DEVOLATILIZATION OF TWO AGRICULTURAL RESIDUES IN FLUIDIZED BED: PRODUCT DISTRIBUTION AND INFLUENCE OF FLUIDIZATION AGENT

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ABSTRACT: Devolatilization of two agricultural residues; corn stover and a solid by-product from enzymatic hydrolysis of biomass (cake), was carried out in a fluidized bed at temperatures between 750 and 900 ºC. The distribution of products and composition of the light gas were determined using N_2 as fluidizing gas and the effect of the fluidizing agent was studied using N_2-steam and N_2-CO_2 mixtures. Dedicated experiments were performed in order to measure the amount of H_2O formed during devolatilization and the results had good repeatability. Expressions for calculating product yields and light gas composition as a function of temperature were obtained. These expressions are useful for gasification modeling. It was found that the composition of the fluidizing gas did not have significant effect on production of light gases during devolatilization.
Keywords: agricultural residues, biomass, fluidized bed, gasification, pyrolysis.

1 INTRODUCTION

Devolatilization is a key step during biomass conversion, since the volatiles represent up to 90% of the dry ash free material. In fluidized bed gasification, the composition of the produced gas depends greatly on the fluidizing gas employed. In addition to air-blown gasification, gasification of biomass using steam and CO_2 are under investigation. For example, in dual fluidized beds the devolatilization usually occurs in a steam atmosphere.

Devolatilization of biomass is usually studied in inert atmosphere. The influence of different reactive gases has been studied in fixed bed furnaces at low heating rates [1] However, in a fluidized bed (FB), the heating rate is high and the volatiles are quickly swept away by the fluidizing gas, influencing the process significantly. Therefore, conduction of tests in an FB is necessary if the data are being applied to scale-up FB combustors and gasifiers.

Despite of the industrial importance of these processes, only a few works have been published in FB.

The presence of reactive gases may influence both primary and secondary reactions during devolatilization and so the yields and distribution of the species generated. In addition, the mode of devolatilization affects the structure and reactivity of the produced char.

In this study biomass devolatilization experiments are carried out in a laboratory fluidized bed at temperatures between 750 ºC and 900 ºC using different fluidizing gases; N_2, N_2-steam mixtures and N_2-CO_2 mixtures.

2 EXPERIMENTAL

2.1 Rig

The experimental setup is represented in Fig. 1 Experiments were carried out in a fluidized bed reactor with internal diameter in the fluidized bed section and freeboard of 51 mm and 81 mm, respectively. The reactor is equipped with an electrical oven and four thermocouples, so the temperatures in the freeboard and in the fluidized bed could be controlled. The gas leaving the reactor passes through cyclone where any entrained material is collected. The flow of N_2 and CO_2 were controlled by means of mass flow controllers and steam was generated by vaporizing a controlled flow of water.

Fuel batches were fed to the upper part of the fluidized bed through two ball valves. The composition of the exit gas was measured by a Siemens analyzer using a non-dispersed infrared method for CO, CO_2 and CH_4 and thermal conductivity and paramagnetic methods for H_2 and O_2, respectively.
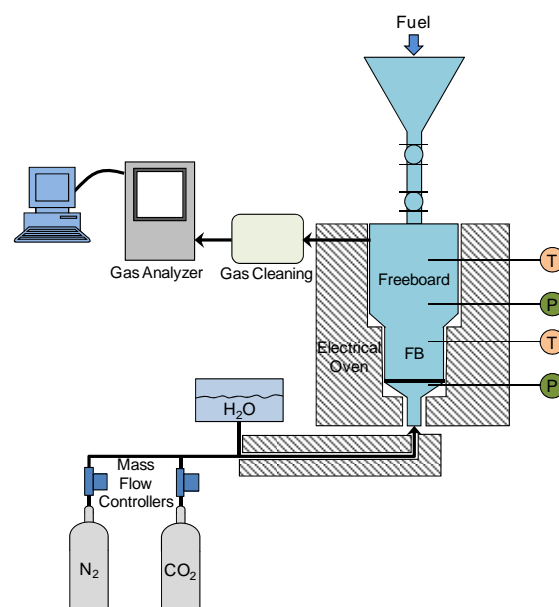

Figure 1: Experimental setup

2.2 Material

The fuels employed were corn stover and a solid by-product from the enzymatic hydrolysis of biomass, here referred to as cake. The corn stover received was milled to a size < 6 mm and afterwards, the fines with size < 500 μm were separated. The cake was received in the form of powder that was dried in an oven at 60 ºC for 48 hours before storage. Pellets were prepared from corn stover and cake by putting 1 g of material in a 1 cm diameter cylindrical mould and applying a pressure of 50 bar.

Afterwards the pellets were dried for 24 h. The weight of the dry pellets was approximately 0.90-0.95 g. The proximate and elemental composition of corn stover and cake is shown in Table I.

The bed material employed was bauxite with a particle size in the range of 250 μm-500 μm and density of 3300 kg/m^3. The minimum fluidization velocity measured for the bauxite was 0.20 m/s. The amount of bauxite in the bed was 300 g.

Table I: Proximate and elemental composition of corn stover and cake

	Corn Stover		Cake	
	As received*	Dry Basis	As received	Dry Basis
HHV, MJ/kg	15.37	16.73	7.24	20.01
Composition, weight %				
C	-	44.82	-	48.31
H	-	5.39	-	4.91
N	-	0.96	-	1.84
S	-	0.09	-	0.22
O	-	41.36	-	27.83
Moisture	8.11	-	63.85	-
Ash	11.89	13.14	6.11	16.89
Volatiles	68.58	74.63	7.98	61.03
Fixed carbon	11.42	12.23	7.98	22.08

* This refers to the composition of the material after separating the fines.

2.3 Experimental procedure

Three types of experiments were carried out in this study; devolatilization experiments using different fluidizing gases, dedicated experiments to measure the amount of chemically formed water during devolatilization and experiments aimed at studying the shrinkage and fragmentation of the pellets. In addition, a blank test was performed to assess the effects of mixing in the gas exit line by injecting a certain flow of CO_2 into the fluidization gas (pure N_2) in a port situated in the upper part of the FB. The effect of mixing was well characterized by a first order model, with a time constant equal to 13 s. This value was used to correct the concentrations of the light gas components measured by the gas analyzer.

The procedure followed during the devolatilization experiments with different fluidizing gases was as follows. First, the reactor was heated to the desired temperature with a continuous flow of air. Once this temperature was reached, the fluidizing gas was switched to N_2 to purge the oxygen. Afterwards, the composition and flow rate of the fluidizing gas were established and the batch of fuel was fed to the reactor. For the tests using pure N_2, after complete devolatilization, the gas feed was switched to air to burn the remaining char. For the experiments using N_2-steam mixtures and N_2-CO_2 mixtures as fluidizing gas, the conditions of the feed gas were maintained for approximately 25 minutes, which is enough for the devolatilization to be complete and for most of the produced char to react with the steam or CO_2.

Afterwards, the feed gas was switched to air to burn the remaining char.

For determination of the amount of water formed during devoltilization, the fuel was devolatilized with N_2 as fluidizing gas and the gases leaving the reactor were passed through six impingers with isopropyl alcohol maintained at -20 ºC. The amount of water was then determined using Karl-Fischer titration.

For studying the shrinkage and fragmentation of the pellet, the fuel batch was devolatilized under N_2 using the same procedure as for the devolatilization experiments, but instead of burning the produced char, after devolatilization, the oven was switched off and the char was cooled down under a reduced N_2 flow.

2.4 Operating conditions

Experiments were carried out at three temperatures; 750, 825 and 900 ºC, using a gas velocity equal to three times the minimum fluidizing velocity. Three different compositions of the fluidizing gas were tested; 100% N_2, N_2-steam mixture with 45 % volume concentration of steam and N_2-CO_2 mixture with 40 % CO_2 concentration.

For the devolatilization experiments, batches of 3 fuel pellets were employed. To measure the amount of water produced, the batch size had to be larger (than in the other experiments) in order to ensure that the water concentration in the isopropyl alcohol was sufficiently high to permit accurate measurements. For each test, a total amount of 30 pellets was employed, but divided into six batches of 5 pellets each. Devolatilization of the four batches was done sequently under N_2 flow.

3 RESULTS AND DISCUSSION

3.1 Distribution of products from devolatilization with N_2 as fluidizing gas.

The devolatilization experiments with N_2 as fluidizing gas were employed to determine the yields of light gas and char, as well as the composition of the light gas. The light gas yield includes the CO, CO_2, CH_4 and H_2 measured during devolatilization and the char yield was calculated as the total amount of carbon measured as CO and CO_2 during the combustion of the produced char.

For corn stover, the water yield was determined in dedicated experiments as explained above and the tar yield was determined by difference and includes both tar and light hydrocarbons (other than methane). For cake, experiments for measuring the water yield are still ongoing and results are not yet available, so a condensate yield that includes both water, tar and light hydrocarbons was defined. All the experiments were repeated at least once, and the repeatability was good. Figs. 2 and 3 show the product yields referred to the carbon, hydrogen and oxygen contained in the dry and ash free fuel, measured at different temperatures, for corn stover and cake respectively. The results show that the light gas yield increases significantly with temperature, while the tar/condensate yield decreases. For corn stover, the char and water yields decrease slightly with increasing temperature while for cake, the char yield is practically constant. The light gas yield is very similar for the two fuels. The char yield is higher for cake, which is consistent, since this fuel is expected to have a high lignin content. The char yields measured for both corn stover and cake agree well with the fixed carbon contents measured during proximate analysis.
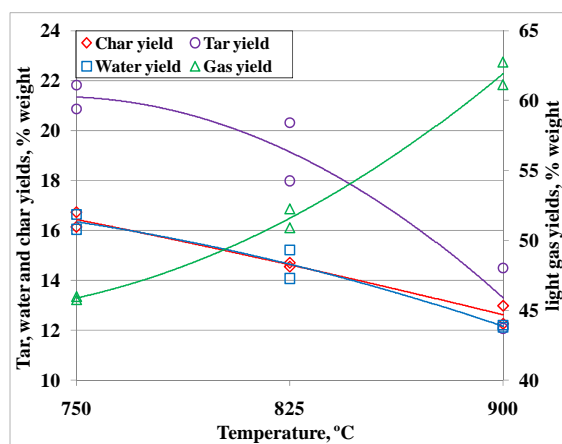
Figure 2: Light gas, tar, water and char yields obtained during devolatilization of corn stover, note that the light gas yield is red on the right side y-axis.
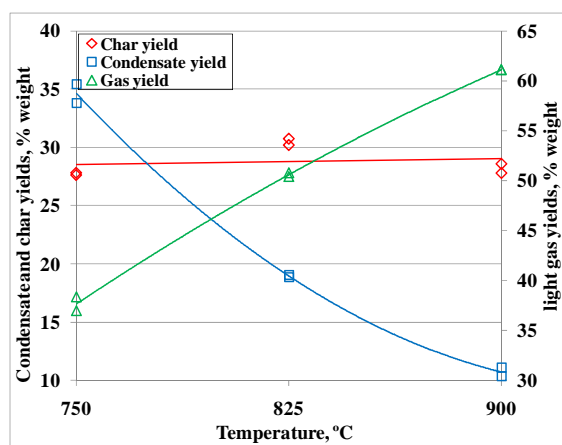

Figure 3: Light gas, condensate and char yields obtained during devolatilization of cake, note that the condensate yield includes both tar and water yields and that the light gas yield is red on the right side y-axis.

The composition of the light gas at different temperatures is shown in Figs. 4 and 5 for corn stover and cake respectively.
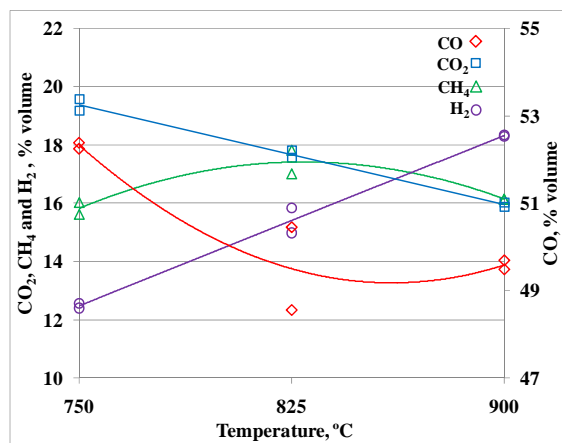

Figure 4: Composition, in volume %, of the light gas produced during devolatilization of corn stover, note that the CO concentration is red on the right side y-axis.
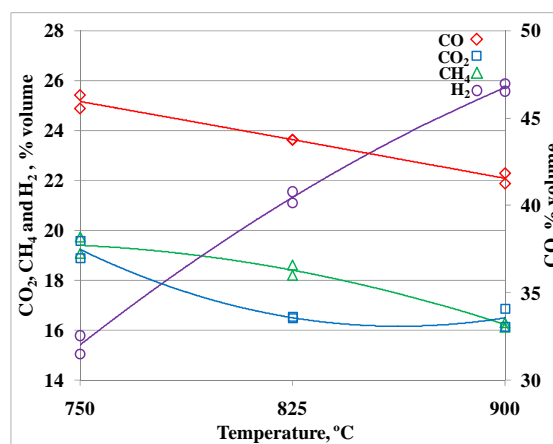

Figure 5: Composition, in volume %, of the light gas produced during devolatilization of cake, note that the CO concentration is red on the right side y-axis.

For both fuels, CO is the main light gas component.

Variations in the light gas composition are not very important, except for the increase in H_2 concentration with rising temperature. This effect is most significant for the devolatilization of cake.

The product yields and the composition of the light gas were fitted to a quadratic function of temperature:

$$y_i = a_0 + a_1T + a_2T^2 \qquad (1)$$

being y_i the light gas, tar, water, condensate or char yield (in % weight) or the CO, CO_2, CH_4 or H_2 concentration in the light gas (volume %). a_o, a_1 and a_2 are empirical fitting parameters and T is the temperature in °C. This type of expression is very useful to include in a fluidized bed gasifier model. The a_o, a_1 and a_2 obtained for devolatilization of corn stover and cake are shown in Tables II and III respectively.

Table II: Values of the fitting parameters, a_o, a_1 and a_2, in Eq. (1) calculated for the product yields and light gas composition obtained during devolatilization of corn stover.

	a0	a1	a2
Gas yield	244.30	-5.74E-01	4.13E-04
Tar yield	-157.70	4.82E-01	-3.25E-04
Water yield	-10.25	8.82E-02	-7.04E-05
Char yield	35.53	-2.54E-02	0
CO %vol	240.30	-4.44E-01	2.58E-04
CO2 %vol	36.48	-2.28E-02	0
CH4 %vol	-156.90	4.21E-01	-2.54E-04
H2 %vol	-16.71	3.89E-02	0

Table III: Values of the fitting parameters, a_0, a_1 and a_2, in Eq. (1) calculated for the product yields and light gas composition obtained during devolatilization of cake.

	a0	a1	a2
Gas yield	-224.16	5.10E-01	-2.14E-04
Condensate yield	597.34	-1.24E+00	6.57E-04
Char yield	28.79	0	0
CO %vol	65.41	-2.32E-02	-3.69E-06
CO2 %vol	196.29	-4.18E-01	2.42E-04
CH4 %vol	-35.96	1.53E-01	-1.06E-04
H2 %vol	-125.74	2.88E-01	-1.33E-04

3.2 Influence of fluidizing gas on devolatilization of corn stover.

In order study the influence of the fluidizing gas, devolvatilization experiments using mixtures of 45 % volume of steam in N_2 and 40 % volume of CO_2 in N_2 were employed and the fuel was corn stover. During these experiments, both devolatilization and gasification of the produced char with steam or CO_2 occur. In order to study the influence of the fluidizing gas on devolatilization it is therefore important to be able to separate these two processes. In order to visualize the different stages of fuel conversion, sample mass loss curves were calculated for the tests using different fluidizing gases. Fig. 6 shows the sample mass loss curves obtained with the three different fluidizing gas compositions at 825 °C. Fig 6 represents $m(t)/m_0$ as a function of time, being m_0 the initial mass of C, H and O in the dry and ash free sample and $m(t)=m_0-m_v(t)$, where m_v is the total mass of light gases measured by the analyzer up to time t. These mass loss curves do not take into account the mass loss due to tar and water formation during devolatilization, but they are useful for visualizing the results.
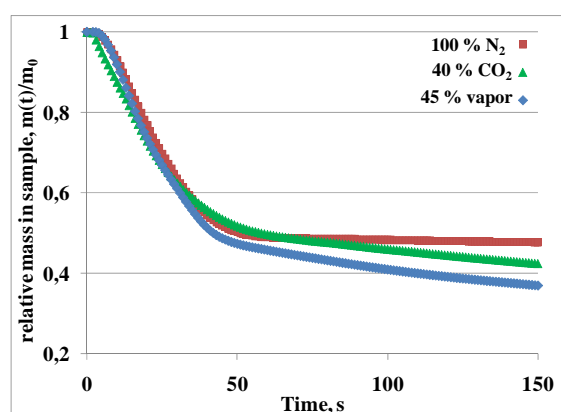

Figure 6: Sample mass loss curves obtained during devolatilization of corn stover at 825 °C using different compositions of the fluidizing gas

Fig. 6 shows that the mass loss curves obtained with N_2-steam mixture and N_2-CO_2 mixture have two distinct sections with different rates of mass loss, so overlapping in time between devolatilization and gasification of char is limited. This result is not unexpected since the flow of volatiles out of the particle during devolatilization, prevents the fluidizing gas to penetrate into it.

The influence of the fluidizing gas on the formation of the different light gas components was also studied.

The productions of the different species in mol/s measured with different fluidizing gases, were compared but no significant difference was observed. Fig. 7 represents the CO production as a function of time measured for different fluidizing gases at 825 °C.
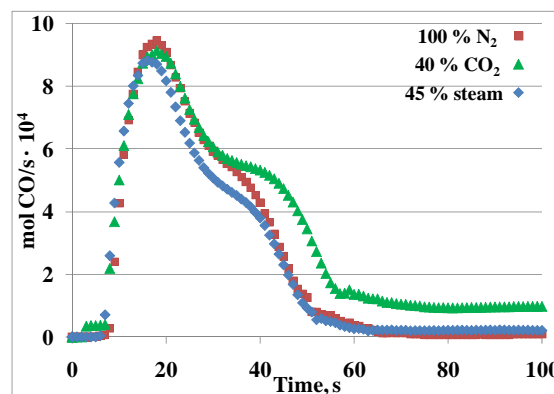

Figure 7: Production of CO during the gasification of corn stover, mol/s·10^4, measured at 825 °C using different compositions of the fluidizing gas.

The composition of the fluidizing gas may affect both primary and secondary reactions during devolatilization.

If penetration of fluidizing gas into the particle is limited, the influence on primary reactions can be expected to be small. On the contrary, at temperatures above 800 °C, the rates of secondary reactions, such as the WGSR can be high. If these reactions were important, the production of the different gas species should be effected by the composition of the fluidizing gas employed. No such effect was observed here. One surprising results is that the production of CO is not affect by the addition of 45 % steam in the fluidizing gas.

Using WGSR kinetics from literature that are, often used for gasifier modelling, [2] it is predicted almost complete conversion of the CO produced during devolatilization before it leaves the reactor. There are many species that can catalyze this reaction, for example the bed material or the reactor walls, so the kinetics of the WGSR in our reactor should be investigated further.

3.3 Shrinking and fragmentation of corn stover pellets during devolatilization

A test was made to check the shrinkage and fragmentation of corn stover pellets by devolatilizing two pellets with 100% N_2 as fluidizig gas. After devolatilizaction the char was cooled and recovered from the reactor. Fig. 8 shows a picture of the virgin and devolatilized pellets.

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Figure 8: Virgin corn stover pellets and the char obtained from devolatilization of these pellets in fluidized bed

It can be seen that the pellets broke into a limited number of pieces and some shrinkage was also observed.

4   CONCLUSIONS

- Devolatilization of two agricultural residues in a fluidized bed has been studied and expressions that permit calculation of the light gas, tar/condensate, water and char yields as well as the light gas composition, as a function of temperature have been obtained.
- The experimental method was modified in order to obtain reliable results of the amount of water formed during devolatilization. The results obtained using this method showed good repeatability.
- Experiments were carried out using N_2-steam and N_2-CO_2 mixtures to study the influence on the results of the composition of the fluidizing gas during devolatilization. No significant influence was found and the overlapping in time between devolatilization and gasification of char was small.

5   ACKNOWLEDGEMENTS

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6   REFERENCES

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