

Optimisation of Gasification Processes for Biomass/Straw By using Additives

OCIFF Summary Report



Lasse Holst Sørensen, Dorthe Posselt, Ulrik Henriksen,
Antero Moilanen, Esa Kurkela,
Per Stoltze, Per Rosenberg, Benny Gøbel, Poul Norby, Jan Fjellerup,
Jens Dahl Bentsen, Håvar Risnes, Maria Barrio, Johan E. Hustad
and Erik Winther

ReaTech, June 2002
Prepared for Energi E2 and Energistyrelsen
EFP-2000 1373/00-0032

Optimisation of Gasification Processes for Biomass/Straw By using Additives

OCIFF Summary Report, 2.ed



Lasse Holst Sørensen¹, Dorthe Posselt², Ulrik Henriksen³,
Antero Moilanen⁴, Esa Kurkela⁴,
Per Stoltze⁵, Per Rosenberg⁶, Benny Gøbel³, Poul Norby⁷, Jan Fjellerup³
Jens Dahl Bentsen⁹, Håvar Risnes⁸, Maria Barrio⁸, Johan E. Hustad⁸
and Erik Winther¹⁰

ReaTech, June 2002, Prepared for Energi E2 and Energistyrelsen
EFP-2000 1373/00-0032

Addresses:

¹ReaTech, Frederiksborgvej 399, P.O.Box 30, DK-4000 Roskilde, Denmark, ²Roskilde University, Dep. of Mathematics and Physics, P.O. Box 260, DK-4000, Roskilde, Denmark, ³Technical University of Denmark, Dep. of Mechanical Engineering, Biomass Gasification Group, DK-2800 Kgs. Lyngby, Denmark, ⁴VTT Energy, P.O. Box 1601, Fin-02044 VTT, Finland, ⁵Ålborg University Esbjerg, Dep. of Chemical Engineering, Niels Bohrs Vej 8, DK-6700 Esbjerg, Danmark, ⁶Danish Geological Survey, Dep. of Geochemistry, GEUS, Thoravej 8, 2400 København NV, ⁷University of Oslo, Dep. of Chemistry, N-0315 Oslo, Norway, ⁸Norwegian University of Science and Technology, Dep. of Thermal Energy and hydropower, N-7491 Trondheim, Norway. ⁹Cowi A/S, Parallelvej 2, 2800 Kgs. Lyngby, Denmark, ¹⁰Energi E2, Lautruphøj 12, 2750 Ballerup, Denmark

1. ed. June 2002. 2. ed. June 2003.

Table of Content

TABLE OF CONTENT	4
ENGLISH ABSTRACT	5
DANISH ABSTRACT	5
1. SUMMARY	6
2. CHARACTERISATION METHOD OF BIOMASS ASH FOR GASIFICATION ³	7
3. REACTIVITY AND INTERNAL AREA STUDY OF STRAW CHAR ⁸	8
4. REACTIVITY IN BIOMASS GASIFICATION IN DEPENDENCE OF THE CALCIUM LOADING PROCEDURE ^{9,14}	9
5. FUNDAMENTAL INVESTIGATIONS OF CALCIUM ADDITION TO STRAW ²	9
6. PHOSPHOROUS AND CALCIUM ADDITION INVESTIGATIONS ⁶	11
7. REACTIVITY ¹ OF STRAW, WOOD AND COKE IN CO ₂	13
8. REACTIVITY STUDY FOR BIRCH AND BEECH CHAR SAMPLES ^{4,5}	13
9. ALKALI CATALYSED GASIFICATION OF CARBON AND TAR MOLECULES ⁷ ..	15
10. TWO STAGE GASIFIER TESTS	16
11. ADDITIVE UTILISATION IN GASIFICATION (ECONOMICAL ASPECTS).....	17
12. FINAL DISCUSSION.....	18
13. CONCLUSION	24
REFERENCES.....	26
ACKNOWLEDGEMENT	28

English Abstract

The present project intends to contribute to the optimisation of the operating conditions and to minimise agglomeration and sintering under gasification of straw in circulating fluidised bed (CFBG) and two-stage gasification. Various combinations of fuels, additives, catalysts and bed materials have been investigated and evaluated. A number of Danish straws were tested. Reactivity, tendencies for ash agglomeration and deposit formation in biomass gasification were first studied in thermo balances, high-temperature X-ray diffraction equipment, and in an atmospheric-pressure fluidising bed reactor. Comprehensive global equilibrium analysis (GEA) has been used for the prediction of important characteristics of the inorganic ash residue. Different additives were tested. One phosphorous calcium combination was tested successfully in the MEK-100 kW two stage gasifier where 2 tons of the pelletised additive-impregnated straw could be gasified during a four days test-run. A dry straw conversion of 98 wt.% was obtained. During the test there were no signs of agglomeration or sintering in the char bed.

Danish Abstract

Dette projekt bidrager til at minimisere agglomerering og sintring ved forgasning af halm i cirkulerende fluidiserende bed forgassere (CFBG) og two-trinsforgasning. Forskellige kombinationer af brændsler, additiver og katalysatorer samt bed materialer er blevet undersøgt og evalueret. Et antal danske halm er blevet testet. Reaktivitet, askeagglomererings- samt aflejringsindeks var først undersøgt med termisk analyse, høj temperatur røntgen diffraktion samt i en atmosfærisk fluid bed reaktor. Omfattende globale ligevægts beregninger (GEA) er anvendt til at estimere vigtige egenskaber af det uorganiske restprodukt. Forskellige additiver er testet. En fosfor-kalk kombination blev testet med god succes i MEK's 100 kW tottrins forgasser, hvor 2 tons pelleteret additiv-imprægneret halm blev forgasset under et 4 dages test forsøg. En omdannelse på 98 wt.% blev opnået. Under denne test var der ingen tegn på agglomerering eller sintring i koksbedden.

1. Summary

It has been the original goal of the present project to contribute to the optimisation of the operating conditions and to minimise agglomeration and sintering under gasification of straw in circulating fluidised bed gasification (CFBG) systems. Since, however, early in the project, it was decided that any CFBG was apparently soon to be build in Denmark, the focus was broadened to include tests with a two-stage gasifier. Various combinations of fuels, additives, catalysts and bed materials have been investigated and evaluated. In particular as a part of the present OCIFF project a number of Danish straws were tested. Moilanen³ presented these results together with gasification tests made in the VTT Process development unit (PDU) where two wheat-straw feedstocks were gasified. Even though the ash sintered strongly below 800°C it was possible to optimise gasification conditions to obtain a carbon efficiency of 95%. The tar content was clearly lower in straw gasification than in wood gasification. No additive addition was tested in the PDU tests. Instead additive addition was tested in the MEK-100 kW two stage gasifier (Bentzen¹⁰). Reactivity, tendencies for ash agglomeration and deposit formation in biomass gasification were first studied in thermo balances^{2,3,11}, high-temperature X-ray diffraction equipment⁶, and in an atmospheric-pressure fluidising bed reactor³. Gasification reactivity of wood samples was measured in steam and CO₂ by using thermal analysis. Comprehensive global equilibrium analysis (GEA) has been used for the prediction of important characteristics of the inorganic ash residue³. Different gasification additives were tested. Calcium addition was thoroughly evaluated. Experiments as well as GEA suggests that abundant Ca-enrichment of the inorganic straw ash in general leads to decreased formation of K-rich SLAG (experimentally observed through the a Sintering and Agglomeration Index, SAI), increased formation of calcium-silicates and an increasing water-soluble and potentially catalytic liquid SALT melt fraction.

It was demonstrated on laboratory scale facilities that a well-balanced mixture of calcium and phosphorous may perform well as an anti-agglomeration and anti-sintering additive^{6, 20}. It was following shown¹⁰ that 2 tons of the pelletized additive-impregnated straw “Wheat 2000+” could be gasified during a four days test-run in a two-stage gasifier with a dry straw conversion of 98 wt.%. During the test there were no signs of agglomeration or sintering in the char bed. Additionally, in tests performed at the Ensted CHP plant the addition of CAP significantly reduced chloride and sulphur from corrosive deposits on test probes.

Calculations made by Stoltze^{7c} suggest that alkali is bound to oxygen containing aromatic compounds as oxygen-alkali salt with a significant heat of bonding. Such compounds will therefore be in the form of e.g. phenol vapour alkali salt instead of phenol and KOH and more abundant due to larger stability during pyrolysis and the early gasification or in general under reducing conditions.

Several groups and individuals have contributed to the results of the project. The result from each individual contribution is briefly described in the following sections. Each contribution is thoroughly described in separate reports or papers. Several of the papers are published^{1,3,4} and others papers are to be published. Some of the papers and reports have been made as a part of educational studies^{1,2,4,5,8,9}.

2. Characterisation method of biomass ash for gasification³

This part of the study was lead by VTT within a test program performed under TEKES. The work is presented in a paper by Moilanen³. The Danish experimental and reporting contribution took place through the project BIOG¹⁵ and the present OCIFF project respectively. Tendencies for ash agglomeration and deposit formation in biomass gasification were studied in two atmospheric-pressure fluidising bed reactors³ together with reactivity tests carried out using a thermo balance. Various herbaceous and woody biomasses of different origin and a selection of Danish straws were tested. The measurements were carried out as a function of temperature, and H₂O and CO₂ were used as gasification agents. The reaction gas pressure was varied between 1 and 30 bar, and the temperature range was 650 - 950 °C. The appearance of the ash residues after the gasification reaction was examined by microscopy. Bed agglomeration and freeboard deposit formation were monitored by collecting samples after the test runs. Samples were analysed by using a computer-controlled scanning electron microscopy (CCSEM) technique developed for ash deposit analyses. The thermo balance measurements gave results comparable to the ash behaviour in the fluidised-bed reactor. The strongest ash sintering was observed for wheat straw both in the thermo balance and in the fluidised-bed reactor. The effect of additives to prevent agglomeration formation was included in the study. A sintering and agglomeration index "SAI" is defined³ in steps of 0.5 in an interval from 0* to 3* as following: SAI=0*: Non-sintered ash residue: ash structure resembling the original fuel particles, easily crumbling when touched. SAI=1*-2*: Partly sintered ash containing clearly fused ash. SAI=3*: Totally sintered ash fused into larger blocks.

In particular interesting for the Danish participation was that the differences between Danish wheat straw qualities were relatively small: almost all tested straws had a rather problematic ash sintering behaviour. When tested in a calcium oxide bed this was in particular the case for a wheat straw rich in silicon while a straw rich in potassium but poor in silicon caused much less sintering.

In this study³ it was also found that the use of kaolin and magnesium oxide additives each had a great preventive effect on bed agglomeration and freeboard deposit formation in the bench-scale bubbling fluidised-bed gasification tests carried out with straw.

3. Reactivity and internal area study of Straw char⁸

A study was performed primarily as a student project⁸ in a co-operation between Dep. of Mathematics and Physics, Roskilde University (RUC) and Dep. of Mechanical Engineering, Biomass Gasification Group, Technical University of Denmark (MEK), Risø National Laboratory and ReaTech.

The specific internal area of a pyrolysed straw char was measured, using the BET technique, as a function of conversion. Several mathematical models were fitted to the data. The raw data are shown in the Table 3.1 below. Clearly the specific BET-area increases greatly from $X=0$ to $X=0.11$ and following the area increases only little until almost complete conversion is obtained, i.e. ($X > 76$ wt. %). At complete conversion the BET area of the ash is only 24 m^2/g .

Sample #	Conversion % (X)		Area (m^2/g)
	dry	daf	
2	0	0	112
3	11	13.75	460
4a	25	31.25	439
4b	25	31.25	451
5	35	43.75	547
6	42	52.50	458
7	46	57.50	709
8	47	58.75	554
9	54	67.50	522
10	61	76.25	662
11	80	100.00	24
12	28	35.00	449

Table 3.1. BET area (m^2/g) of pyrolysed straw char measured as a function of conversion. Data are as presented on dry basis “dry” and dry and ash free basis “daf”.

4. Reactivity in Biomass Gasification in Dependence of the Calcium Loading Procedure^{9,14}

The work was performed primarily as student projects in a co-operation between Dep. of Mathematics and Physics, Roskilde University (RUC) and Dep. of Mechanical Engineering, Biomass Gasification Group, Technical University of Denmark (MEK) and Fachhochschule Darmstadt (FD), Germany and ReaTech.

Larsen and Nielsen⁹ found that addition of calcium carbonate to straw did not increase the char gasification reactivity in the temperature range [700-850°C] when the calcium carbonate was added either in a dry form or impregnated in a suspension of calcium carbonate and water.

As a direct continuation on this work Papadakis¹⁴ at ReaTech investigated the reactivity of straw char in dependence of the calcium loading procedure. He found that it is of major importance that the calcium is distributed throughout the char and that this is mainly possible if the calcium is added in an ionic form, for example in the form of calcium acetate or calcium hydroxide/calcium saccharate in solution into straw pellets. When calcium was added as calcium acetate a few samples (washed in hydro fluoric acid) showed an increased reactivity, but in general significant and reproducible catalytic effect directly attributable to the calcium addition was difficult to get from the experiments. One major finding during this work was that the addition of around 2-3 wt.% Ca(OH)₂ in the form of calcium hydroxide/saccharate reduced the sintering tendency of a silicon-poor barley char significantly, while this was not the case, when 3 wt.% Ca(OH)₂ was added to a silicon-rich wheat sample.

In order to get a better understanding of these results a thorough theoretical investigation was performed using the global equilibrium analysis (GEA)² and experiments were performed using Time resolved in-situ high-temperature combustion and synchrotron X-ray diffraction studies at the Swiss-Norwegian beam line (BM01B) at the European Synchrotron Radiation Facility, ESRF in Grenoble¹¹

5. Fundamental Investigations of Calcium Addition to Straw²

The global equilibrium approach is useful for a first description of the complex reactions taking place in a reactor during biomass gasification. Risnes² carries out Global Equilibrium Analysis (GEA) using the FACT equilibrium program⁷. FACT incorporates the CHEMSAGE algorithm for free energy minimisation.

The chemical equilibrium composition of a complex mixture indicates which compounds are possibly expected in fairly large amounts and how the amounts of such compounds can be affected by the mixing of fuels and by addition of specific compounds, i.e. additives. The success of GEA depends of its ability to describe the relevant reactor results.

How well GEA adequately reproduce reactor results depends on the completeness of the thermodynamic data set used. If important compounds or solution phases are not available

within the database misleading results are obtained. This is also the case if the calculations include very thermodynamically stable but kinetically prohibited compounds or phases. In order to obtain good results modelling and experimental verification has to be conducted in an iterative procedure based on detailed knowledge about the chemical systems of interest. Experimental verification may be made from Scanning Electron Microscopy, SEM-EDX and from In-situ high-temperature X-ray diffraction and combustion measurements¹¹ in combination with indirect methods like reactivity measurements and sintering and agglomeration measures.

The input for the equilibrium model is the input flows in terms of the elemental composition of the selected fuels and additives as given in Table 1 and 2, together with air and steam (air ratio of 0.26). The elements: C, H, N, O and K, Ca, Si, Al, Fe, Mg, Na, Cl, P and S, are studied. Additionally possible output species and compounds as well as 19 solution phases are evaluated during the calculations, made in the range from 700 to 1000°C in steps of 10°C.

A summary of the solution phases included in our analysis is given in the paper². Of particular importance are the Si rich glass/liquid solution “SLAG”-phase, a solid KCl/NaCl mixture phase “ACLA”, a solid and a liquid K_2CO_3 – $CaCO_3$ “SCSO”/“LCSO”-phase respectively and a liquid alkali (K, Na) -chlorides/carbonates “SALT” solution phase. The chemically distinctive oxide/silicate and salt system are assumed to be non-miscible. Clearly the extrapolation of miscibility/non miscibility observed for well-defined limited compositions to multi-component systems is uncertain as are the kinetics of the possible reactions between inorganic compounds and the presence of carbonaceous material.

The SLAG database contains more than 20 oxide components and is obtained from optimisation of more than 150 binary, ternary and higher order systems. Not all of the ternary combinations have been optimised, and only a few higher-order systems have been studied. The properties of higher-order systems are estimated automatically from low order systems using the quasi-chemical model⁹.

Conclusions:

The influence of Ca addition in straw gasification was investigated² and compared to experimental results obtained using thermal gravimetric analysis. It was in the study experimentally found that the reactivity was little affected by the Ca added. In-situ high-temperature X-ray diffraction and combustion measurements¹¹ indicated that major parts of the inorganic-inorganic reactions take place late in the char conversion process. The results support the suggestion that in the present case the catalytic activity of the mobile K is significantly larger than that of Ca. Ca may, however, indirectly affect the reactivity by primarily binding silicon as calcium silicates and less into potassium calcium silicates and hereby generate or maintain potassium into a catalytic water soluble form.

Fuels with silica rich ash tend to produce a viscous K and Si- oxide/silicate slag with a low melting point. Although small amounts of Ca result in a low melting point (due to ternary eutectics) we find that abundant Ca-enrichment of the inorganic straw ash in general leads to decreased formation of K-rich SLAG (experimentally observed through the reduced Sintering and Agglomeration Index, SAI) and increased formation of calcium-silicates and a

water-soluble and potentially catalytic liquid SALT melt fraction. The fact that a significant reactivity enhancement from calcium addition was not observed in the study supports the assumption that formation of viscous oxide/silicate melts and the derived catalytic salt formation mainly takes place at the end of the char conversion process.

For a Si-poor barley sample experimental addition of 2 to 3 wt.% $\text{Ca}(\text{OH})_2$ was sufficient to obtain a low sintering and agglomeration index, while addition of 3 wt.% $\text{Ca}(\text{OH})_2$ was not enough for the Si-rich “Wheat 2000”, in agreement with the theoretical calculations. Wheat 2000 contains about three times higher Si-content than the barley sample, addition about 2-3 times more of the CAM solution (i.e. about 6-9 wt% $\text{Ca}(\text{OH})_2$) is therefore expected to reduce the slag formation to an acceptable level.

Equilibrium calculations predict the formation of liquid salt if sufficient amounts of Ca are added. In several combustion and gasification systems salt formation may by itself cause problems due to problematic deposit formation. Hence, an adverse slag formation problem might be replaced by increased corrosion on heat transfer surfaces and high temperature filters.

The experimental observation by in-situ high temperature X-ray diffraction of K_2CaSiO_4 and $\text{CaSiO}_3/\text{Ca}_2\text{Si}_2\text{O}_5$ formation from Ca enriched straw ash we considered important with respect to improved modelling of the viscous oxide/silicate melt.

6. Phosphorous and Calcium Addition Investigations⁶

According to the results obtained in the previous section rather large amounts of calcium are required for ash- and silicate rich straws in order to prevent significant slag formation. That work suggests that calcium mainly binds silicon and that an increased amount of a separate chlorides, hydroxides and carbonates salt phase of potassium and sodium is therefore formed. Such salt mixtures may lead to corrosion on super heater surfaces. We⁶ investigate the ability of dissolved or organically bound calcium *and* phosphate calcium additive mixtures to effectively bind corrosive potassium and sodium elements into very stable and less-corroding compounds present in the quaternary system $\text{K}_2\text{O}-\text{Na}_2\text{O}-\text{CaO}-\text{P}_2\text{O}_5$ and in the much more complex compounds obtained in biomass gasification – or combustion systems.

Considering the relevant binary systems, the lowest melting temperatures in the $\text{CaO}-\text{P}_2\text{O}_5$ binary are below 500°C and generated when the mixtures are very rich in phosphorous, i.e. $\text{CaO}/\text{P}_2\text{O}_5 < 0.2$ on a mass basis. Above this ratio in general an increasing $\text{CaO}/\text{P}_2\text{O}_5$ ratio leads to increasing melting temperatures. Calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$ has a high melting point (1780°C) and is very stable and normally present in gasification. In the $\text{K}_2\text{O}-\text{P}_2\text{O}_5$ binary system fusion temperatures as low as around 600°C are seen. The highest melting temperatures are observed for $\text{K}_4\text{P}_2\text{O}_7$ (1105°C) and K_3PO_4 (1340°C). In the $\text{Na}_2\text{O}-\text{P}_2\text{O}_5$ binary system fusion temperatures are observed around 552°C . For $\text{Na}_2\text{O}/\text{P}_2\text{O}_5 > 2$ on a molar basis a fusion points above 940°C is obtained. From the binary data it appears that adding relatively large amounts of phosphate to a potassium and sodium rich fuel may lead to mixtures with low melting points. For the ternary $\text{K}_2\text{O}-\text{CaO}-\text{P}_2\text{O}_5$ phase, experimental data are still too scarce for any useful modelling and phosphates can melt around 800°C but no experimental information is available about the solubility between this melt and salt

melts of carbonate, chloride and sulphate. Thus a fair description of the quaternary system $K_2O-Na_2O-CaO-P_2O_5$ and systems with a higher number of elements is not available. Such a complex system may, however, be relevant in combustion and gasification. We have found experimentally that $CaK_2P_2O_7$ ($T_m=1143^\circ C$) and $KCaPO_4$ ($T_m=1560^\circ C$) are fairly stable and possible to synthesize. Apparently potassium and sodium are well bound into the complex quaternary matrices.

In case $KCaPO_4$ is the product aimed at and if the effect of sodium is calculated as equivalent to that of potassium one gets in case potassium as well as sodium is present in the fuel, the amount of phosphorous P_{added} by weight per 100 parts by weight of the inorganic portion in the fuel is

$$P_{added} = q1 \times (31/39 K_w + 31/23 Na_w - P_w - 31/35.4 Cl_w) \quad 6.1$$

Where K_w , Na_w , P_w and Cl_w are the amounts of potassium, sodium, phosphorous and chloride already available in the inorganic portion of the fuel calculated in parts by weight per 100 parts by weight of the inorganic portion in the fuel. $q1$ is a variable parameter with a typical value of $q1=0.5$ or $q1=1$. Some sintering reduction is observed already for lower values, e.g. $q1=1/3$. A value for $q1$ larger than one is suggested in order to bind most potassium and sodium otherwise bound as KCl and $NaCl$.

Calcium should be added according to the rules:

$$Ca_{added} = q2 \times (40/31 \times (P_{added} + P_w) - Ca_w) \quad 6.2$$

Where typical values for $q2 = 0.5$ or $q2 = 1$. Ca_w is the amounts of calcium by weight per 100 parts by weight of the inorganic portion of the fuel. For to large values of $q1$, gaseous phosphorous compounds may form. A surplus of phosphorous may effectively be reacted with calcium.

Time resolved in-situ synchrotron X-ray powder diffraction studies¹¹, measurements in a macro-TGA, tests in an atmospheric fluidised bed test facility^{12,13} and finally results from a two-stage gasifier are briefed.

It was demonstrated that a well-balanced mixture of calcium and phosphorous may perform well as an anti-agglomeration and anti-sintering additive. Since potassium is bound in products as $K_2CaP_2O_7$, $KCaPO_4$ and various related mixtures as for example $Ca_{13}P_{13}K_7Na_7Si_2MgO_{57}$, the potassium and sodium salts formation and consequently the sintering- and corroding potential from these elements are greatly reduced.

It was following demonstrated¹⁰ that 2 tons of the pelletized additive impregnated Wheat 2000+ straw could be gasified during a four days test run in a two-stage gasifier with a dry straw conversion of 98 wt.%. During the test there were no signs of agglomeration or sintering in the char bed.

A patent application²⁰ have been made on this method of additive addition.

7. Reactivity¹ of straw, wood and Coke in CO₂

Risnes¹ measured CO₂-gasification reactivity for two biomass char species: Danish wheat straw (dp<150µm, prior to devolatilisation) and Norwegian spruce char (dp< 63µm); and a dense metallurgical coke from Longyear coal (dp < 45 µm). The reactivity was thermo gravimetrically determined using 4-10 mg of pre-pyrolised char samples, CO₂-partial pressure (0.03-1 bar) and sample temperature (700-1000°C). Char reactivity (R) is expressed by separating the effects arising from true kinetics (r_C) and structural development (F(X)). The resulting function: $R = r_C \cdot F(X)$. r_C is modelled by nth order kinetics. F(X) was separated from r_C by normalising R with respect to a reference profile (R_{ref}). Over the considered pressure and temperature range, reactivity varies considerable, but the structural profile is in general approximately invariant, i.e. each sample apparently exhibits consistently the same structural evolution for a broad span of kinetic conditions as one prerequisite for good kinetics determination. The structural profile is dependent on reactant gas (O₂ or CO₂) and different for each carbonaceous material. Significant structural profile invariance to conversion and CO₂ partial pressure was illustrated for a Longyear coke at 1000°C.

For all fuels tested the nth order kinetic models used well represents the CO₂-reactivity measured by thermogravimetry. Since normalised reactivity was approximately independent of conversion, for each char, one reaction order, and activation energy could be estimated for the whole range of temperature and CO₂ partial pressures. Applying nth order kinetics (for r_C(X=0.5)) the following kinetic parameters were obtained (atmospheric experiments): apparent activation energies (E) for wheat straw char; 205.6 [kJ/mol], spruce char; 219.9 [kJ/mol] and Longyear coke; 233.1 [kJ/mol], the respective reaction orders equals 0.59, 0.36 and 0.51. In the investigated temperature (T) and CO₂-partial pressure (P_i) range, using normalised reactivity (R_n) and the reactivity at 20, 40, 60 and 80% conversion for kinetics determination gives similar results, as expected in the case of an invariant structural profile. For the Longyear coke partial pressure dependent reactivity profiles were measured and discussed. A simple nth order reaction and an invariant structural profile assumption were used under the evaluation of experimental data for kinetics determination. However, the results indicated that a more complex mechanism must be considered if the results, even for a single pure gas, are to be extrapolated to their limits for the purposes of modelling reactor data under realistic conditions. Additionally it was found that the reactivity profiles measured in CO₂ and in O₂ are significantly different.

8. Reactivity study for birch and beech char samples^{4, 5}

Barrio derived gasification kinetics parameters for birch and beech char samples⁴ (45µm<d<60µm) pyrolised under identical conditions. Reactivity experiments were made in steam-hydrogen-nitrogen mixtures at atmospheric pressure. Reactivity profiles was obtained in the temperature range from 750 °C to 950 °C, for H₂O partial pressures of 0.05, 0.1, 0.2, 0.5 and 1.0 bar and H₂ partial pressures of 0.1, 0.2 and 0.3 bar. Assuming nth order kinetics for pure steam experiments, the activation energy and the reaction order were found to E=211 kJ/mol and n=0.51 for beech and E=237 kJ/mol and n=0.57 for birch. A kinetic

expression based on Langmuir-Hinchelwood kinetics fairly describes the observed hydrogen inhibition effect on the steam-carbon reaction.

The differences between the kinetics determined for birch and beech were relatively small. The kinetic parameters obtained are presented using a kinetic compensation diagram and compared with literature data and discussed. The influence of the calculation procedure on the results is also discussed. The data evaluation procedure mostly influences the pre-exponential factor and less the activation energy and reaction order. It was found that

- 1) The kinetic parameters according to the n^{th} order reaction model for steam gasification of wood char are $E= 237 \text{ kJ/mol}$, $k_0= 2.62 \cdot 10^8$ and $n= 0.57$ for birch, $E= 211 \text{ kJ/mol}$, $k_0= 1.71 \cdot 10^7$ and $n= 0.51$ for beech char.
- 2) Hydrogen inhibits the steam gasification reaction. The char gasification reaction with steam and hydrogen can be modelled based on Langmuir-Hinchelwood kinetics. The model fits well the results.

Wood char gasification experiments⁵ were following conducted in mixtures of $\text{H}_2\text{O}/\text{N}_2$, CO_2/N_2 and $\text{H}_2\text{O}/\text{CO}_2/\text{N}_2$ in a temperature range $750^\circ\text{C} - 950^\circ\text{C}$. The objective of this investigation was to thoroughly evaluate kinetic models that predict the gasification rate in complex gas mixtures based on Langmuir-Hinchelwood kinetics. It was investigated if kinetics obtained from $\text{H}_2\text{O}/\text{N}_2$ and CO_2/N_2 experiments can be used to predict gasification in the more complex $\text{H}_2\text{O}/\text{CO}_2/\text{N}_2$ mixtures.

The results suggest that the rate of desorption of the $\text{C}(\text{O})$ complex varies depending on the gas mixture surrounding the char. They also show that experiments with $\text{H}_2\text{O}/\text{N}_2$ and CO_2/N_2 could give a fair approximation for gasification in complex mixtures.

It was, however, found that kinetic models based on $\text{H}_2\text{O}/\text{N}_2$, CO_2/N_2 and $\text{H}_2\text{O}/\text{CO}_2/\text{N}_2$ combined experimental data and Langmuir-Hinchelwood kinetics tends to under predict the gasification rate in $\text{H}_2\text{O}/\text{CO}_2$ mixtures.

The results suggest that the rate of desorption for the complex $\text{C}(\text{O})$ varies depending on the gas mixture surrounding the char and that k_{3w} , is different from k_{3c} , see section 11 for possible reaction schemes. It has been found that when experimental data are obtained from separate $\text{H}_2\text{O}/\text{N}_2$ and CO_2/N_2 experiments. According to Barrio, the reactivity of the char in mixtures of CO_2 and H_2O were well predicted assuming that $k_3=k_{3w}$. Since eight constants have to be calculated, a larger number of experiments should be conducted to find these constants.

Additionally it was found that the type of wood affected very little the kinetic parameters but in particular showed some influence on the reactivity profile.

9. Alkali Catalysed gasification of carbon and tar molecules⁷

Stoltze^{7,a,b,c,d} made a comprehensive literature search for relevant studies on the gasification mechanism of carbon. Attempts of quantum mechanical calculations relevant for gasification of carbon and for alkali-catalysed gasification of tar molecules were made.

The most important results are:

A. Numerous studies of coal exist in the literature that relatively consistently points towards one specific mechanism. Unfortunately the results of the studies mutually point at weaknesses of each other.

B. The reaction is more complex than usually assumed due to the coupling between the distributions of the catalyst, the carbon and the other ash elements and the reaction rate the degree of conversion and area evolution.

C. The reaction is less complex than usually assumed since the mechanism by and large is the same independent of gas and used catalyst.

D. Results from studies on individual crystal of graphite are a possible source for information about details in the reaction mechanism, but it is necessary to analyse the large content of oxygen in partially gasified coal thoroughly before it is possible to determine if graphite is a relevant model system.

E. The electron structure for pure carbon is difficult. This explains why results of the present calculations do not exist in literature. It must therefore be concluded that in the development of a kinetic model, quantum mechanical calculations for pure carbon are not a possibility.

F. For gasification of tar molecules, the calculations show that it is not possible to make quantum mechanical calculations. The calculations show that the heat of bonding for K is too small to give significant alkali-aromatic bonding.

G. For oxygen containing molecules (Phenol, formic acid, benzoic acid) the calculations show that alkali is bound as salt with a significant heat of bonding. The molecules will therefore be in the form of e.g. phenol vapour alkali salt instead of phenol and KOH.

H. Intercalation compounds are not important for gasification. Carbon-alkali as graphite-alkali compounds are only very stable under inert conditions and therefore cannot be made from coal and alkali-carbonates, -oxides and hydroxides.

In summary it is concluded that for gasification of solid carbonaceous material it is possible to formulate a mechanism, but a number of kinetic parameters are not known, cannot be calculated, but may be estimated from experiments on graphite or other carbonaceous materials. For tar molecules a calculation of kinetic data is possible, but relatively few data are available in the literature and systematic calculations are necessary.

It was not possible to produce reliable data that could be used to estimate Gibbs free energy function for solid carbonaceous compounds like Cn-O and Cn-O-K. The idea was to be able to estimate distribution functions of the catalyst on the carbon surfaces as a function the inorganic elemental composition.

10. Two Stage Gasifier Tests

A 100 kW two-stage gasifier test was performed with approximately 2 tons of the pelletized Wheat 2000+ straw. During the test there were no signs of agglomeration or sintering in the char bed. The test did run for four days and the total conversion during the last two days test were 98 wt.% which is a fairly high degree of conversion for this type of gasifier and as large that would be expected if no additive was used. A more comprehensive description of the gasification tests are made by Bentzen¹⁰

11. Additive utilisation in gasification (Economical aspects)

In chapter 6, it was suggested to add phosphorous to potassium rich fuels in order to reduce their agglomeration and sintering tendency. Furthermore roughly the same treatment is suggested for reduction of salt induced corrosion. The latter is observed in high temperature combustion systems.

Additive cost

For wood containing around 1 wt.% ash (dry fuel basis) and 15 wt.% (K_2O+Na_2O) in the ash the K_2O+Na_2O content is around 0.15 wt.% (dry fuel basis). If $K_2O \gg Na_2O$ we find $K_w=0.13$ wt.% (dry fuel basis). If the amounts of chloride and phosphorous inherent in the fuel are relatively small and if we chose $q_1=0.5-1$ in equation 6.1, we get that the necessary amount of phosphorous to be added to the wood is $P_w=0.05-0.10$ wt.% (dry fuel basis) or 0.5-1 kg P/ton dry wood. The price value for 1 kg of P is approximately $V_p = 1$ Euro/kg P if phosphorous is derived from technical grade phosphorous acid or calcium phosphate compounds. In this case if the additive price is set to 1 Euro/ton dry wood. The total cost for the conversion of dry wood or straw may be set to around 200 Euro/ton. In this case the cost of the additives are less than 0.25-0.5 % of the total costs for conversion of wood. For straw the content of potassium may be up to 5-10 times higher, i.e. the necessary additive amounts are $P_w=0.25-1$ wt.% (dry fuel basis) cost are in these cases up to 1.25 - 5 % of the total conversion costs per ton fuel. In the cases, where straw is converted at fairly low temperatures, values in the range $q_1=1/3$ to 0.5 are realistic, so that the additive cost typically should be around 2-3% of the total conversion costs per ton fuel.

Value added combustion residues

Furthermore phosphorous and calcium may likely be derived from treated bone ash, which is at present a cheap phosphorous source. In this case it may be economically favourable to use even more additive, i.e. values for $q_1 > 1$. It should here be stressed that the residues contain a relatively high content of phosphorous, potassium and calcium. Therefore the residue (eventually after some treatment) may have a fairly high positive economic value (e.g. 1-2 % of the total conversion costs) as a P-K or Ca-P-K fertilizer.

We suggest the combination of the phosphorous additive with other well-known additives like calcium or dolomite in gasification - and in combustion eventually fly ash, kaolin or sulphur. Furthermore the combining of the utilisation of additives with systematic fuels mixing or fuels preparation may reduce a part of the cost.

12. Final Discussion

Various combinations of wood, straw and additives, catalysts and bed materials have been evaluated and a number of tests have been made.

Reactivity

Stoltze⁷ made a comprehensive literature search for relevant fundamental studies on the catalysed gasification mechanisms of char and tar. For oxygen containing molecules (Phenol, formic acid, benzoic acid) the quantum mechanical calculations showed that alkali is bound as a salt with a significant heat of bonding. The molecules will therefore be in the form of e.g. phenol vapour alkali salt instead of phenol and KOH during pyrolysis and early gasification. Furthermore a high alkali loading may increase the amount of evaporated phenol during pyrolysis while these molecules may also be more rapidly converted at gasification or combustion conditions.

Also attempts of quantum mechanical calculations on alkaline carbonaceous compounds were made. According to these calculation, carbon-alkali as graphite-alkali compounds little stable under gasification conditions; i.e. intercalation compounds, C_n-K , are not important for gasification and cannot be made from coal and alkali-carbonates, -oxides and hydroxides. Instead Stoltze found it necessary to analyse the large content of oxygen (20-40 mol %) found in partially gasified coal.

If alkali is bound to oxygen with a similar heat of bonding as in the phenol vapour salts, we suggest, that a large surface-coverage of oxygen as well as of alkali as C_n-O-K , may be available during gasification of carbonaceous surfaces. In the present study Gibbs free energy functions and thus distribution functions for compounds or clusters of C_n-O or C_n-O-K could not be estimated. Such a distributions function would be valuable for the understanding of gasification kinetics of complex carbonaceous material containing complex inorganic compounds.

Char reactivity is generally determined as $R = dX/dt/(1-X)$, where X is the degree of conversion. The present study⁸ on internal area suggested that the specific internal area increases only moderately with increasing degree of conversion. In a former study¹⁶ we found for one silicon-rich wheat straw and one leached barley straw that char reactivity decreased as a function of conversion. The reactivity of the unleached potassium-rich - as well as a salt-enriched barley straw char increased significantly as a function of conversion.

According to the experiments made by Moilanen³, for straws with high potassium to silicon ratio, a water-soluble catalytic liquid SALT melt fraction coexists with other ash residues even at complete conversion. This is in accord with the results obtained by global equilibrium analysis². Such straws typical have increasing reactivity as a function of conversion.

This behaviour suggest that chars from straws with a high alkali-salt to silicon ratio causes a steadily increasing catalyst/carbon ratio and thus increasing reactivity as a function of conversion. Oppositely chars from straws with low alkali-salt to silicon ratio, e.g. washed

straws, may lead to decreasing reactivity as a function of conversion since available alkali is completely absorbed by the surplus silicon content in the ash residue as the gasification reaction progresses.

In a simple attempt to quantify relevant catalyst data we chose data given by McKee²¹ for 5 wt.% pure catalysts loaded on spectroscopic grade graphite. He found (steam gasification at 800°C & 900°C) the catalytic activity of K₂CO₃ to be ~2.8 times larger than of KCl, ~9 times larger than of K₃PO₄ and ~50 times larger than the pure graphite. From the following simplified relation may be made

$$R = R_0 \left\{ 1 + \sum_i \alpha_i \gamma_{k,i} \left\{ \frac{M_{w_k}}{M_{w_i}} N_k \right\} \right\} \quad (1)$$

R₀ denotes the reactivity of the catalyst-free carbonaceous fuel. The reactivity for a fuel loaded with catalyst/(daf-fuel), α_i, weight fraction of the i'th mobile catalytic compound, i ∈ {K₂CO₃, KOH, KCl, NaOH, etc.} is denoted R_i. γ_{k,i} is a catalyst element and compound mixture-dependent coefficient calculated for α_k = 1 wt.%, for the k'th element in the i'th compound as

$$\gamma_{k,i} = \frac{1}{N_k} \left(\frac{R_i - R_0}{R_0} \frac{1}{\alpha_i \frac{M_{w_k}}{M_{w_i}}} \right) \quad (2)$$

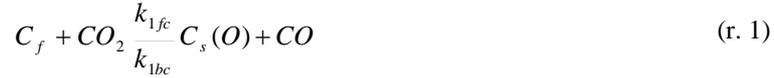
Where R(α_i=0) ≡ R₀ for the pure carbonaceous catalyst-free fuel of relevance. Structural properties have here not been taken into account. M_{wi} is the molecular weight of the catalytic compound and M_{wk} and N_k is the atomic weight and the number of catalyst elements, k, in the i'th catalytic compound. We find values for γ_{k,i} from the data presented by McKee²¹ as γ_{K,K₂CO₃}=17.3, γ_{K,KCl}=6.43, γ_{K,K₃PO₄}=1.65. These numbers says that a potassium- to carbon fraction of 1 wt.% increases the reactivity a factor of 17.3 if potassium is present as K₂CO₃ but only a factor of 1.65 if present as K₃PO₄. It also says that KCl is a better catalyst than K₃PO₄. Assuming that the catalytic effect decreases with the compound stability this indicates that K₃PO₄ is more stable at the carbon surface than KCl.

For a Danish wheat straw Moilanen observed a reduction in the total amount of potassium (K_{tot}) and the water-soluble potassium (K_{ws}) to (X_C, K_{tot}, K_{ws}) = (0, ~90%, ~75%) during pyrolysis at 800°C in a thermo balance. This reduction continued to (0.5, ~85%, 50%) and (1, ~80%, ~15%) during char gasification at 800°C. since K_{ws} → 15wt% for X → 1, we in principle find α_K → ∞ (where α_K = M_{K,ws}/ M_C). Therefore R → ∞ for X → 1 until kinetics or mass transfer becomes limiting. It is here important that salt co-exist with the formed slag where SAI=3* ("Wheat 95" where used for the studies).

According to this simplified formulation the reactivity is proportional to the amount of independent water-soluble catalyst compounds weighed by coefficients characteristic for the individual compounds. Therefore when catalysts are reacted into non-soluble compounds like potassium calcium silicates or catalysts with low catalytic coefficients, γ_{k,i}, like K₃PO₄ or potassium aluminium silicates the reactivity is decreased as observed earlier¹⁵.

Kinetics

Experimental results made in cooperation between NTNU, DTU and ReaTech are discussed in the following. The experiments are made in a H₂O and CO₂ atmosphere with very little H₂ and CO available. The experimental facility is ReaTech's thermal gravimetric analysis equipment. One possible reaction scheme is the following:



This scheme is made from an interpretation from results of Kapteijn¹⁹, suggesting that two significantly different types of CO desorption step are important, one fast and one slow reaction pathway. Here the r. 1 reaction gives slowly decomposing semiquinone sites, C_s, while the r.2 reaction gives the less stable diketone sites, C_{dk}. In this case if k_{1bc} and k_{1bw} are neglected due to the absence of H₂ and CO, and if C_s(O)=zC(O) and C_{dk}=(1-z)C(O), where 0 ≤ z ≤ 1, one may get the following Langmuir type equation

$$dC(O)/dt = (k_{1fc}P_{CO_2} + k_{1fw}P_{H_2O})(C_t - C(O)) - k_{3c}zC(O) - k_{3w}(1-z)C(O) = 0 \quad (r. 5)$$

From which

$$(k_{1fc}P_{CO_2} + k_{1fw}P_{H_2O})C_t = (k_{1fc}P_{CO_2} + k_{1fw}P_{H_2O} + (k_{3c}z + k_{3w}(1-z)))C(O) \quad (r.6)$$

$$C(O) = \frac{k_{1fc}P_{CO_2} + k_{1fw}P_{H_2O}}{k_{1fc}P_{CO_2} + k_{1fw}P_{H_2O} + (k_{3c}z + k_{3w}(1-z))} C_t \quad (r.7)$$

$$-\frac{dC_t}{dt} = (k_{3c}z + k_{3w}(1-z))C(O) \quad (r.8)$$

$$-\frac{dC_t}{dt} = \frac{k_{1fc}P_{CO_2} + k_{1fw}P_{H_2O}}{1 + \frac{k_{1fc}}{k_{3c}z + k_{3w}(1-z)}P_{CO_2} + \frac{k_{1fw}}{k_{3c}z + k_{3w}(1-z)}P_{H_2O}} \frac{C_t}{C_{tot}} C_{tot} \quad (r.9)$$

In terms of reactivity one gets:

$$R = \frac{k_{1fc}P_{CO_2} + k_{1fw}P_{H_2O}}{1 + \frac{k_{1fc}}{k_{3c}z + k_{3w}(1-z)}P_{CO_2} + \frac{k_{1fw}}{k_{3c}z + k_{3w}(1-z)}P_{H_2O}} f(X) \quad (r.10)$$

Barrio⁴ tested a number of conditions and found that the following equation well fitted all data where just a small steam partial pressure were present:

$$R = \frac{k_{1fc}P_{CO_2} + k_{1fw}P_{H_2O}}{1 + \frac{k_{1fc}}{k_{3w}}P_{CO_2} + \frac{k_{1fw}}{k_{3w}}P_{H_2O}} f(X) \quad (r.11)$$

This was the case even if $P_{CO_2} \gg P_{H_2O}$. Using k_{3c} instead of k_{3w} , i.e. $z=1$ instead of $z=0$, was not successful except for the fitting of pure CO_2 data. The reason for this may be due to the fact that - according to the data evaluation -, the value of k_{3w} was 3-5 times larger than k_{3c} in the investigated temperature range.

Another explanation may be that low or moderate steam partial pressures rapidly convert the semiquinone structure to the diketone structure.



This is the case if $k_{3s}P_{H_2O}^n \gg k_{3c}$. Such behaviour may explain that equation r.11 well describes the gasification rates. This may also be the case if r.1. as well as r.3. both form a semiquinone structure, while the formation of the diketone structure primarily takes place through equation r.12.

Stoltze^{7b} find in the literature study that also phenolic hydroxyl groups, ether, carbonyl, lactone, quinone, anhydride and carboxyl groups are present on gasified surfaces.

Reactivity and catalysis are important topics in gasification. Another aspect, which is related due to its dependence of the fuels alkali-content, is the problem of agglomeration and sintering.

Agglomeration and sintering

The catalytic elements K and Na are abundant in biomass. In particular in straw K and Na are present in volatile compounds at typical combustion and gasification temperatures. This introduces significant problems due to salt deposit or slag formation. In particular we found from thermo-balance - and fluidised-bed reactor test that the strongest ash sintering was observed for wheat straw³. Furthermore the differences between Danish wheat straw qualities were relatively small. When tested in a calcium oxide bed this was in particular the case for a wheat straw rich in silicon.

One straw rich in potassium but poor in silicon caused much less sintering. According to Global Equilibrium Analysis (GEA) calculations little slag formation but significant salt formation takes place for such a straw. This is also in accordance with the observation that char gasification reactivity is very high for salt rich straws^{2, 3, 15}. Such straws may be attractive in low-temperature gasifiers and CHP plants according to their high reactivity. In high-temperature gasification and CHP plants increased corrosive salt deposit formation may result in costly maintenance or materials replacement.

In order to reduce the sintering tendency of fuels rich in potassium various additives as well as bed materials may be tested. The use of kaolin and magnesium oxide additives had a great preventive effect on bed agglomeration and freeboard deposit formation in the VTT bench-scale bubbling fluidised-bed gasification tests carried out with straw³. These additives are, however, relatively expensive. Calcium is an abundant and fairly clean low-cost source and therefore we have thoroughly tested calcium as an additive experimentally as well as theoretically. A combination of calcium and phosphorous has also been tested.

The initial tests made by Larsen and Nielsen indicated that calcium carbonate, when added dry or in suspension to straw (not pelletized) did not influence char gasification reactivity. One reason for this is that calcium carbonate is very little dissolvable in water and in both the tested cases no good contact between the calcium and the char appeared until eventually very late in the char conversion process. These results supports the fluidised bed results³, where the gasification of a wheat straw rich in silicon in a calcium oxide bed did not prevent agglomeration and sintering of the straw residues, i.e. the calcium bed and the straw ash likely behaved almost as two independent phases.

From the continuing work¹⁴, it was found that calcium added in the form of ions increased the reactivity of straw chars washed in hydrofluoric acid. Relatively large amount of calcium was added. Similar effects were not significantly observed for calcium added in the form of a calcium hydroxide/calcium saccharate solution into straw pellets. Here it was, however, found that the addition of 2-3 wt.% Ca(OH)₂ in the form of calcium hydroxide/saccharate reduced the sintering tendency of a silicon-poor barley char from SAI=3* to SAI = 0-1*. The fact that such results could not be obtained even by similarly adding 3 wt.% Ca(OH)₂ to a silicon-rich wheat sample indicated that the major role of reactive calcium is to bind silicon.

In order to get a better understanding of these results a thorough theoretical investigation was performed. Global equilibrium analysis², GEA, was made. Experiments were performed using time resolved in-situ high-temperature combustion and synchrotron X-ray diffraction studies at the Swiss-Norwegian beam line (BM01B) at the European Synchrotron Radiation Facility, ESRF in Grenoble¹¹. Here a dramatic effect already at fairly low temperatures was observed from mixing well calcium hydroxide/calcium saccharate to straw ash. The reaction took place rapidly after that the carbonaceous material (molasses/saccharate) was converted between 500 and 550°C.

The theoretical GEA studies² supported the experimental results obtained for the Si-poor barley sample as well as for the Si-rich Wheat 2000 sample. From these calculations we suggest that Ca primarily binds silicon as calcium silicates and less into potassium calcium

silicates. Hereby increasing amounts of potassium salts are generated in the ash residue. Although small amounts of Ca results in a low melting point (due to ternary eutectics), calculations suggests that abundant Ca-enrichment of the inorganic straw ash in general leads to decreased formation of K-rich SLAG (experimentally observed through the decreased “Sintering and Agglomeration Index”, SAI), and increased formation of calcium-silicates and an increasing water-soluble and potentially catalytic liquid SALT melt fraction.

The theoretical results agreed well with diffraction studies¹¹ as well as studies on the amount of water-soluble potassium as a function of char conversion³. From these experimental studies, it is suggested that the calcium silicate formation reactions are mainly taking place at high degrees of conversion. This may explain why a significant reactivity enhancement from calcium addition was not observed in the study.

Since calcium addition leads to an increased amounts of chlorides, hydroxides and carbonates salt phases of potassium and sodium that may possibly lead to corrosion on e.g. super heater surfaces we instead investigated the ability of using a dissolved or activated calcium *and* phosphate additive mixture⁶. This mixture, “CAP”, apparently effectively binds corrosive potassium and sodium elements into very stable and less-corroding compounds present in the quaternary system $K_2O-Na_2O-CaO-P_2O_5$ and in the even more complex systems characteristic for gasification – or combustion systems.

Time resolved in-situ synchrotron X-ray powder diffraction studies¹¹, measurements in a macro-TGA¹⁶, tests in an atmospheric fluidised bed test facility and finally results from a two-stage gasifier demonstrated that a well-balanced mixture of calcium and phosphorous may perform well as anti-agglomeration and anti-sintering additive. The sintering liquid potassium silicate slag formation and the potassium and sodium salt formation and consequently the sintering- and corroding potential from these elements was greatly reduced. Since the addition of CAP as well as kaolin binds potassium and sodium the char gasification reactivity is significantly reduced, as these additives are used as anti-sintering additives¹⁵.

Two stage gasifier tests demonstrated¹⁰, that 2 tons of the pelletized additive-impregnated Wheat 2000+ straw could be gasified during a four days test-run in the two-stage gasifier with a dry straw conversion of 98 wt.%. During the test there were no signs of agglomeration or sintering in the char bed.

In combustion tests performed at the Ensted CHP plant the addition of CAP significantly reduced chloride and sulphur from corrosive deposits on test probes.

13. Conclusion

Various combinations of wood, straw and additives, catalysts and bed materials have been evaluated and a number of tests have been made.

1. A comprehensive literature search and quantum mechanical calculations^{7c} made by Stoltze^{7c} suggest that alkali is bound as oxygen-alkali salt with a significant heat of bonding. Such compounds will therefore be in the form of e.g. phenol vapour alkali salt instead of phenol and KOH and more abundant due to larger stability during pyrolysis and the early gasification or in general under reducing conditions. Carbon-alkali as graphite-alkali compounds are little stable under gasification conditions; i.e. intercalation compounds, C_n-K, are not important for gasification
2. According to the experiments made by Moilanen³, for straws with high potassium to silicon ratio, a water-soluble catalytic liquid SALT melt fraction coexists with other ash residues even at complete conversion. This is in accord with our results obtained by global equilibrium analysis (GEA)². Such straws typical have increasing reactivity as a function of conversion.
3. The results suggest that chars from straws with a high alkali-salt to silicon ratio causes a steadily increasing catalyst/carbon ratio and thus increasing reactivity as a function of conversion. Furthermore, the internal area⁸ evolution as measured by the BET technique does not support a steeply increasing reactivity as a function of conversion caused by internal area evolution only. Chars from straws with low alkali-salt to silicon ratio, e.g. washed straws, may lead to decreasing reactivity as a function of conversion since alkali is completely absorbed by the surplus silicon content in the ash residue as the gasification reaction progresses.
4. According to a simplified formulation the reactivity is proportional to the amount of independent water-soluble catalyst compounds weighed by coefficients characteristic for the individual compounds. Therefore when catalysts are reacted into non-soluble compounds like potassium calcium silicates or catalysts with low catalytic coefficients, $\gamma_{k,i}$, like K₃PO₄ or potassium aluminium silicates the reactivity is decreased as observed earlier¹⁵.
5. Experiments made in a H₂O and CO₂ atmosphere with very little H₂ and CO available suggests that at least two significantly different types of CO desorption step are important, one fast and one slow reaction pathway. Barrio⁴ tested a number of conditions and found that the following equation well fitted all data where just a small steam partial pressure were present:

$$R = \frac{k_{1fc}P_{CO_2} + k_{1fw}P_{H_2O}}{1 + \frac{k_{1fc}}{k_{3w}}P_{CO_2} + \frac{k_{1fw}}{k_{3w}}P_{H_2O}} f(X) \quad (r.11)$$

This was the case even if $P_{CO_2} \gg P_{H_2O}$.

6. In accordance to Global Equilibrium Analysis (GEA) the strongest ash sintering was experimentally observed for wheat straws³ rich in silicon and with a medium to rich potassium content and thus reactivity. Highly reactive straw rich in potassium but poor in silicon caused much less sintering, little slag formation but significant salt formation.
7. In order to reduce the sintering tendency of fuels rich in potassium the use of kaolin and magnesium oxide additives had a great preventive effect on bed agglomeration and freeboard deposit formation in the VTT bench-scale bubbling fluidised-bed gasification tests carried out with straw³.
8. Theoretical calculations and high temperature diffraction measurements suggest that Calcium added as calcium carbonate, when added dry or in suspension to silicon rich straw or used as a calcium oxide bed material due to a poor calcium-fuel contact did not influence char gasification reactivity or prevent agglomeration or sintering.
9. A better effect was observed by using calcium added in the form of ions in the form of calcium acetate to straw or a calcium hydroxide/calcium saccharate solution into straw pellets. Here it was found that the addition of 2-3 wt.% $\text{Ca}(\text{OH})_2$ in the form of calcium hydroxide/saccharate reduced the sintering tendency of a silicon-poor barley char from $\text{SAI}=3^*$ to $\text{SAI} = 0-1^*$. The fact that such results could not be obtained even by similarly adding 3 wt.% $\text{Ca}(\text{OH})_2$ to a silicon-rich wheat sample indicated that the major role of reactive calcium is to bind silicon. High-temperature diffraction measurements suggest that the inorganic reactions primarily takes place rapidly after that the carbonaceous material (molasses/saccharate) is converted, i.e. at high degrees of conversion. This may explain why a significant reactivity enhancement from calcium addition to raw straws was not observed in the study.
10. A dissolved or activated calcium and phosphate additive mixture⁶, “CAP”, apparently effectively binds corrosive potassium and sodium elements into very stable and less-corroding compounds.
11. 2 tons of the pelletized additive-impregnated Wheat 2000+ straw could be gasified during a four days test-run in a two-stage gasifier with a dry straw conversion of 98 wt.%. During the test there were no signs of agglomeration or sintering in the char bed.
12. Additionally: in combustion tests performed at the Ensted CHP plant the addition of CAP significantly reduced chloride and sulphur from corrosive deposits on test probes.

References

1. Risnes H., Sørensen L.H. and Hustad J.E. (2001). CO₂ reactivity of chars from wheat, spruce and coal. Progress in Thermochemical Biomass Conversion, Tyrol, Austria, pp-61-72
2. Risnes, H., Fjellerup J., Henriksen, U., Moilanen, A., Norby, P., Papadakis, K., Posselt, D. and Sørensen, L. H. (2002). Calcium addition in Straw Gasification, [Fuel.Vol. 82, Issue 6, 2003. pp. 641-651.](#)
3. Moilanen A., Sørensen L.H., Gustafsson T.E., Laatikainen-Luntama J., Kurkela E. (2001). Characterisation method of biomass ash for gasification. Progress in Thermochemical Biomass Conversion, Tyrol, Austria, pp. 122-136
4. Barrio M., Gøbel B., Risnes H., Henriksen U., Hustad J.E., Sørensen L.H., (2001). Steam gasification of wood char and the effect of hydrogen inhibition on the chemical kinetics, Progress in Thermochemical Biomass Conversion, Tyrol, Austria, pp. 32-46
5. Barrio M., Gøbel B., Henriksen U., Hustad J.E., Sørensen L.H. Wood char gasification chemical kinetics in mixtures of CO₂ and H₂O. To be published 2003.
6. Sørensen L.H., Henriksen U., Norby P., Posselt D., Moilanen A., Kurkela E., Rosenberg P., Winther E. (2002). Phosphorous and Calcium Addition in Biomass Conversion. Internal report.
7. Stoltze P., Sørensen L.H. (2002). Aalborg Universitet Esbjerg Report, Denmark.
 - a. Gasification of coal and tar (In Danish).
 - b. The content of oxygen in partly gasified coal (In Danish).
 - c. Calculations for tar compounds (In Danish)
 - d. Suggestion for further studies on straw gasification mechanisms. (In Danish),
8. Gunnarsdóttir I., Hansen J.K., Jankvist U.T.V., Madsen T.H., Tiedemann P., supervisor Dorthe Posselt (2000). Development of Internal Area under Gasification of Straw Char. Project report, IMFUFA, Roskilde University, Roskilde, Denmark
9. Karen-Anne Holt Larsen, Heidi Kolmorgen Nielsen, supervisor, Dorthe Posselt (2000). Reaktiviteten for Hvedehalm, Fysik OB, Toning-Anvender projekt, Roskilde University, Roskilde, Danmark
10. Bentzen J.D., Hindsgaul C., Henriksen U., Sørensen L.H. (2002). Straw gasification in a two-stage gasifier. Presented in 12th European Conference and Technology Exhibition on Biomass for Energy, Industry and Climate Protection. Amsterdam, The Netherlands 17-21 June 2002
11. Norby P., Posselt D., Sørensen L.H. (2002). To be published.

12. Kurkela E., Kurkela M., Noroaho E., Moilanen A., Sørensen L.H. [2000]. Fluidised-Bed Gasification of Straw Using Additives – Bench-Scale Tests, Internal Final report, VTT Energy, Espoo, Finland.
13. Kurkela M., Grommi M., Kurkela E. [2001]. Bench-Scale Fluidised-Bed Gasification Tests with Straw, Internal test report, VTT Energy, Espoo, Finland
14. Papadakis K. [2000]. Reactivity in Biomass Gasification in Dependence on the Calcium Loading Procedure. Master Thesis (FA Darmstadt) and ReaTech Report. Roskilde Denmark.
15. Sørensen L.H., Fjellerup J., Henriksen U., Moilanen U., Moilanen A., Kurkela E., Winther E. [2000]. An Evaluation of Char Reactivity and Ash Properties in Biomass Gasification. EFP-98 1383/98-0003, ReaTech, Roskilde, Denmark,
16. Sørensen, L.H., Henriksen U., Risnes H., Tarp Poulsen K., Hansen L.K., Olsen A., Rathman O. (1997). Straw - H₂O gasification kinetics. Determination and discussion, Nordic Seminar on Thermochemical Conversion of Solid Fuels, 3rd December, 1997, Chalmers University of Technology, Sweden.
17. Hansen, L.K., Rathmann, O., Olsen, A. & Poulsen, K.(1997). Steam gasification of wheat straw, barley straw, willow and giganteus, Risø National Laboratory, Optics and Fluid Dynamics Department, Project No. ENS-1323/95-0010
18. Hurt R.H. & Calo J.M. (2001). Semi-global intrinsic kinetics for char combustion modelling. *Combustion and Flame*, Vol. 125, pp. 1138-1149.
19. Kapteijn, F., Meijer, R. & Moulijn, J.A. (1991). A transient kinetic study of the gasification of carbon in CO₂, American Chemical Society, Preprints of papers, Division of fuel chemistry, pp. 906-913.
20. Sørensen L.H., Fjellerup J., Henriksen U. (2000). A Method for Reducing Agglomeration, Sintering and Deposit Formation in Gasification and Combustion of Biomass, PCT/DK00/00404 & WO 01/05911 A2
21. McKee D.W. *Carbon* 1982, **20**, 59

Acknowledgement

The research was supported by Energy E2, the Danish Ministry of Energy, RITTS Greater Copenhagen and the Nordic Energy Research Programme (Biomass combustion programme).

Several students have participated to the results obtained in OCIFP by doing very good experimental and theoretical work. Thanks to Karen-Anne Holt Larsen, Heidi Kolmorgen Nielsen Ingunn Gunnarsdóttir, Jacob Kirkensgaard Hansen, Uffe Thomas Volmer Jankvist, Thomas Helverskov Madsen and Peter Tiedemann all from IMFUFA, University of Roskilde. Thanks also to Klaus Papadakis and Anja Heselich from Fachhochschule Darmstadt, Germany. John Kjøller, Bent Larsen and Allan Schrøder Pedersen from Risø National laboratory are acknowledged for providing assistance with BET adsorption measurements.

We acknowledge Lars Nicolaisen (Teknologisk Institut, Århus), Klaus Hjuler (dk-Teknik) and Jørgen Busk (Bioteknologisk Institut) for providing assistance during preparation of the straw pellets with additives for the two-stage gasifier tests.

ReaTech
ISBN 87-988105-1-0



ISBN 87-988105-1-0