

# PRESSURIZED THERMOGRAVIMETRIC REACTIVITY STUDY OF WHEAT STRAW COMBUSTION AND CO<sub>2</sub>-GASIFICATION.

Ole Rathmann and Jytte B. Illerup  
Department of Combustion Research  
Risø National Laboratory  
DK-4000 Roskilde, DENMARK.

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## Abstract.

Biomass fuel reactivity is interesting since biomass, as e.g. wheat straw, is a relevant fuel for advanced pressurized power plants due to the CO<sub>2</sub> neutrality. In this study combustion- and CO<sub>2</sub>-gasification reactivities of pulverized wheat straw char up to 40 bar were investigated by isothermal thermogravimetric analysis, and the results were compared to a typical subbituminous coal. A recently built pressurized thermogravimetric analyzer of the horizontal type, with operating conditions at least up to 1200°C, 45 bar, was used. In the study the effects of temperature and partial pressure of the reactants O<sub>2</sub> and CO<sub>2</sub>, respectively, were seen, for gasification also the inhibition effect of CO, whereas a distinct total pressure effect could not be observed. Also the effect of using non-pulverized straw pieces was investigated.

## INTRODUCTION

The use of biomass fuels for power generation and heat production has a number of advantages with the CO<sub>2</sub> neutrality and saving of depletable fossil fuels among the most obvious. In addition, national legislation in Denmark urge to use locally available biomass as e.g. wood waste and straw. Considering the future, characterization of biomass fuel will thus be relevant in relation to combustion and gasification for high efficiency pressurized power plant types (as IGCC). As a result, research groups in Scandinavia and elsewhere have been active in characterizing the biomass fuels relevant in their respective countries, and main issues have been influence of pressure, temperature and gas composition on the reaction rate.

Especially wood, straw and black liquor char gasification reactivities at moderate reaction rates have been studied using large-sample vertical Pressurized ThermoGravimetric Analyzer (PTGA) instruments. Blackadder & Rensfelt (1985) studied pyrolysis of wood, cellulose and lignine up to 800 °C at 1 to 40 bar. Moilanen et al. (1993) investigated atmospheric steam gasification of chars of wood, peat and black-liquor in comparison with coal and brown-coal, while Whitty et al. (1993b) investigated pyrolysis and char CO<sub>2</sub>-gasification of coarsely pulverized wood and peat at 850°C at 1-20 bar. Stoltze et al. (1993) studied atmospheric steam gasification of large samples of barley straw char at 750°C-950°C. Black liquor char was investigated by Backman et al. (1993) and by Whitty (1993) regarding pressurized CO<sub>2</sub>- and steam gasification in presence of CO at 650-800°C and 1-30 bar. The following overall picture is seen: In pyrolysis, wood char yield increases clearly with increasing pyrolysis pressure, while the reactivity displays a weak decrease. Wood char reactivity is similar to that of peat and brown coal and about 1 order of magnitude faster than for coal, black liquor displays a reactivity 2 orders of magnitude faster than wood, and gasification with steam has a reactivity about 4 times faster than with CO<sub>2</sub>. The reactivity increases strongly with increasing temperature and as seen for coal. Increase in total pressure at constant gas percentage composition has a weak, enhancing effect for wood while for black liquor the effect is directly reducing, attributed to inhibition by CO or H<sub>2</sub> inside the char pores.

In this work we have investigated combustion and CO<sub>2</sub>-gasification reaction rates of straw as this fuel is expected to be one of the important biomass fuels in future advanced Danish power/heating stations. The work was performed under contract with and the Danish utility associations Elsam and Elkraft within the European Union APAS programme, and was supported by the Danish Ministry of Energy.

## EXPERIMENTAL

The fuel samples were prepared from wheat straw normally used in Danish electrical-power/district-heating stations. Entire straws were ground to pulverized, average straw samples with a particle diameter smaller than 200µm. Char of pulverized straw, straw inter-node pieces, straw nodes and grains were produced in a furnace by a 7 minutes 900 °C pyrolysis heat treatment at atmospheric pressure without oxygen access. The raw fuel compositions given in table 1 indicate rather similar proximate compositions while ash compositions differ, especially with respect to K<sub>2</sub>O and P<sub>2</sub>O<sub>5</sub>.

The PTGA-instrument used for the study (fig.1) is a modified DuPont thermogravimetric analyzer of the horizontal type, recently built at RISØ. The fuel sample is placed on a small 1cm diameter Platinum tray hanging on a horizontal balance arm, situated in a reaction tube together with thermocouples. The reaction tube is heated from outside by a heater element, and the entire thermobalance arrangement is placed inside a 35 l pressure vessel. Pressure and flow control are performed by a number of valves and gas mass flow controllers. The test gas, selectable from either an inert gas (N<sub>2</sub>) source or a premixed reactive gas source, is supplied to the rear end of the reaction tube with a filler element to heat the test gas to operating temperature. A test gas rate corresponding to a linear velocity in the reaction tube of about 1 cm/s at 1000 °C is used giving a switching time for the gas composition at the sample position of about 100 s. The balance system is the original DuPont component, while reaction tube, oven and all external systems are new. The PTGA can operate up to 45 bar and 1200°C simultaneously. Samples up to about 150 mg can be investigated, but for low density fuels the practical limit is set by the fuel volume and may be 5 to 10 mg. Data logging is performed once per 2 seconds.

Pyrolysis experiments were performed in an inert test gas with a ramped temperature. The combustion and gasification reactivity experiments were performed isothermally with the operating temperature established in inert test gas after which the reactive test gas (N<sub>2</sub>/O<sub>2</sub> or N<sub>2</sub>/CO<sub>2</sub>/CO mixture) was selected. The maximum conversion rate that could be measured was set by the test gas switching time and the maximum diffusion rate of reactant to the sample and within the sample.

The experimental weight signals were compensated for bouyancy and balance arm length expansion, based on calibration tests. For the reactivity experiments a transformation then followed of the compensated weight to a conversion degree X and a reactivity R(= reaction rate per remaining char)

$$X = (m_{c0} - m_c) / m_c \quad (1)$$

$$R = -dm_c/dt / m_c = dX/dt / (1-X) \quad (2)$$

where  $m_c$  and  $m_{c0}$  are the instantaneous and initial char mass on dry and ash free basis, respectively. Each reactivity experiment was characterized by the reactivity at 50% conversion,  $R_{0.5}$ , and the variation of R with conversion X was, as an approximation, described by a single normalized reactivity profile  $f(X)$  (normalized to 1.0 at  $X=0.5$ ) for each of the reaction types, i.e.  $R(X) \approx R_{0.5} f(X)$ . An estimate of the reaction time to a certain conversion degree could then be calculated as

$$t_X \approx 1/R_{0.5} \int_0^X \frac{f(X')}{(1-X')} dX' \quad (3)$$

## RESULTS

A minor number of pyrolysis experiments were performed on raw, pulverized straw samples to see the influence of heating rate and pressure in the temperature range 150-1000°C. At 20 bar, heating rates of 10, 30 or 50°C/min had no effect on char yield. With a heating rate of 30°C/min the char yield seemed to increase weakly with pressure: 15%, 20% and 22% char yield (2.5% uncertainty) for 1.5, 20 bar and 40 bar, and the maximum pyrolysis rate occurred in a narrow range from 342°C to 355°C. More accurate experimental results are necessary to quantify the pressure effect on the char yield. As these results showed little effect of pyrolysis pressure it was assumed that the atmospheric pyrolysis pressure was of no importance for the resulting char.

Combustion reactivity was measured at temperatures from 300°C to 410°C, pressures from 1.5 bar to 40 bar and O<sub>2</sub> pressures from 0.08 bar to 0.8 bar. The results for  $R_{0.5}$  are shown in fig.2. The reactivity increased with increasing conversion degree, with values at  $X=0.2$  and  $X=0.8$  about 0.6 and 1.7 times the value at  $X=0.5$ , respectively. While results at such low temperatures are not directly applicable to practical conditions they permit comparison to corresponding reference coal data. At 400°C and 0.26 bar O<sub>2</sub>, the reactivity was found to be about 0.002s<sup>-1</sup>, about 30 times higher than the reactivity for the reference coal. The dependence on temperature and O<sub>2</sub> partial pressure corresponds to an activation energy of 110 kJ/mole and a reaction order of 0.61. The activation energy is similar to that of the reference coal but the reaction order is a little lower. No significant effect of the total pressure was observed.

CO<sub>2</sub> gasification reactivity was measured in the fluidized-bed relevant temperature range 850°C-1050°C at 20 bar and with 3 different gas compositions, including one with the inhibitor-component CO, as shown in fig.3. A few of these experiments were repeated at 4 and 40 bar total pressure with unchanged CO<sub>2</sub>/CO partial pressures. At 1000°C the reactivity R<sub>0.5</sub> was found to be about 0.006s<sup>-1</sup> in 0.7 bar CO<sub>2</sub> and no CO. The reactivity increased with conversion degree, with values at X=0.2 and X=0.8 about 0.6 and 2 times the value at X=0.5, respectively. The present straw reactivity is about 16 times faster than for the reference coal and 1.5-2 times faster than for the wood reactivity as measured by Whitty et al.(1993a). The results for R<sub>0.5</sub> could be interpreted in terms of Langmuir-Hinshelwood kinetics (see e.g. Laurendeau (1978)):

$$R_{0.5} = k_1 P_{CO_2} / (1 + aP_{CO} + bP_{CO_2}),$$

where k<sub>1</sub>, a, and b have Arrhenius temperature dependence, for a and b, however, with negative activation energies. In spite of some unsystematic variation in the experimental data, saturation (described by the 'b' parameter) was clearly observed as the reactivity increased less than proportionally to the increase in CO<sub>2</sub> pressure from 0.7 to 2.2 bar in absence of CO. Also, the clear decrease in reactivity from 1.5 to 5 times, when changing from a 2/0 bar to a 2/2 bar CO<sub>2</sub>/CO test gas, indicates clearly inhibition (described by the 'a' parameter) at the test temperatures. Both the saturation and inhibition effects showed an expected reduction with increasing temperature. The present results are too scarce to permit an unambiguous determination of kinetic parameters, but as shown in fig.3, a Langmuir-Hinshelwood representation could be obtained using a- and b-parameters from the reference coal in combination with a fitted k<sub>1</sub>-parameter. However, the value of this k<sub>1</sub>-parameter in dependence of temperature is strongly dependent on the applied values of the a- and b- parameters. The measurements suggest a moderate reactivity reduction with increasing total pressure, may be up to 2 times when the pressure is increased from 4 to 40 bar at constant CO<sub>2</sub> and CO partial pressures. In contrast to black liquor reactivity, the present data suggest an increasing reactivity when increasing the pressure at constant gas percentage composition.

The reactivity of char of non-pulverized 'straw particles' was measured at 900-1000°C with 20 bar pressure and 2/2 bar CO<sub>2</sub>/CO partial pressure. Relative to the char of average, pulverized straw the inter-node particles showed a reactivity more than 2.5 times faster, node-particles showed a reactivity 2 times slower at 900°C while at 950°C and 1000°C it was more than 3 times faster than for pulverized straw. Grains showed a reactivity about 2.5 times slower than pulverized straw. The surprising faster reactions of inter-node and node particles may be due to the non-packed structure of the sample, but for the nodes this behavior may also be due to the higher concentration of the catalyst K<sub>2</sub>O in the ash (see table 1).

#### DISCUSSION AND CONCLUSION

The present PTGA instrument has proved to be a valuable instrument for biomass fuel reactivity analysis at moderate reaction rates, in the present study of wheat straw.

Pyrolysis of pulverized straw suggested a small increase in char yield with increasing pressure. Pressurized combustion and gasification reactivity of straw char samples, pyrolyzed at low heating rate, was investigated up to 40 bar but with the main part of the investigations at 20 bar.

The combustion reactivity at low temperature (around 350°C) with 0.08 to 0.8 bar O<sub>2</sub> was somewhat more than one order of magnitude higher than for a reference coal and with the same relative temperature dependence. The dependence on O<sub>2</sub> partial pressure was weaker, and no significant dependence on total pressure (at constant partial pressure) could be observed.

CO<sub>2</sub>-Gasification reactivity was investigated around 950°C at CO<sub>2</sub> and CO pressures around 1 bar. The results, displaying both CO<sub>2</sub>-saturation and Co-inhibition, could be understood in terms of Langmuir-Hinshelwood kinetics, but more accurate measurements are necessary to actually determine the kinetic parameters. In absolute magnitude the straw char reactivity was found to be an order of magnitude higher than for the reference coal and also a little higher than for wood biomass. Char of non-pulverized 'straw-particles', including grains, displayed reaction rates moderately scattering above (3 times) and below (2 times) that of the pulverized samples, presumably as a combined result of size effect, compactness and composition of the non-pulverized particles. The pulverized fuel reactivity results displayed a moderate decrease with total pressure, but more accurate measurements are needed to tell whether this is a significant effect. Also, experiments with chars pyrolyzed at high heating rates at various pressures would be relevant to distinguish between the effects of total pressure through pyrolysis and through char gasification.

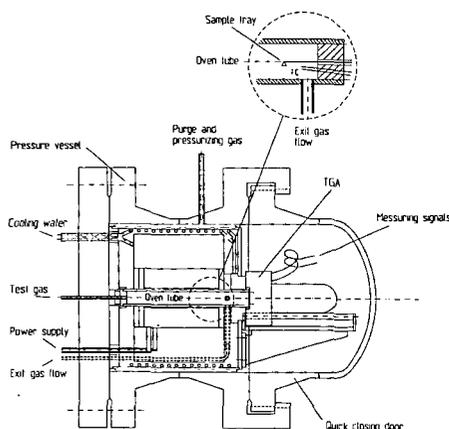
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## TABLES AND FIGURES

*Table 1. Fuel proximate-ultimate analysis.  
Most relevant species and compounds are included.*

w% in dry non-pyrolyzed fuel	Pulv. straw (average)	Straw-nodes	Grain
Ash	6.4	9.0	1.6
Volatiles	77.3	75.1	83.2
Hydrogen	5.8		6.8
Carbon	47.2		44.6
w% in ash			
SiO <sub>2</sub>	62	2.7	1.4
CaO	8.1	11	3.7
MgO	1.8	3.4	11
Na <sub>2</sub> O	0.4	0.2	0.2
K <sub>2</sub> O	14	55	34
P <sub>2</sub> O <sub>5</sub>	2.4	2.0	45



*Fig 1. Recently built Pressurized Thermogravimetric Analyzer instrument used in this study.  
All electrical connection fit-throughs are placed in the rear flange (left side) of the pressure vessel.*

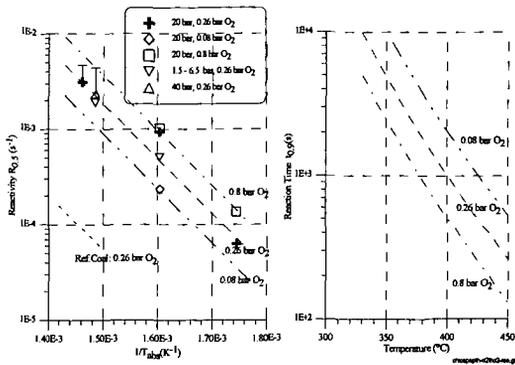


Fig.2. Straw char combustion reactivity experimental results.

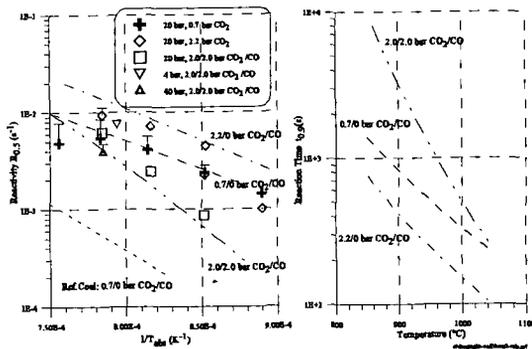


Fig.3. Straw char  $CO_2$ -gasification reactivity experimental results.

In both fig.2 and fig.3 representative Langmuir-Hinshelwood kinetic model values are shown by dashed and dash-dotted lines. Error bars indicate uncertainty due to large instrument diffusion limitation. The over-all accuracy is 10-15%. Preliminary results from a reference pulverized coal char (Colombian Cerrejón) are included. Predictions of conversion times to a conversion degree of 0.9 are shown in the right part of the figures.