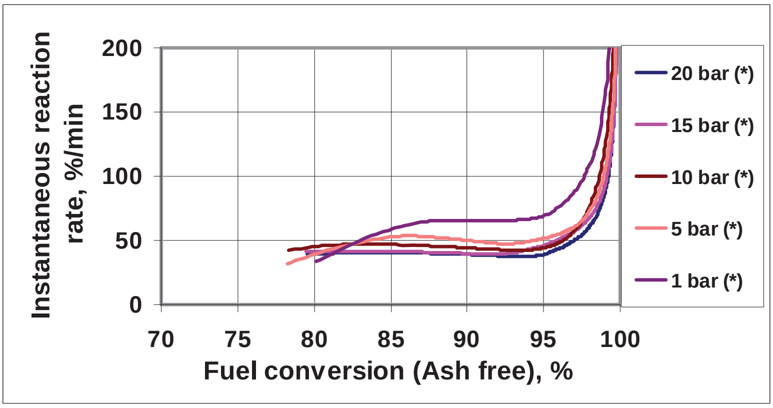


Figure 24: Effect of pressure on fuel reactivity and ash sintering of spruce bark at 850°C with CO_2 (100%) as gasifying medium.

Weak ash sintering is observed at all the given pressures (1–20 bar) and 850°C.

The ash sintering is not increasing here with increase in pressure; it is because at higher pressure the fuel reactivity is decreasing using CO_2 as gasifying medium. The ash sintering behavior shown in table 7 is described in figure 17.

Table 7: Effect of pressure on instantaneous rate of reaction and ash sintering of spruce bark at 850°C with CO_2 (100%) as gasifying medium.

Pressure (bar)	Instantaneous reaction rate at 90% fuel conversion (%/min)	Ash sintering
1	65.4	*
5	49.8	*
10	44.2	*
15	39.7	*
20	39.1	*

On higher pressure it takes more time for 100% char conversion because of slower fuel reactivity as explained below by figure 25.

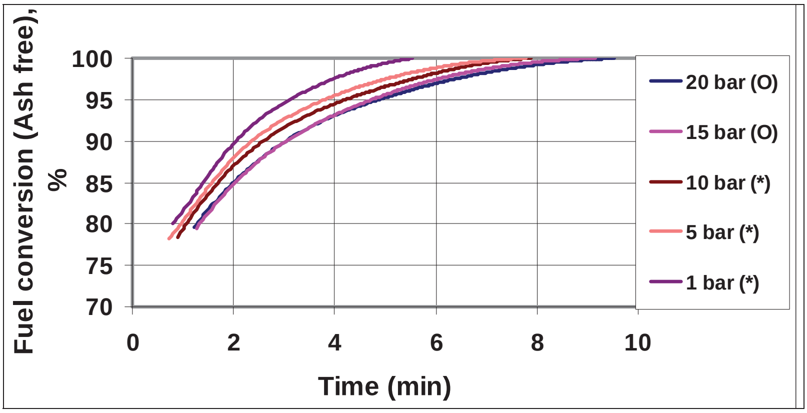


Figure 25: Effect of pressure on time taken for completion of char conversion of spruce bark at 850°C with CO_2 (100%) as a gasifying medium.

- So it can be seen from figure 25 that increase in pressure makes it longer to reach 100% char conversion because reactivity is relatively lower at higher pressures than that at lower ones for CO_2 as a gasifying medium.

7.4.3 Effect of gasifying medium

Mainly, two gasifying mediums have been used in the tests performed here i.e. steam and carbon dioxide (See figure 26.)

- With steam as a gasifying medium, fuel reactivity is higher and completion of char conversion takes lesser time as compared with carbon dioxide as a gasifying medium.
- At higher pressure (15 bar and 20 bar), weak ash sintering is observed with carbon dioxide as a gasifying medium, whereas strong ash sintering is noticed with steam as a gasifying medium.

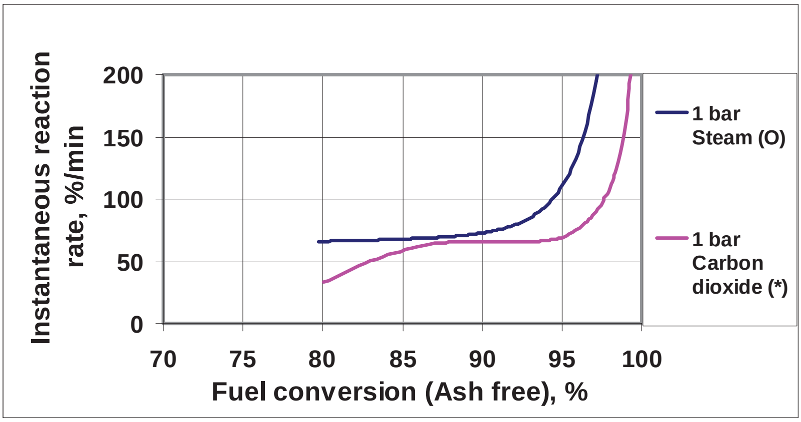


Figure 26: a) Effect of gasifying medium on fuel reactivity and ash sintering of spruce bark at 850°C and 1 bar.

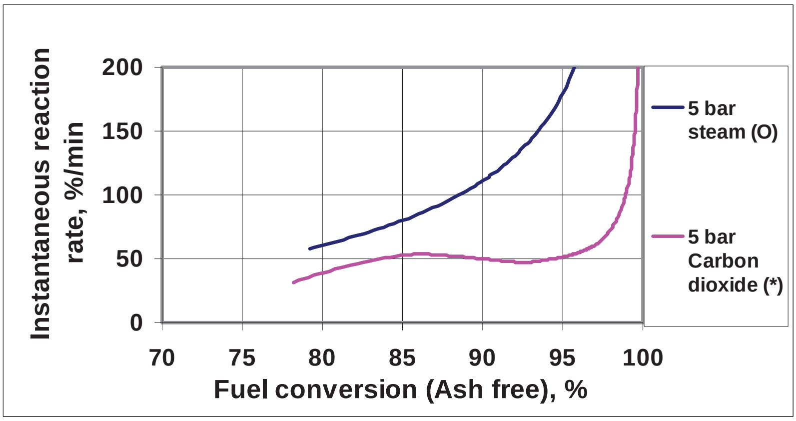


Figure 26: b) Effect of gasifying medium on fuel reactivity and ash sintering of spruce bark at 850°C and 5 bar.

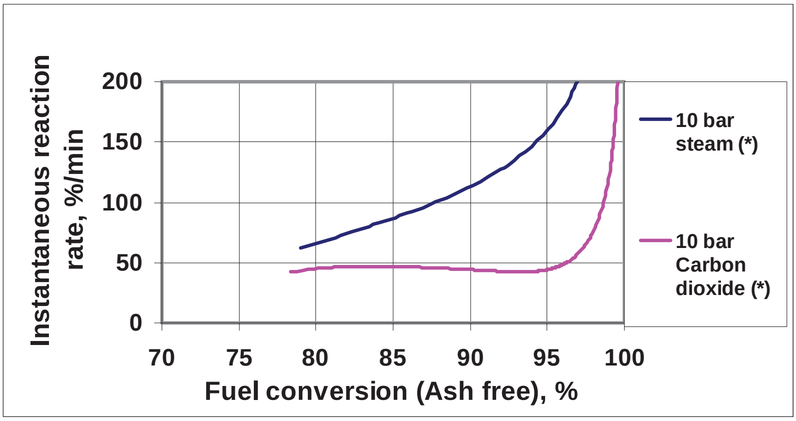


Figure 26: c) Effect of gasifying medium on fuel reactivity and ash sintering of spruce bark at 850°C and 10 bar.

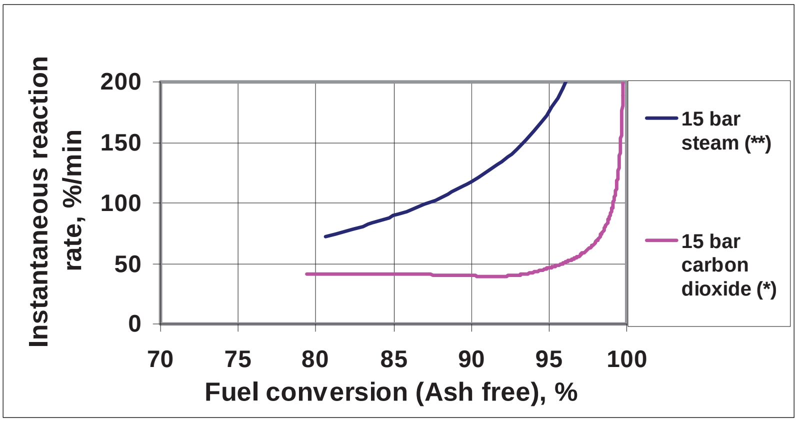


Figure 26: d) Effect of gasifying medium on fuel reactivity and ash sintering of spruce bark at 850°C and 15 bar.

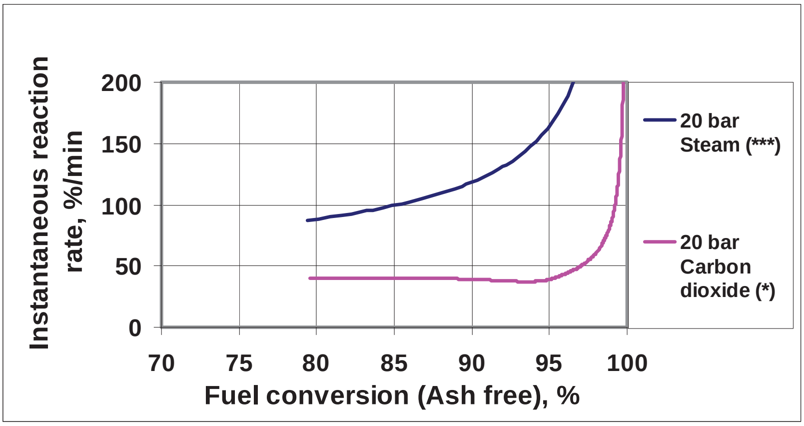


Figure 26: e) Effect of gasifying medium on fuel reactivity and ash sintering of spruce bark at 850°C and 20 bar.

7.5 Effect of type of feedstock (biomass)

It has been observed that gasification characteristics can vary to a great extent between various biomass species [42, 43, 44]. Different barks are tested on same conditions of temperature, pressure and gasifying medium to study the difference in their characteristics. These barks are, aspen bark, birch bark, spruce bark and pine bark, tested at 850°C and atmospheric pressure with steam (100%) as a gasifying medium as shown below by figure 27.

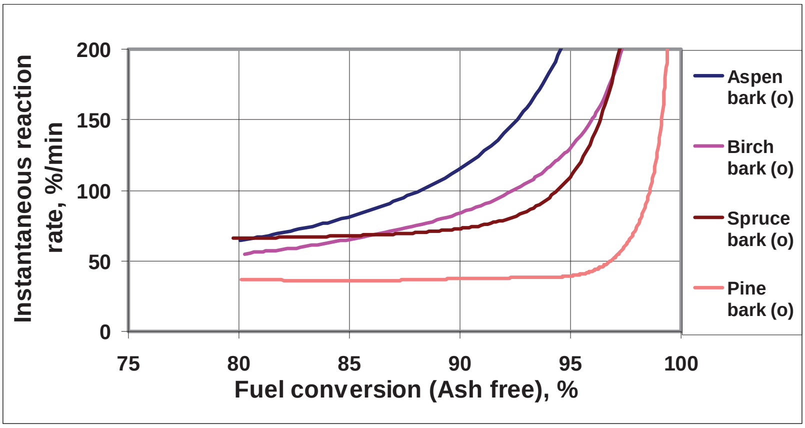


Figure 27: Different barks at 850°C and 1 bar with steam (100%) as gasifying medium.

- Fuel reactivity of aspen bark> birch bark> spruce bark> pine bark

- Whereas no ash sintering is observed for these barks at given conditions

Similarly, difference of characteristics is observed among forest residue, crushed bark mixture and stump chips. This is shown in figure 4 of publication paper according to that,

- Fuel reactivity for crushed bark mixture> forest residue> stump chips
- At the given conditions, ash sintering is observed in stump chips but not in crushed bark mixture and forest residue.

7.6 Same type of biomass collected from different locations

There are characteristics differences in forest biomass harvested at different sites [37]. The difference in the characteristics is observed even in same type of biomass collected from different locations of Finland. This may be because of different growing environment for trees on various locations i.e. climate and the fertility etc. of ground which may affect on internal structure and composition of biomass. This behavior of same type of biomass collected from different locations and tested at same process conditions is shown in figures 5, 6 and 7 of publication paper in Appendix 1 for spruce bark, pine bark and forest residue respectively.

7.7 Variation in ash sintering behavior due to storage, transportation and debarking method of biomass

The general fuel characteristics of biomass feedstock can be affected by harvesting time, biomass growth location, transportation, storage and debarking processes etc. [37]. During storage (outdoor), transportation (through water) and debarking methods of biomass, it remains in contact with (water) for certain period of time, which can cause leaching/extraction of minerals matter (Na, K, Ca, Mg etc.) which are naturally present inside the biomass. To study this behavior of biomass, two tests are performed separately; one with spruce bark gets after normal processes like outdoor storage, and debarked by keeping in contact with water and second spruce bark sample taken directly from spruce tree without these normal processes (storage and debarking). A strong ash sintering is observed at 10 bar and 850°C with steam as gasifying medium for spruce bark taken from tree directly, whereas weak ash sintering is observed for other spruce bark sample collected from plant after those normal processes. But the fuel reactivity is almost same in both the cases. This is also explained by figure 8 of publication paper in Appendix 1.

7.8 Mixing of different feedstocks

At industrial level or at plant scale, normally not one type of biomass is used as a raw material, but it is the mixture of different types. So how does it effect on overall fuel reactivity on mixing different types of biomass in feedstock. The following figure 28 shows the effect of mixing stump chips in spruce bark on fuel reactivity and ash sintering behavior at 850°C and 5 bar.

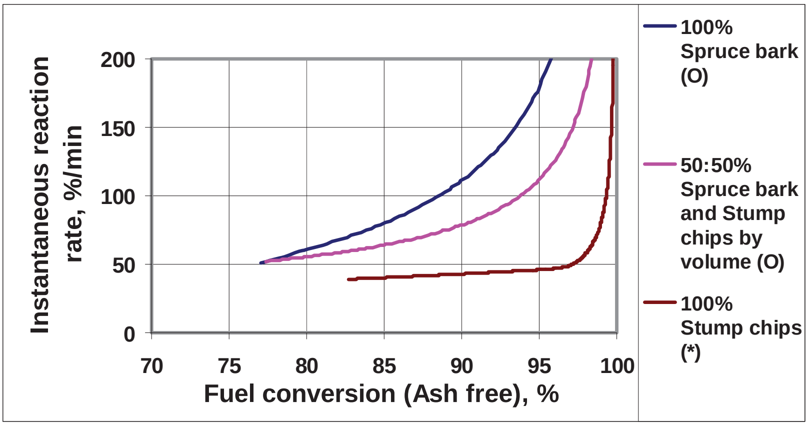


Figure 28: Mixing stump chips in spruce bark at 850°C and 5 bar with steam (100%) as gasifying medium.

7.9 Difference in fuel reactivities of different parts of the same biomass

Two parts of pine bark i.e. pine bark thick and pine bark thin are tested on the same process conditions of temperature, pressure and gasifying medium, a considerable difference is observed in fuel reactivity of both barks. The thick part of pine bark is considerably less reactive than that of thin part as shown in figures 29 and 30 at 850°C and 1 bar and 5 bar respectively. There maybe two explanations for this,

- Since thicker part of pine bark represents the older age cells which are becoming dead and less active and reactive with the passage of time as compared with thin part of the pine bark.
- Secondly, older age part (outer part) of pine bark remains in contact with water for longer time as compared with thin part (inner part), which may cause more leaching and extraction of active catalytic substances present inside the thicker part.

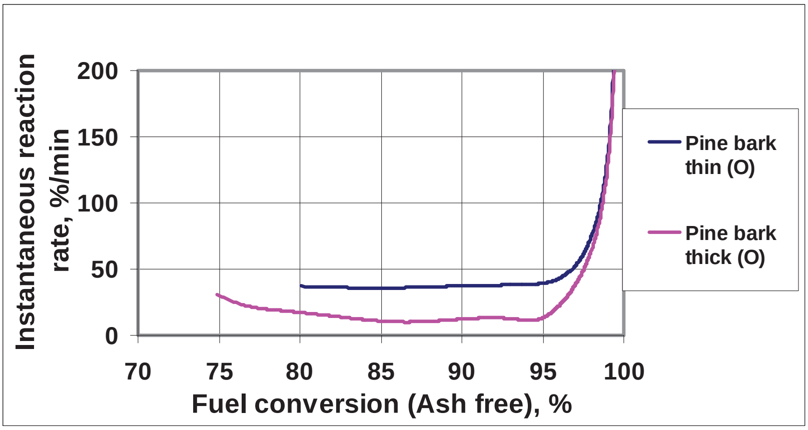


Figure 29: Pine bark thin and pine bark thick at 850°C and 1 bar with steam (100%) as gasifying medium.

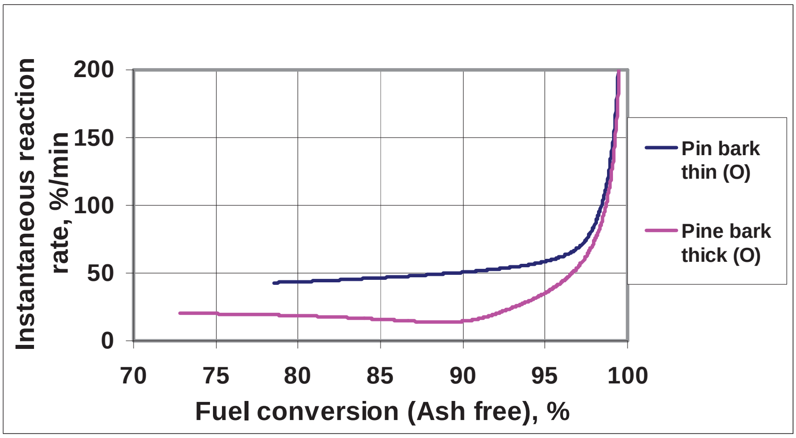


Figure 30: Pine bark thin and pine bark thick at 850°C and 5 bar with steam (100%) as gasifying medium.

8. Inhibition Effect of Product Gas on Biomass gasification

It has been observed that product gas inhibits the gasification reactions in various ways for biomasses [45]. In this work, focus is paid on determining the inhibition effect of product gas on biomass gasification process. This effect is studied here by adding hydrogen (H_2) to steam gasification, carbon monoxide (CO) to carbon dioxide (CO_2) gasification and mixture of all gases (steam+H_2+CO_2+CO). The carbon conversion is influenced by the product gas component since they inhibit the reactivity [44].

8.1 Activation energy of spruce bark

This is the amount of 'energy required for a chemical reaction to take place as a result of which reactants are converted into products'. It can be calculated by Arrhenius equation (20).

$$\ln k = (-E_a / R) 1/T + \ln A \qquad (20)$$

Where,

E_a is the activation energy
R expresses gas constant i.e. 8.314472 J/K mol
T is temperature in Kelvin
k denotes rate coefficient.

A is frequency factor i.e. an empirical relationship between temperature and rate coefficient.

To determine the activation energy of spruce bark, tests are performed at constant pressure but different temperatures. The temperature range is from 700°C to 950°C and pressure is 1 bar. The activation energy is determined by plotting lnr (r is rate measured from tests) against 1/T (in 1/Kelivin). This number (shown in linear equation slope in graphs) is multiplied by R (gas constant) value 8.314 J/K mol and divided with 1 000 to convert the energy value into kJ/mol. The activation energy calculated of spruce bark is 211.8kJ/mol as shown in figure 31.

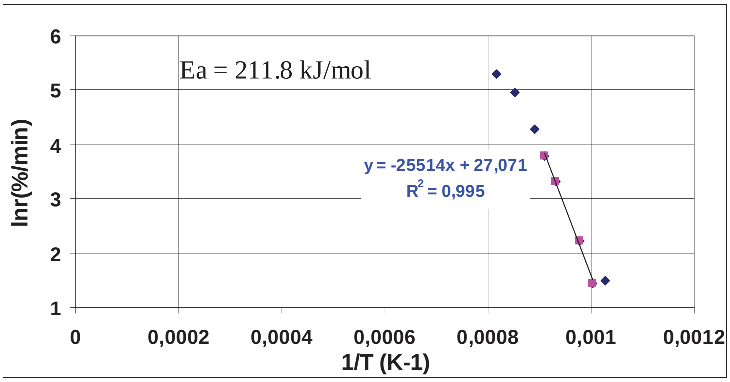


Figure 31: Calculation of activation energy of spruce bark at atmospheric pressure.

8.2 Inhibition effect on steam gasification by adding hydrogen (H_2) gas

It is observed that the presence of hydrogen gas inhibits the process of biomass gasification in the gasifier. This inhibition effect is studied here by adding hydrogen gas into steam gasification. The reactivity and char conversion are observed lesser with hydrogen addition as compared with steam (100%) gasification. The figure 32 explains this inhibition effect due to the presence of hydrogen.

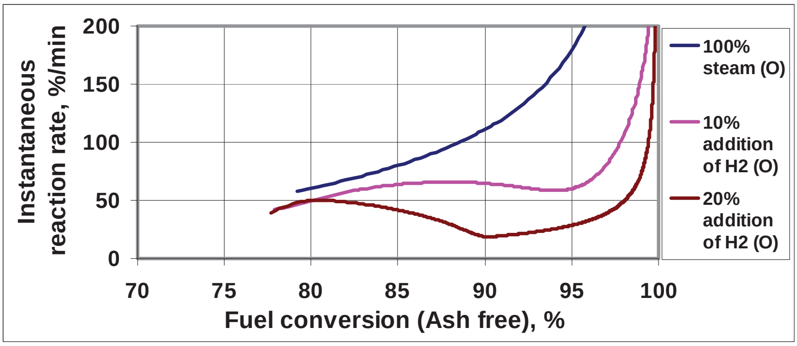


Figure 32: Inhibition effect of H_2 to steam gasification on spruce bark at 850°C and 5 bar.

Figure 33 explains this inhibition on char conversion with respect to time.

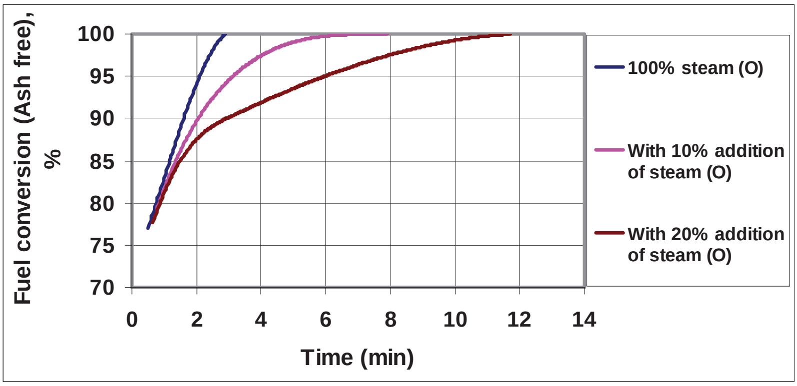


Figure 33: Inhibition effect of H_2 to steam gasification on time taken for complete charconversion of spruce bark at 850°C and 5 bar.

Figure 33 shows that due to the presence of hydrogen the fuel reactivity becomes slower and it takes longer time for the 100% completion of char as compared with steam (100%) gasification.

The inhibition effect of hydrogen gas (H_2) to steam gasification is also explained by figure 34. This shows the effect of partial pressure of H_2 on fuel reactivity in the steam gasification of spruce bark. The process conditions for these tests are 850°C and 5 bar (total pressure). The nitrogen is used as an inert gas.

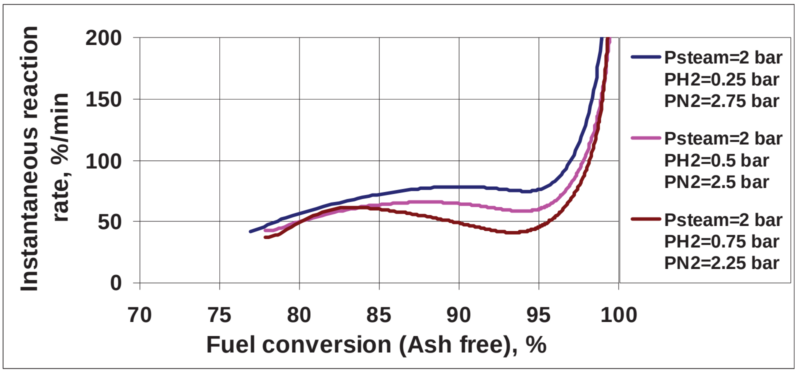


Figure 34: Inhibition effect of H_2 in steam gasification on fuel reactivity of spruce bark at 850°C and 5 bar (total pressure).

8.3 Inhibition effect on CO_2 gasification by adding CO

The inhibition effect of CO to CO_2 gasification is studied by adding 20% and 30% CO to CO_2 gasification. The fuel reactivity is lesser in case of 20% and 30% addition of CO respectively as compared with CO_2 (100%) as gasifying medium as shown by figure 35.

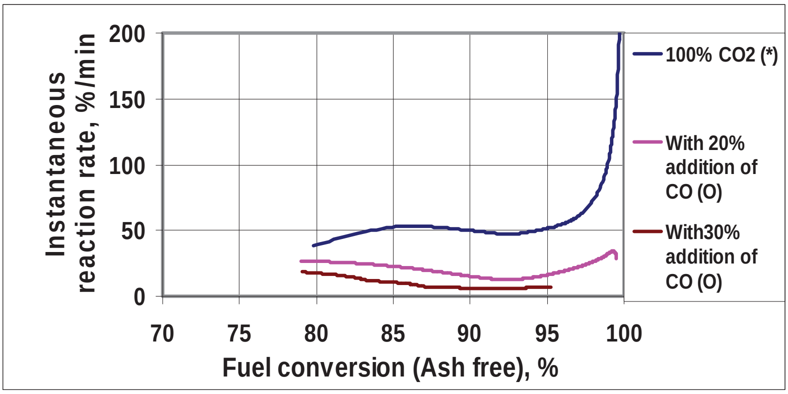


Figure 35: Inhibition effect of CO to CO_2 gasification on spruce bark at 850°C and 5 bar.

The presence of CO during gasification process makes the fuel reactivity slower, because of which it takes longer time for the completion of char conversion, figure 36 shows this.

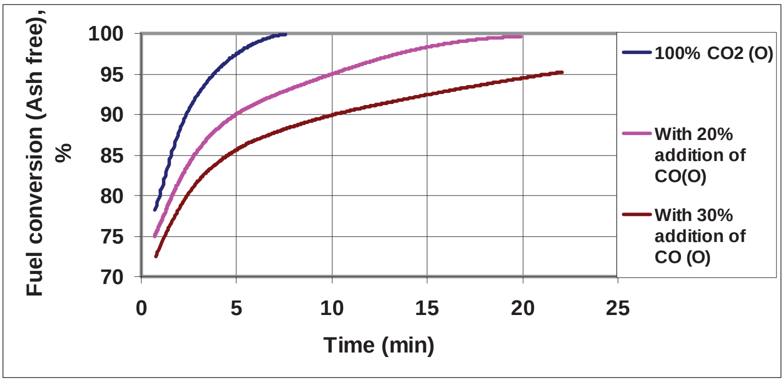


Figure 36: Inhibition effect of CO to CO_2 gasification on time taken for complete char conversion of spruce bark at 850°C and 5 bar.

The inhibition effect of CO to CO_2 gasification is also explained by figure 37. This shows the effect of partial pressure of CO on fuel reactivity in the CO_2 gasification of Spruce bark. The process conditions for these tests are 850°C and 5 bar (total pressure). The nitrogen is an inert gas used here for dilution of gases.

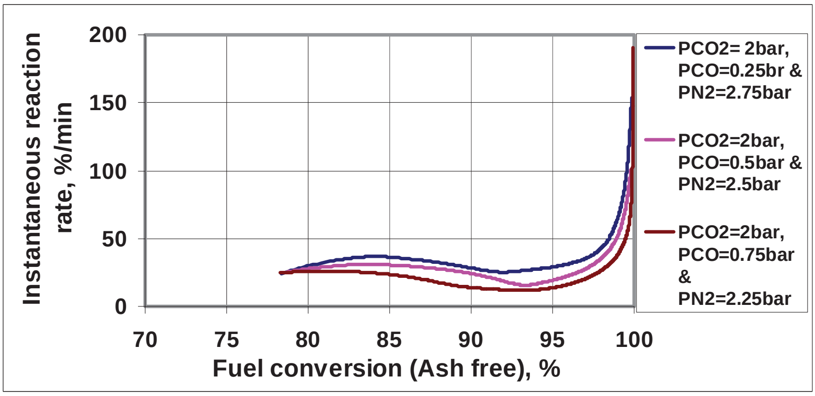


Figure 37: Inhibition effect of H_2 in steam gasification on fuel reactivity of spruce bark at 850°C and 5 bar (total pressure).

8.4 Effect of temperature and pressure on biomass gasification in the presence of product gas

To study effect of temperature and pressure on biomass gasification in the presence of product gas/gas mixture, product gas (H_2 + CO) is added along with steam and CO_2 in the thermobalance. This situation is closer to large scale gasification, where the gas mixture (steam, H_2, CO_2 and CO) is present in the gasifier. The effect of temperature on spruce bark at 1.5 bar steam, 1 bar H_2, 1.25 bar CO_2, 0.75 bar CO and 0.5 bar N_2 (5 bar total pressure) and varying temperature in the presence of product gas is shown by figure 38. The composition of product gas used her is 30% steam, 20% H_2, 25% CO_2, 15% CO and 10% N_2.

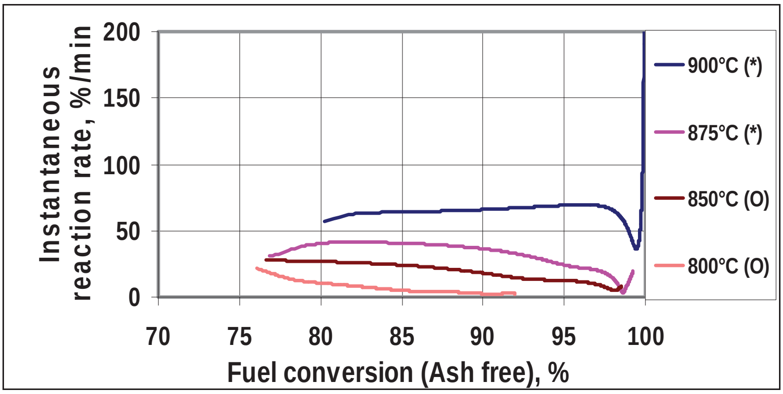


Figure 38: Spruce bark at 5 bar (1.5 bar steam, 1 bar H_2, 1.25 bar CO_2, 0.75 bar CO and 0.5 bar N_2) and varying temperature in the presence of product gas.

Similarly, figure 39 shows the effect of pressure on spruce bark at 875°C. The composition of product gas is 30% steam, 20% H_2, 25% CO_2, 15% CO and 10% $N_{2,}$ varying pressures i.e. 1 bar, 5 bar, 10 bar, 15 bar and 20 bar respectively.

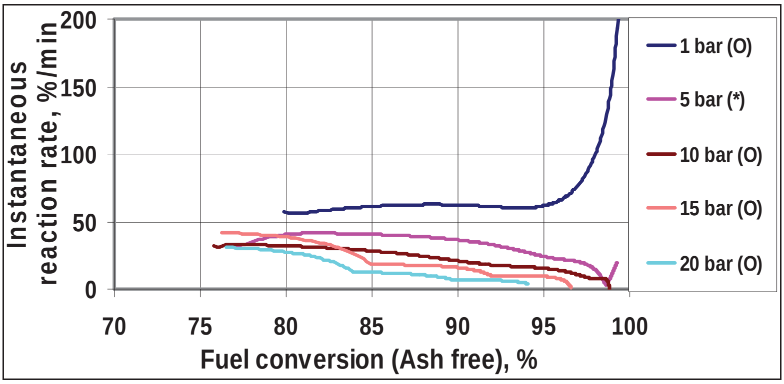


Figure 39: Spruce bark at 875°C with varying total pressure in the presence of product gas.

As shown in figure 39 that by increasing pressure, fuel reactivity decrease in the presence of gas product gas or gas mixture therefore, slow reactivity causes delay in completion of char conversion with respect to time, it is shown in figure 40.

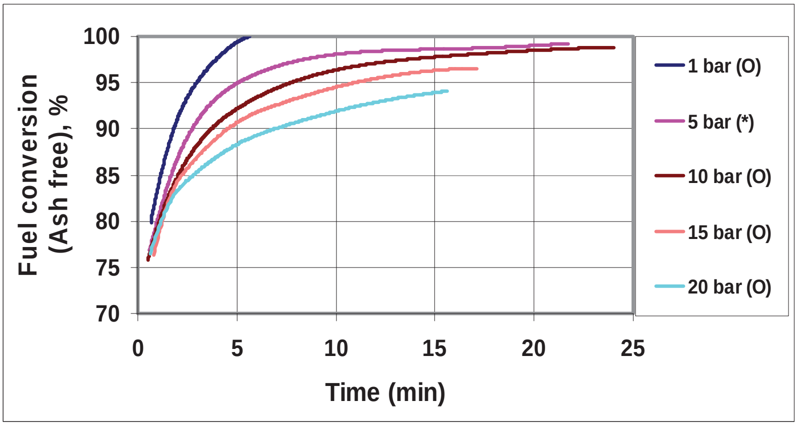


Figure 40: Effect of pressure time taken for complete char conversion of spruce bark at 875°C in the presence of product gas.

The effect of pressure at constant temperature in the presence of product gas on fuel reactivity, char conversion and ash sintering behavior of spruce bark is found very interesting. It is so that by increasing pressure, fuel reactivity decreases (as shown by figure 39) as a result of slower fuel reactivity it takes longer time for the completion of char conversion even (as shown in figure 40). Since, at higher pressures reactivity is slower, so no ash sintering is observed at higher pressures in the presence of product gas.

There can be different reasons for this interesting behavior of spruce bark of decreasing reactivity with the increase in pressure at constant temperature in the presence of product gas as explained.

- As the total pressure (process pressure) increases, the partial pressures of steam, CO_2, H_2 and CO also increases in the process. It has been experimentally observed that H_2 and CO inhibit the gasification process; even increasing partial pressure of CO_2 seemed to have inhibiting effect on gasification process. So, except steam the other gases (CO_2, CO and H_2) are inhibiting the gasification process as their partial pressures increase. Therefore, by in creasing total process pressure, the net effect on gasification is of inhibition which causes slower down the fuel reactivity and char conversion also.
- The alkali and earth alkaline metals naturally present in the biomass in the form of compound of calcium, potassium, magnesium, aluminium and silicon including small amount of nitrogen and phosphorus play a significant role during the gasification process. Detailed study is required to predict their role and behaviour in the biomass gasification process.

8.5 Different type of feedstock in the presence of product gas

Different types of barks are tested at 850°C and 1 bar to study how they differ in their characteristics in the presence of product gas. Their fuel reactivities are observed in the order of aspen bark>

spruce bark> birch bark > pine bark. This is shown in figure 11 of publication in appendix 1, no ash sintering is observed for these barks at the given conditions of temperature, pressure and gasifying medium.

8.6 Rate (char gasification reactivity of spruce bark) calculations for model and comparison with measured values

The rate calculations for gasification of spruce bark are done by using Langmuir-Hinshelwood and Arrhenius equations. The rate constants r_1 to r_6 are calculated by using Arrhenius equation. According to Arrhenius equation (21),

$$r = ke^{-E/RT} \tag{21}$$

Where,

r is the rate constant
k is rate coefficient
E is expresses activation energy
R is the gas constant
T is temperature in Kelvin.

The value of rate constant r can be replaced in equations (10), (11), (15), (16) and (11). By replacing r values the following equations (22), (23), (24), (25) and (26) are obtained for rate calculation for different values of temperature and pressure.

Steam gasification: $$r_s = \frac{k_1 e^{-E_1/RT} * P_{H_2O}}{1 + k_2 e^{-E_2/RT} * P_{H_2O}} \tag{22}$$

Steam + H_2 gasification: $$r_s = \frac{k_1 e^{-E_1/RT} * P_{H_2O}}{1 + k_2 e^{-E_2/RT} * P_{H_2O} + k_3 e^{-E_3/RT} * P_{H_2}} \tag{23}$$

CO_2 gasification: $$r_s = \frac{k_4 e^{-E_4/RT} * P_{CO2}}{1 + + k_5 e^{-E_5/RT} * P_{CO_2}} \tag{24}$$

CO_2 + CO gasification: $$r_s = \frac{k_4 e^{-E_4/RT} * P_{CO2}}{1 + + k_5 e^{-E_5/RT} * P_{CO_2} + k_6 e^{-E_6/RT} * P_{CO}} \tag{25}$$

Gas mixture (steam+CO_2+H_2+CO) gasification:

$$r_s = \frac{k_1 e^{-E_1/RT} * P_{H_2O} + k_4 e^{-E_4/RT} * P_{CO2}}{1 + k_2 e^{-E_2/RT} * P_{H_2O} + k_3 e^{-E_3/RT} * P_{H_2} + k_5 e^{-E_5/RT} * P_{CO_2} + k_6 e^{-E_6/RT} * P_{CO}} \tag{26}$$

A Langmuir-Hinshelwood equation based model is formed here which holds for different temperatures i.e. 800°C to 900°C and pressures i.e. 5 bar to 20 bar. The values of k_1 to k_6 and E_1 to E_6 are determined graphically from data collected from measurements and by iterations with solver in MS Excel. These values are given in table 25.

Table 25: Values of rate coefficients and activation energy calculated by iteration method.

Rate coefficients		**Activation Energy (kJ/mol)**	
k_1	7.48E+12	E_1	306.285
k_2	5.12E+09	E_1	201.812
k_3	1.22E-09	E_1	-214.046
k_4	-1053.633557	E_1	115.512
k_5	-0.000136566	E_1	-80.198
k_6	-3.22803E-22	E_1	-474.986

8.6.1 Comparison of measured and calculated values of char gasification reactivity for steam and steam + H_2 gasification of spruce bark

The calculated rates are compared with measured rates both at 90% of fuel conversion for steam gasification and steam + H_2 gasification in figure 41 and 42 respectively. At 90% of fuel conversion, the char conversion is at about half way i.e. 50% completes. It is taken as reference for comparison of measured and calculated rate values.

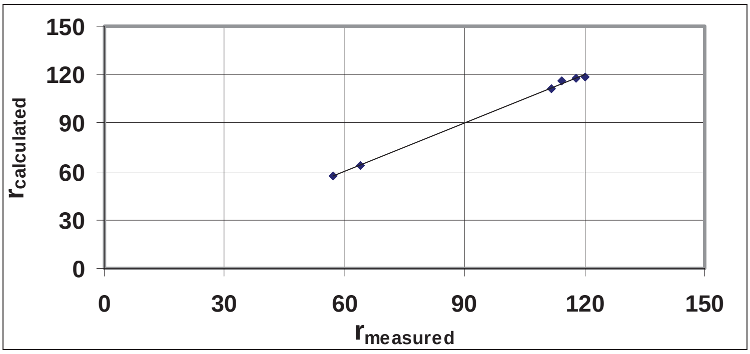


Figure 41: Comparison of measured and calculated char gasification rates for steam gasification of spruce bark.

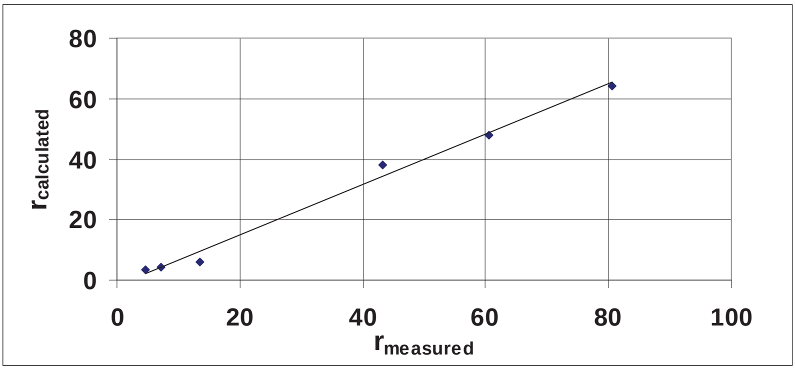


Figure 42: Comparison of measured and calculated char gasification rates for steam + H_2 gasification of spruce bark.

The calculated rate values match with measured ones very well for steam gasification as shown in figure 41, but for steam + H_2 gasification vary to some extent at some points and match well on most of the points as shown in figure 42.

8.6.2 Comparison of measured and calculated values of char gasification reactivity for CO_2 and CO_2 + CO gasification of spruce bark

The comparison of calculated and measured rates for CO_2 and CO_2 + CO gasification is given in figures 43 and 44 respectively.

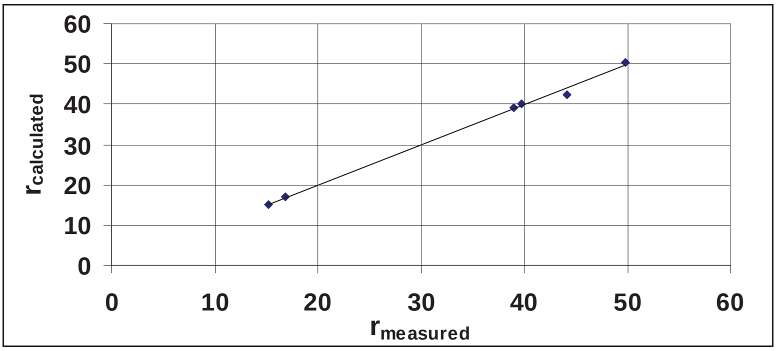


Figure 43: Comparison of measured and calculated rates for CO_2 gasification of spruce bark.

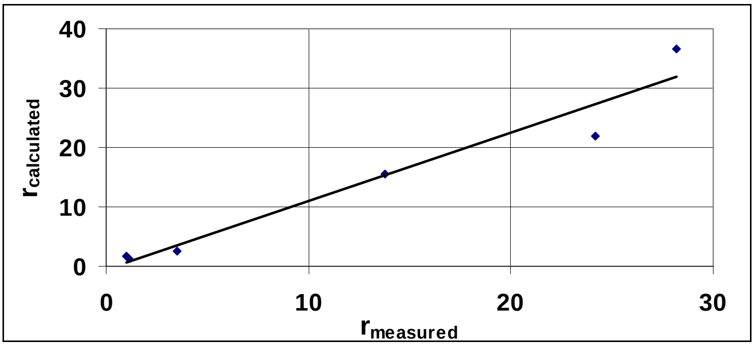


Figure 44: Comparison of measured and calculated rates for CO_2 + CO gasification of spruce bark.

For CO_2 and CO_2 + CO gasification the calculated rate values fit well with the measured ones.

8.6.3 Comparison of measured and calculated values of char gasification reactivity for gas mixture (steam+CO_2+H_2+CO+N_2) gasification of spruce bark

The presence of gas mixture during gasification process also reveals the inhibition effect of product gas (H_2 + CO). The comparison of calculated and measured rates for gas mixture gasification is shown in figure 45. This can be observed from figure 45 that values of rate calculated and measured are not the same on different points but also fit well on some points. This is because of the unpredictable behavior of biomass gasification on the application of pressure which needs to be studied further in detail. It also includes the role of alkaline and earth-alkaline metals (Na, k, Ca, Mg, Al, and Si etc.) naturally present in the biomass on gasification process.

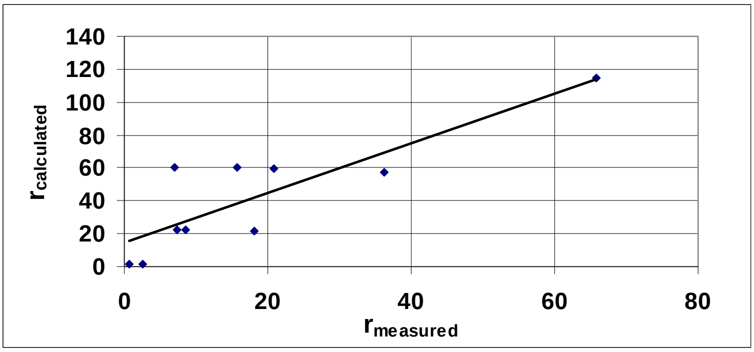


Figure 45: Comparison of measured and calculated rates for gas mixture (steam + CO_2 + H_2 + CO) gasification of spruce bark.

The figure 45 shows that calculated and measured rates are fitting well on some points but also varying to some extent on other points.

9. Block Model Approach for CFBG and Effect of Process Parameters to Improve char conversion in the gasifier

The model developed for calculating char gasification reactivity of biomass in fluidized bed gasifier will be used in future to make further a block model for gasifier.

The concentration of gas mixture and specifically of product gas varies in different sections of circulated fluidized bed gasifier during gasification process. To understand the variation in concentration of gas mixture with the length or height of gasifier, it is important to study the different phenomena like, flow structure in a circulated fluidized bed, mechanism of gasification reactions in the gasifier, temperature and pressure profile in the gasifier, fragmentation of particles, completion of char reactivity and time required for complete conversion in the gasifier. There are two different prominent zones in the reactor or circulated fluidized bed combustor, the dense bed at the bottom and dilute bed above it. The flow conditions in the dense bed can be compared with bubbling fluidized bed. The gas solid phase can be divided into two phases i.e. bubble phase and emulsion phase [45]. The axial riser flow profile is shown in figure 46.

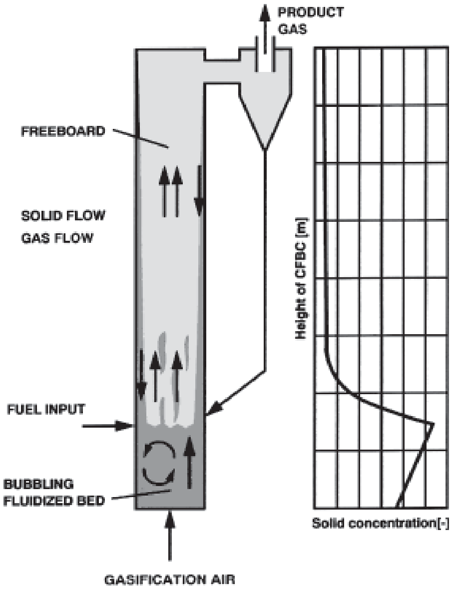


Figure 46: Axial solid concentration in a circulating fluidized bed reactor [45].

Figure 47 shows the temperature and pressure drop profile with the height of circulated fluidized bed combustor.

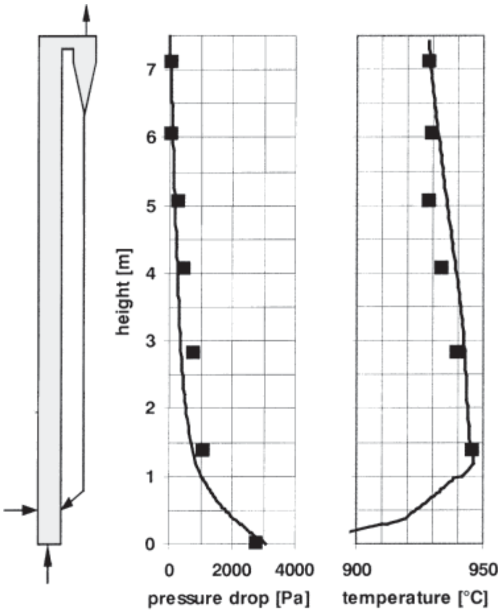


Figure 47: Comparison between measured (points) and calculated (curves) pressure drop pressure drop and temperature in the circulating fluidized bed reactor [45].

9.1 Gasification reactions [45]

The gasification reactions take place in the gasifier can be divided into four steps.

Primary pyrolysis:

In primary pyrolysis wood (biomass) is converted into primary tar, H_2O, CO_2, CO, CH_4, C_2H_4 and carbon (C) or char.

Secondary pyrolysis:

Here, primary tar is converted into secondary tar, CO, CO_2, C_2H_4, CH_4 and H_2.

Gas phase reactions:

After pyrolysis, gas phase reactions start in which following reactions take place.

$CO + 0.5O_2 \rightarrow CO_2$
$H_2 + 0.5O_2 \rightarrow H_2O$
$CO_2 + H_2 \leftrightarrow CO + H_2O$
Secondary tar → C, CO, H_2

Solid phase reactions:

Carbon/char reacts with gases in gas-solid phase reactions.

$C + O_2 \rightarrow CO_2$
$C + CO_2 \rightarrow 2CO$
$C + H_2O \rightarrow CO + H_2$
$C + 2H_2 \rightarrow CH_4$
$CH_4 + H_2O \rightarrow CO + 3H_2$

9.2 Fragmentation and particle size distribution in the gasifier

Particle size distribution and fragmentation of particles affect on gasification process. Figure 48 shows the behavior of different particles in the furnace (reactor) according to their sizes. The trajectory or location of feed input can be optimized to increase the residence time of char particle in the gasifier for better conversion.

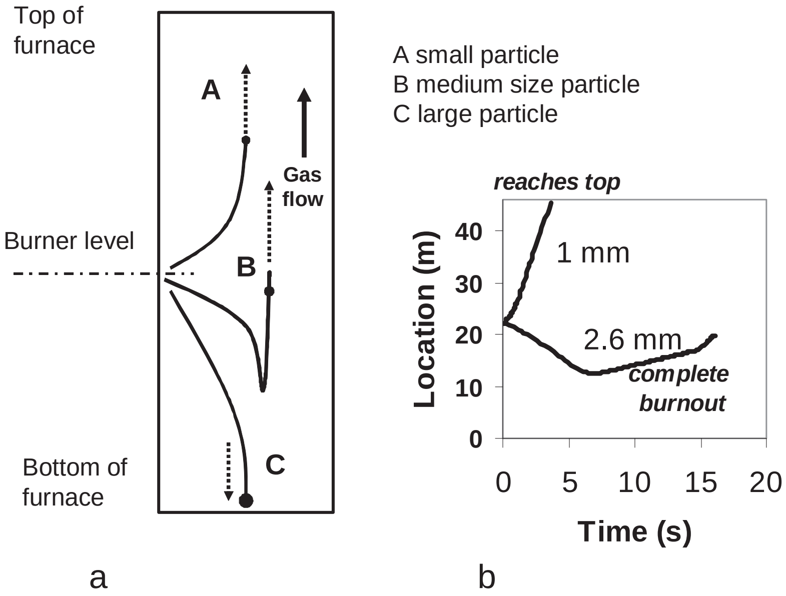


Figure 48: a) Schematic trajectories in the furnace, b) Vertical locations of two burning particles with different sizes in the furnace [46].

The effect of particle size on char conversion is so that lesser the size of particle, char conversion completes in shorter time and vice versa. For smaller particles, diffusion rate is faster than that of in larger particles. The influence of particle diameter on changes in the conversion rate is explained by figure 49.

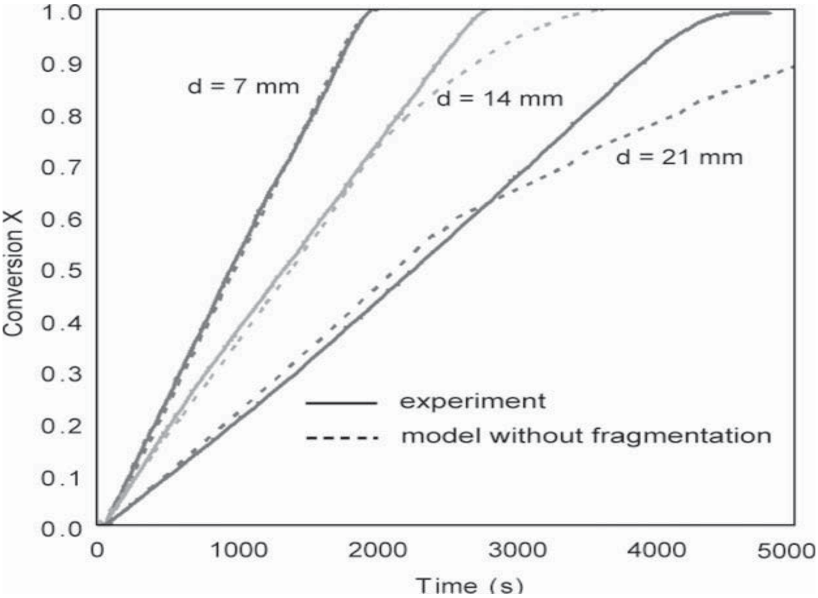


Figure 49: Influence of particle diameter on changes in the conversion rate (T= 930°C, P_{H2O} = 0.2 bar) [47].

In this figure, solid lines describe experimental values and the other (- - -) to model without fragmentation.

9.3 Behavior of completion of carbon/char conversion with respect to time

The tests performed in thermobalance with spruce bark in the presence of product gas/gas mixture (steam + CO_2 + H_2 + CO) also describe the behavior of char conversion with respect to time. This behavior can be observed form following figure 50.

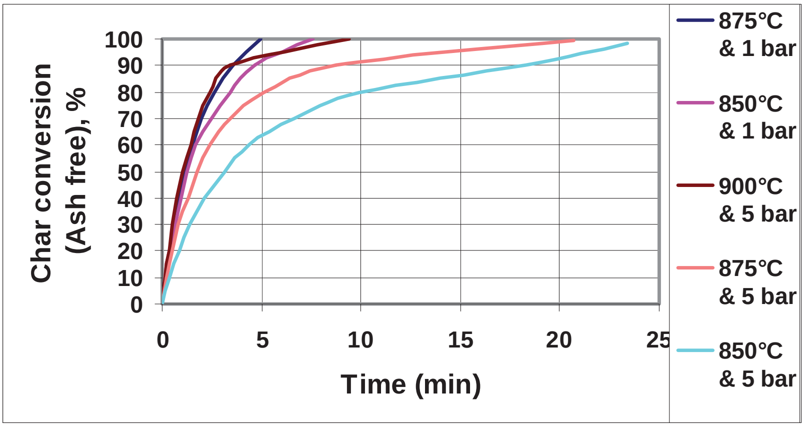


Figure 50: Char conversion of spruce bark with respect to time at different temperatures and pressures (total and partial) in the presence of gas mixture (steam + CO_2 + H_2 + CO). 1 bar (0.3 bar steam, 0.2 bar H_2, 0.25 bar CO_2, 0.15 bar CO and 0.1 bar N_2) and 5 bar (1.5 bar steam, 1 bar H_2, 1.25 bar CO_2, 0.75 bar CO and 0.5 bar N_2)

- ➢ It can be observed from graph 33 that the rate of char conversion varies during gasification process with respect to time. Initially, the conversion of char takes place quickly but later becomes slow, especially after 80% and 90% conversion it becomes very slow. A comparison of char conversion rate is given in table 26 for every 10% of conversion with respect to time.

Table 26: Comparison of every 10% of char conversion measured during gasification process of spruce bark at different temperatures (850°C, 875°C and 900°C) and pressures i.e. 1 bar (0.3 bar steam, 0.2 bar H_2, 0.25 bar CO_2, 0.15 bar CO and 0.1 bar N_2) and 5 bar (1.5 bar steam, 1 bar H_2, 1.25 bar CO_2, 0.75 bar CO and 0.5 bar N_2).

Char conversion Ash free, %	0–10	10–20	20–30	30–40	40–50	50–60	60–70	70–80	80–90	90–100	Total time (min)
Time req. at 850°C & 1 bar (min)	0.16	0.2	0.3	0.3	0.3	0.4	0.8	1.0	1.2	2.9	7.56
Time req. at 850°C & 5 bar(min)	0.4	0.5	0.5	0.7	1.0	1.3	2.2	3.3	8.4	6.7	25
Time req. at 875°C & 1 bar (min)	0.14	0.25	0.25	0.3	0.3	0.4	0.4	0.7	0.9	1.4	5.04
Time req. at 875°C & 5 bar (min)	0.22	0.3	0.3	0.5	0.4	0.7	1.0	1.7	3.6	12	20.72
Time req. at 900°C & 5 bar (min)	0.17	0.16	0.2	0.2	0.3	0.4	0.4	0.6	1	6	9.43

According to table 26, the rate of char conversion decreases as gasification progresses. The second last column of the table 26 shows that the conversion of char from 90–100% takes longer time as compared with conversion at previous stages (before 90%). It is interesting to know the reason of this kind of behavior of char conversion.

9.4 Variation of gases (steam, CO_2, H_2, CO) concentration with the height of gasifier

The production and concentration of gases in the gasifier depend on the chemical reactions (pyrolysis, gas phase and gas-solid phase) taking place during biomass gasification process. The transformation of solid fuel into gaseous form is also based on the extent of char conversion in the gasifier. In the dense (bottom) section of gasifier different reactions take place simultaneously, pyrolysis of biomass takes place after that gas-phase reactions start then absorption and desorption processes of gases with solid char occure and gas-solid phase reactions take place according to Langmuir-Hinshelwood equation. The amount of oxygen is consumed to maximum extent in the dense or bottom section of the gasifier. The figure 51 shows the concentration of different gases including product gas (CO + H_2) in different section of gasifier/combustor. More variation takes place in the concentration of gases at the bottom section of gasifier as compared with upper one i.e. freeboard section.

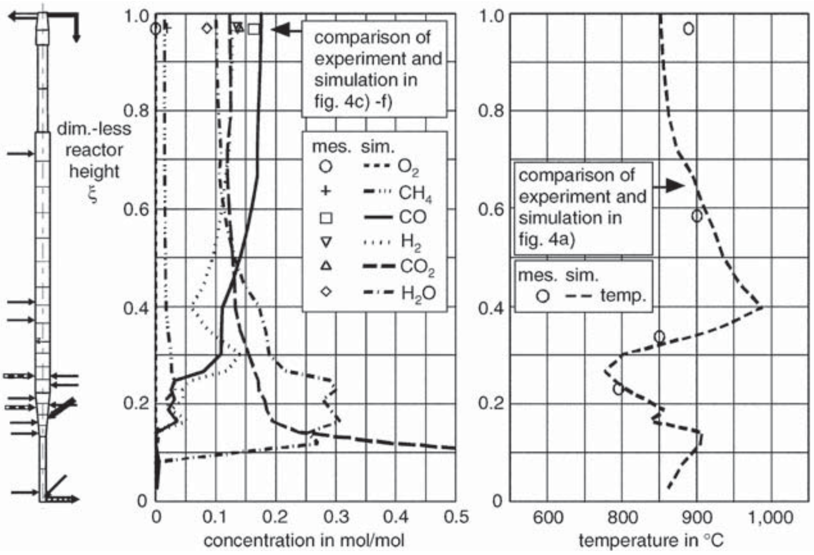


Figure 51: Calculated results in comparison with experimental data of air/ steam gasification of the HTW pressurized gasification reactor [48].

More variation in the concentration of different gases can be assumed in the lower section of gasifier than that of in upper one as shown in figure 51. The right side section of figure 51 shows the temperature profile in the gasifier.

10. Summary

In first section of experimental part of this thesis, thermogravimetric characteristics of different biomass types (different barks, forest residue, stump chips etc.) are studied at different process conditions using steam and carbon dioxide separately as gasifying mediums. Thermogravimetric characteristics of biomass are studied in terms of effects of different parameters like temperature, partial pressure of gasifying components on char reactivity, char conversion and ash sintering behavior of biomass in the gasification process.

In steam (100%) gasification, it is observed that by increasing process temperature at constant pressure, fuel/char reactivity increases and completion of char conversion takes place in relatively lesser time. On the other hand, the chances of ash sintering become more with the increase in temperature. By increasing total pressure, fuel/char reactivity normally increases but unpredictably starts decreasing at some stages of gasification and ash sintering is observed at higher pressure also.

In CO_2 (100%) gasification, the char reactivity increases with the increase in temperature at constant pressure as in steam gasification. But interestingly, by increasing pressure at constant temperature the fuel/char reactivity is observed to be decreasing for all the tests performed in this regard. It seems that maybe the presence of CO_2 inhibits the gasification process. Weak ash sintering is observed at different pressures.

In the presence of gas mixture (steam+CO_2+H_2+CO) gasification, the effect of temperature at constant pressure is same as in case of steam (100%) gasification and CO_2 (100%) gasification i.e. fuel/char reactivity increases by increasing temperature and completion of char conversion takes lesser time at higher temperature than that at lower one and probability of ash sintering becomes more at higher temperature. But by increasing total pressure at constant temperature, fuel/char reactivity decrease and completion of char conversion takes longer time than that at lower pressure. So, the optimum conditions of temperature and pressure for biomass gasification can be those at which fuel/char reactivity is higher with no or very weak as sintering/melting.

The variation in fuel/char reactivity of different types of biomass has been observed at same process conditions. For example, reactivities of different barks are measured in the order of Aspen bark>Spruce bark>Birch bark>Pine bark and similarly reactivity of forest residue>stump chips. The reactivity difference is also observed in different parts of same plant or biomass for example, fuel/char reactivity of thin part of pine bark> thick part of pine bark.

In second section, inhibition effect of product gas on biomass gasification is studied by adding H_2 to steam gasification and CO to CO_2 gasification and finally by adding H_2 and CO to gas mixture i.e. steam+CO_2+H_2+CO. This is observed that presence of product gas (H_2+CO) inhibits the biomass gasification process in the gasifier.

In the third section, a mathematical model is developed to calculate char gasification reactivity for biomass in the fluidized bed gasifier. The model fits well for single and binary gases gasification but does not fit well with the gas mixture. The significance of different parameters on completion of char conversion like process conditions, location and trajectory of biomass particles input and location of oxygen/air supplied and char particles retuning back to gasifier in circulated fluidized bed gasifier are also studied and described in this section.

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Appendix

Nasrullah, M., & Moilanen, A., Variation in fuel reactivity and ash characteristics of biomass feedstock for large-scale gasification, Proceedings of the 17th European Biomass Conference and Exhibition, Hamburg 2009.

Series title, number and
report code of publication

VTT Publications 769
VTT-PUBS-769

Author(s)
Antero Moilanen & Muhammad Nasrullah

Title

Gasification reactivity and ash sintering behaviour of biomass feedstocks

Abstract

Char gasification reactivity and ash sintering properties of forestry biomass feedstocks selected for large-scale gasification process was characterised. The study was divided into two parts: 1) Internal variation of the reactivity and the ash sintering of feedstocks. 2) Measurement of kinetic parameters of char gasification reactions to be used in the modelling of a gasifier. The tests were carried out in gases relevant to pressurized oxygen gasification, i.e. steam and carbon dioxide, as well as their mixtures with the product gases H_2 and CO. The work was based on experimental measurements using pressurized thermobalance. In the tests, the temperatures were below 1000 ˚C, and the pressure range was between 1 and 20 bar. In the first part, it was tested the effect of growing location, storage, plant parts and debarking method. The following biomass types were tested: spruce bark, pine bark, aspen bark, birch bark, forestry residue, bark feedstock mixture, stump chips and hemp. Thick pine bark had the lowest reactivity (instantaneous reaction rate 14%/min) and hemp the highest (250%/min); all other biomasses lay between these values. There was practically no difference in the reactivities among the spruce barks collected from the different locations. For pine bark, the differences were greater, but they were probably due to the thickness of the bark rather than to the growth location (see Ch. 3.4). For the spruce barks, the instantaneous reaction rate measured at 90% fuel conversion was 100%/min for pine barks it varied between 14 and 75%/min. During storage, quite large local differences in reactivity seem to develop. Stump had significantly lower reactivity compared with the others. No clear difference in the reactivity was observed between barks obtained with the wet and dry debarking, but, the sintering of the ash was more enhanced for the bark from dry debarking. Char gasification rate could not be modelled in the gas mixture of H_2O + CO_2 + H_2 + CO, similarly as it can be done for coal. The reasons were assumed to be that in the carbon dioxide gasification, the gasification rate was negatively dependent on the CO_2 pressure, the opposite of what is observed in steam gasification and the dependence of the gasification reaction rate on the conversion had three patterns. Normally it increases with the conversion, but it may also decrease or go through a minimum. According to the sintering tests, the ash residues were not totally sintered but they consisted of molten particles (spheres), unreacted char particles and powdery ash. The strongest sintering was observed for hemp, spruce bark obtained by dry debarking, and aspen bark. Increased pressure and CO_2 resulted in intensified sintering, as has been observed in earlier studies.

ISBN
978-951-38-7748-4 (soft back ed.)
978-951-38-7749-1 (URL: http://www.vtt.fi/publications/index.jsp)

Series title and ISSN
VTT Publications
1235-0621 (soft back ed.)
1455-0849 (URL: http://www.vtt.fi/publications/index.jsp)

Project number

Date
December 2011

Language
English

Pages
39 p. + app. 96 p.

Name of project

Commissioned by

Keywords
Biomass, fuel, gasification, reactivity, ash, sintering, pressure, bio diesel

Publisher
VTT Technical Research Centre of Finland
P.O. Box 1000, FI-02044 VTT, Finland
Phone internat. +358 20 722 4520
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ISSN 1235-0621 (soft back ed.)
ISBN 978-951-38-7749-1 (URL: http://www.vtt.fi/publications/index.jsp)
ISSN 1455-0849 (URL: http://www.vtt.fi/publications/index.jsp)

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