

Degradation characteristics of straw and washed straw

Colomba Di Blasi^{*}, Carmen Branca, Gaetano D'Errico

Dipartimento di Ingegneria Chimica, Università degli Studi di Napoli Federico II P.le V. Tecchio, 80125 Napoli, Italy

Received 29 March 2000; received in revised form 14 July 2000; accepted 27 July 2000

Abstract

Product distribution from straw and washed straw pyrolysis shows the usual temperature (660–990 K) dependence, but the pretreatment makes the initial degradation temperature slightly higher and gives rise to larger yields of condensable products (mainly at the expenses of char). Water washing also affects decomposition of straw in air. Devolatilization again takes place at higher temperatures and with a higher peak rate, but char combustion reactivities are always lower. Hot water washing of large (0.5–1 mm) straw char particles is less effective for ash removal than straw washing, independently of the temperature and the atmosphere where chars were formed. In particular, for low temperature (520 K) and air, the ash removed decreases as successively higher conversion levels are examined. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Degradation; Straw; Product yields; Reactivity

1. Introduction

It is well known that ashes present in biomass exert a catalytic action in the thermal decomposition of the cellulose content [1]. More precisely, as the inorganic salts shift cellulose decomposition to lower temperatures, the DTG peaks of cellulose and hemicellulose overlap each other. By reducing the inorganic content through water (or mild acid) washing, a better resolution is observed for several herbaceous biomasses, in particular straw [2–4]. Washing, however, is not only a technique applied to simplify the reaction kinetic studies. It has received significant attention for practical applications also, because it is an effective means to remove large parts of potassium and chlorine from

biofuels [5,6], thus improving the performances of high-temperature conversion systems. Indeed, alkali metals (Cl, K, Mg, Na) give rise to several drawbacks during high-temperature treatments [7,8], which include deposits in the combustion chamber and super heater coils, bed agglomeration, corrosion (high HCl or KCl concentrations in the flue gas) and poisoning (K) of the catalysts in power plants equipped with selective catalytic reduction (SCR). However, an extensive study is not available on the temperature dependence of pyrolysis products from untreated and washed biomass.

In [2,3], a packed-bed reactor was used to investigate the influence of deashing on total volatile and char yields for a chosen temperature and different biomasses (663–668 K for wheat straw). Other studies [9–11] were carried out with bench-scale fluid-bed reactors for wood in a narrow temperature range, with the aim of investigating the effects of demineralization on the yield and composition of pyrolysis oil. In all cases, it has been observed that ash removal causes a

^{*} Corresponding author. Tel.: +39-81-7682232;
fax: +39-81-2391800.
E-mail address: diblasi@unina.it (C.D. Blasi).

reduction in the char yields with a corresponding increase in the liquid products [9–11], which also present higher contents of levoglucosan (at the expense of lighter volatiles such as hydroxyacetaldehyde). In this study, the influence of water washing on the pyrolysis product yields is examined over a wide temperature range for (wheat) straw which, among agricultural residues, is probably the most abundant and available fuel worldwide.

As an alternative to biomass washing, two-stage conversion processes have also been proposed (for instance, [4,12,13]), corresponding to devolatilization and combustion/gasification, respectively. The chief idea of the process is that the low temperatures of the devolatilization stage allow the alkali metals to be retained in the solid phase product (char); consequently, only the resulting charred residue has to be submitted to water washing before conversion (about 30–40% of the original mass). In two-stage conversion processes, devolatilization can be carried out in the presence of moderate oxygen levels, so that partial oxidation can provide the heat needed to preheat and pyrolyze the fuel. In addition, innovative approaches in the design of pyrolysis units, for instance through proper injection of hot air [13], can reduce the scaling difficulties of indirectly heated reactors. However, again a limited understanding has been achieved of the influence of water washing on the straw reactivity in air and the effectiveness of water washing for ash removal from straw chars.

The degradation kinetics of untreated and rain-washed straw for isothermal conditions (500–650 K) in a weakly oxidative atmosphere have been examined in [14]. For both cases, weight loss curves follow a two-reaction zone mechanism, but washing significantly reduces the reaction rates. However, this pretreatment exerts a small influence on the ignition temperature (about 515–565 K) for conditions of heat and mass transfer control [15]. As in practical applications the range of temperatures of interest is significantly wider, further analysis is presented in this study for straw decomposition under dynamic conditions (and slow heating rates). Finally, although extraction of chlorine and potassium from straw chars has been shown to depend on the water temperature and the particle size [7,16], there is no indication about the influences of the pyrolysis temperatures and the reaction atmosphere. These aspects are also investi-

gated in this study and comparisons are made with straw washing.

2. Experimental

2.1. Material

Tests have been carried out for Danish (wheat) straw (elemental composition reported in Table 1 and ash composition in Table 2). Apart from feedstock heterogeneity, the ash content is somewhat dependent on the straw sampling (from a 50 kg bale), but the range of variation is relatively narrow (5–5.5%). In order to investigate the influence of the water treatment on the degradation characteristics, together with untreated straw, the case of washed straw with a residence time of 2 h at 263 K, that is, for the conditions of maximum extraction and an ash content of 2–2.3%, has been considered. Unless otherwise indicated, straw obtained with this treatment is indicated as washed straw.

The contents of K, Mg, Na and Ca (expressed on an oxide basis) are determined by atomic absorption spectrophotometry, after dissolution of straw in nitric, perchloric and chloric acids at 413–423 K for about 2 h. Values are those typical of Danish straw [17,18] which also includes Cl contents of 0.2–0.5% (a large contribution, 1.3–2.6%, is given by SiO₂). In agreement with previous studies [5], water washing removes almost completely potassium. Although

Table 1
Elemental composition of straw and washed straw, expressed as percent of the initial dry mass

	%C	%H	%N	%O	%S
Straw	43.57	6.24	0.3	45.79	0.09
Washed straw	45.14	6.42	0.3	46.51	0.05

Table 2
Ash analysis on oxide basis (as percent of the initial mass) for untreated and washed straw

	%Ash	%MgO	%CaO	%K ₂ O	%Na ₂ O
Straw	5.25	0.085	0.541	2.14	0.032
Washed straw	2.20	0.039	0.510	0.16	0.022

not measured, as can be inferred by difference on the total ash removed, chlorine is also removed (reduction up to 90%, [5,6,19]) and small part of the other constituents (also SiO₂, SO₃, Al₂O₃, [5]).

2.2. Reactivity tests

Degradation tests have been conducted with the thermogravimetric system already applied for studies on the pyrolysis kinetics of biomass and biomass chars [20–22]. It consists of (1) a radiant heating chamber, (2) a quartz reactor, (3) a PID temperature controller, (4) a gas feeding system, (5) a data acquisition system (PC and related accessories) and (6) a precision balance. In this system, a thin biomass layer is exposed to thermal radiation (corresponding to a known temperature history either of the sample or the sample holder) and its weight is continuously monitored (accuracy 0.1 mg), while the proper reaction environment is established by a continuous flow of assigned composition. In this study, the reaction atmosphere is air (1000 cm³ min⁻¹, corresponding to a nominal velocity of 35 cm³ min⁻¹), in order to simulate straw reactivity under combustion conditions. Prior to reaction, feedstocks are milled to powder (particle sizes below 80 μm) and dried. For the tests, the samples consist of about 20 mg, giving thicknesses of about 0.2 mm, or 60 mg, giving thicknesses of 0.6 mm. The sample is heated to 1100 K with a heating rate of 20 K min⁻¹.

2.3. Pyrolysis tests

A bench-scale system, already presented elsewhere [23,24] and developed to reproduce the devolatilization stage of fixed-bed pyrolyzers and gasifiers, has been used to investigate the pyrolysis of straw and washed straw. Straw particles (sizes in the range 0.5–1 mm and initial moisture content of 7% (untreated straw) and 5% (washed straw), on a moisture free (mf) basis) are packed in a stainless steel mesh, cylindrical shaped holder (4 × 10⁻² m diameter), so that the desired bed density can be achieved (110 kg m⁻³ in this study). The bed is exposed to high external heat transfer rates, simulated by a radiant heater, so that heating (and conversion) characteristics are essentially determined by its physicochemical properties. To avoid interaction between the volatile pyrolysis

products and the heating system, a quartz tube transparent to infrared radiation is located inside the furnace and used as a reaction chamber. A nitrogen flow is applied at the top of the quartz tube in order to reduce the extra-bed residence time of volatile pyrolysis products and to establish the proper reaction environment.

The final temperature, attained by the bed at a distance of 0.1 × 10⁻² m from the heat-exposed surface, T_s , is taken as the characteristic process temperature and radiation intensities have been varied to obtain values in the range 660–990 K. The experimental systems allow for temperature measurements along the bed radius at the median section and product collection (with gas analysis by means of gas chromatography). These are grouped into “liquids”, which include all the condensable products collected and weighed from the traps (organic compounds and product water formed), “char”, the solid residue left in the position initially occupied by the bed, and “gas”, all the non-condensable gaseous components.

2.4. Washing tests

The water treatment consists of submerging and soaking straw (cut in 2–3 cm length pieces) or char (particles 0.5–1 mm) in twice-distilled water. About 100 ml of water for 1 g of straw/char, at 363 K, are used. The residence time of the sample in water (washing time) has been varied from 0 to 7200 s. For each selected residence time, after filtration in order to retain fine particles, sample drying is carried out for about 4 h at 388 K. Then, the ash content is determined through calcination (about 1 g sample milled to millimeter-sized particles) in porcelain crucibles heated up to temperatures in the range 690–790 K for 135 min.

3. Results

Reactivity in air of untreated and washed straw is investigated for thermogravimetric conditions (heating rate 20 K min⁻¹ and a final temperature of 1100 K). Product yields and gas composition from the pyrolysis of untreated and washed straw have also been determined for a packed bed under fast external heat transfer rates (radiation) and maximum (surface)

temperatures in the range 660–990 K. Finally, the effectiveness of hot water treatment on straw and straw chars, resulting from thermal and oxidative degradation, is tested.

3.1. Influences of water washing on straw reactivity in air

Weight loss curves and time derivative of the solid mass fraction for straw and washed straw are reported in Fig. 1 for a layer thickness of 0.2 mm, when the effects of transport phenomena and reaction exothermicity are small. The processes show a first fast stage, corresponding to straw devolatilization, and a second slower stage of char combustion. The first stage presents the same qualitative trends as those already discussed for degradation in inert atmosphere [1–4]. That is, devolatilization of washed straw begins at higher temperatures (515 against 465 K) and is characterized by two different zones, corresponding to hemicellulose and cellulose degradation. Furthermore, a slightly higher peak is also observed due to cellulose devolatilization occurring within a shorter time interval (peak temperature of about 630 K against a value of 580 K for untreated straw). However, although the degradation characteristics are qualitatively the same in inert and oxidative atmosphere, oxygen may also play an important role for devolatilization. Combustion is likely to occur to some extent even at relatively low temperatures, especially when catalyzed by ashes (untreated straw). This explains

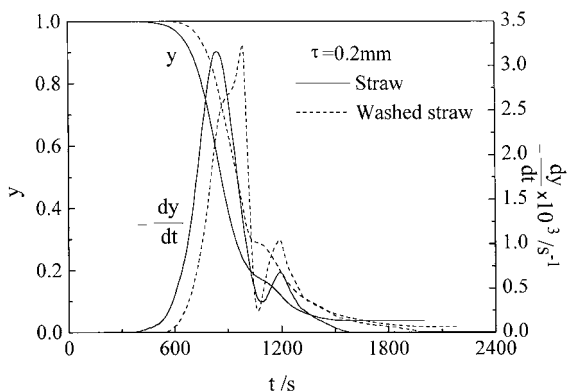


Fig. 1. Solid mass fraction and time derivative of total solid mass fraction as function of time for straw (solid lines) and washed straw (dashed lines) (20 mg heated with 20 K min^{-1} up to 1100 K).

why, in the presence of air, the char yields from the devolatilization stage are lower for untreated straw. On the other hand, it should be noted that the first stage of cellulosic fuel degradation in air is exothermic [25] and it is possible that, despite the small amount of straw, this results in temperatures higher than those recorded in the absence of the sample. Finally, the peak of the volatile release rate for the stage of char combustion is higher for washed straw because of the larger initial mass fraction. However, the duration of the process is longer.

The influence of water washing on straw reactivity (specific reaction rate, defined as $-1/Y_s \times dY_s/dt$, $Y_s = (W - M_a)/(M_0 - M_a)$, M_0 being the initial sample mass, M_a the ash mass and W being the current sample weight) for different conversions and $\tau = 0.2 \text{ mm}$ can be studied through Fig. 2. As anticipated by the weight loss characteristics, devolatilization occurs at a larger extent for untreated straw (up to conversions of about 0.85, corresponding to a minimum in the reactivity) and presents a wide region of high values (conversion of about 0.55–0.75), where degradation rates of all the components are enhanced mainly by the catalytic action of ashes (mild exothermicity). Apart from the higher maximum associated with cellulose devolatilization for conversions of about 0.6 (preceded by a shoulder resulting from hemicellulose decomposition), reactivities of washed straw, for the devolatilization stage, are comparable with those of untreated straw. However, this stage is completed for lower conversions, that is, about 0.725

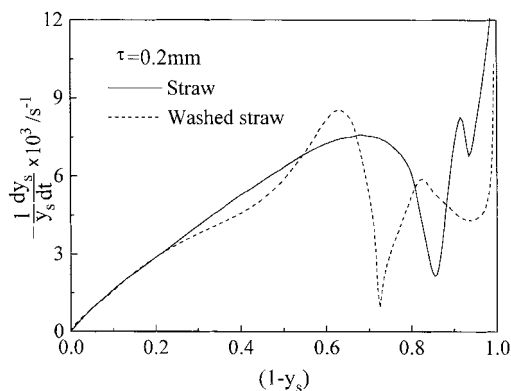


Fig. 2. Reactivity ($-1/Y_s \times dY_s/dt$, $Y_s = (W - M_a)/(M_0 - M_a)$, M_0 being the initial sample mass, M_a the ash mass and W being the current sample weight) of straw in air as function of conversion (20 mg heated with 20 K min^{-1} up to 1100 K).

(again corresponding to a minimum in the reactivity). For both cases, in the char combustion zone (conversion higher than 0.725 and 0.85 for washed and untreated straw, respectively), a new increase in the reactivity is seen, corresponding to temperatures high enough for the combustion reaction to start, followed by the attainment of a maximum (trends qualitatively similar to those discussed for the combustion of biomass chars [22]). The most interesting result of the comparison is, however, that the combustion reactivity is always lower for washed straw.

Fig. 3 reports the weight loss characteristics for untreated and washed straw when the layer thickness is 0.6 mm and the conversion process is highly affected by heat and mass transfer limitations (oxygen diffusion through the thick layer and temperatures different from those measured in the absence of the sample) and combustion exothermicity. Indeed, untreated straw decomposition and char combustion take place simultaneously, so that only one peak appears in the global devolatilization rate. This is a consequence of the high degradation (and heat release) rates which enhance, through temperature, the degradation process. On the contrary, the higher initial degradation temperatures of washed straw still allow the stages of devolatilization and combustion to be observed. As expected, reactivities, reported as function of the conversion in Fig. 4, are always higher for untreated straw, due to the higher actual temperatures of the sample while degrading. In conclusion, devolatilization in air appears as a single stage only when the process is relatively slow, that is, when the

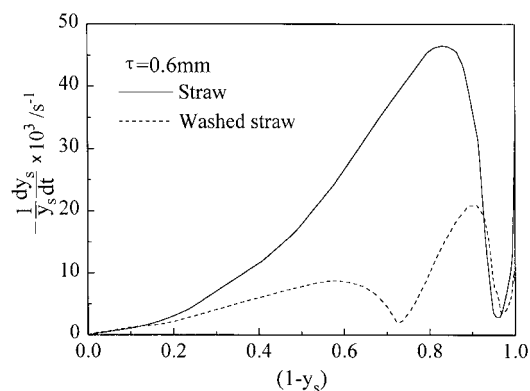


Fig. 4. Reactivity ($-1/Y_s \times dY_s/dt$, $Y_s = (W - M_a)/(M_0 - M_a)$, M_0 being the initial sample mass, M_a the ash mass and W being the current sample weight) of straw in air as function of conversion (60 mg heated at a rate of 20 K min^{-1} up to 1100 K).

amount of heat released by the exothermic combustion reactions is small (thin layers) or in the absence of ashes (washed straw for both thin and thick layers) when the combustion rates are significant slower.

3.2. Pyrolysis products

An example of the dynamics of bed heating and gas species evolution during the pyrolysis of packed biomass beds has already been discussed in the presentation of the degradation characteristics of some agricultural residues [23]. Bed heating occurs in the presence of spatial temperature gradients, which increase with the intensity of the applied radiation. This affects significantly the maximum (final) temperatures, which are, however, attained only after solid devolatilization. Thus, due to intra-bed heat transfer resistances and a narrow range of temperatures where biomass pyrolysis takes place, primary degradation is successively less affected by variation in the external heating conditions for T_s values above 750 K. From the qualitative point of view, all the gas-phase species profiles are similar, that is, they present a maximum as a function of the release time, which becomes successively shorter with the increase in the applied radiation intensity. The position of the maximum, is, however, dependent on both the reaction temperature (applied radiation intensity) and the component. More precisely, the species CO_2 and CO are released at shorter times (degradation of hemicellulose and low-tempera-

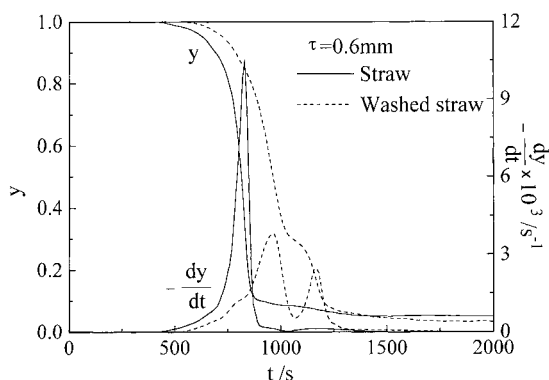


Fig. 3. Solid mass fraction and time derivative of total solid mass fraction as function of time for straw (solid lines) and washed straw (dashed lines) (60 mg heated at a rate of 20 K min^{-1} up to 1100 K).

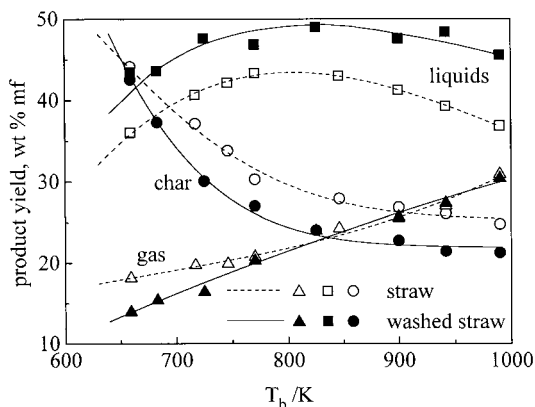


Fig. 5. Product yields (expressed as percent of the initial moisture free (mf) mass) for straw (dashed lines) and washed straw (solid lines) as function of the temperature.

ture path in cellulose degradation), as compared to the other components (H_2 , CH_4 , C_2H_4 , C_2H_6) (formation of tar vapor from cellulose decomposition, lignin degradation and secondary tar decomposition).

Process dynamics are roughly the same for the two straws, but product yields and gas composition are quantitatively different. The former variables (expressed as percent of the initial moisture free (mf) straw) are reported in Fig. 5 as functions of the final surface temperature (mass closure is within 3–6%). For both cases, an increase in the gas and liquid yields at the expense of char yields is observed as the temperature increases from about 660 to 850 K. This trend is due essentially to the increase of the degradation temperature, so that the formation of primary char is successively less favored, compared to volatile formation. For temperatures higher than 850 K, a slight reduction in the liquid and char yields is associated with a further increase in the amount of gas formed. While the slight decrease in the char yield can be due to further devolatilization of the lignin components, the slight decrease in the liquid yields is due to secondary tar degradation reactions, which become active for temperatures above 750 K [26]. However, the forced nitrogen flow, fed at ambient temperature, reduces the residence times of tar vapors along the heated section of the reactor and also keeps the volatile temperature lower than that of the solid phase, as reported by thermocouples [24]. Consequently, the activity of secondary reactions is very

small in this experimental configuration, compared to fluid bed reactors [27].

As already observed in previous studies [2,9–11], the most evident difference between the two straws is that, for the whole range of thermal conditions examined, the liquid yields are always higher for washed straw (a maximum of about 49 against 43%). Due to the higher initial degradation temperature of washed straw, part of the lignin fraction of straw is not completely degraded at the lowest heat flux, so that the solid residue collected at the completion of the process is about the same as for untreated straw. However, when temperatures become sufficiently high for the degradation of all the main straw components, the char yields are always lower for washed straw (a minimum of about 21 against 25%). Also, the lower char yields of washed straw are associated with lower gas yields for T_s below 850 K, as a consequence of the linked formation of these two product classes, as indicated by the Broido–Shafizadeh mechanism [28] of cellulose pyrolysis. On the other hand, for T_s above 850 K, gaseous products become about the same due to the significant contribution of lignin degradation to gas production. Fig. 6, which reports the yields of the main gas components as function of the reaction temperature, indicates that the yields of CO_2 , a product of the primary pyrolysis of cellulose and hemicellulose, are always higher for untreated straw (higher char yields). The same trend is also observed for the CO yields and low temperatures. Differences in the other gas products (CH_4 , H_2 , C_2H_6 and C_2H_4) are

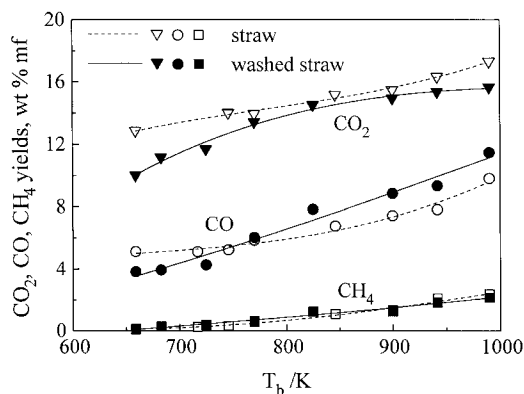


Fig. 6. Yields of some gas species (expressed as percent of the initial moisture free (mf) mass) for straw (dashed lines) washed straw (solid lines) as functions of temperature.

negligible (furthermore, H_2 , and C_2 hydrocarbons are present in small quantities, about 0.1–0.4%).

On the whole, the differences in the gas yields for untreated and washed straw are small, compared to the other two product classes. The differences between liquid and char yields can be attributed to a different content of alkaline metals (in particular, potassium) which act as catalysts for promoting char formation (and also char gasification) [2,9,10] against tar formation.

3.3. Washing of straw and straw char

The ash content, expressed as percent of the initial dry straw mass is reported in Fig. 7 as a function of the washing time (dashed line and open symbols). It can be seen that large part of the extraction process takes place during the first 600 s, when the ash content from the initial value lowers to 2.6%. However, after a time of about 150 s, a value of 3.3% has already been achieved, whereas for times longer than 600 s the extraction process is very slow and a minimum ash content of about 2–2.3% is observed only after 7200 s.

From the practical point of view, a residence time of about 600 s in hot water can remove large part of ash from straw. The hot water treatment is also more effective than a cold water treatment which requires longer residence times or rain leaching when the ash content is lowered to only 3.5% [14,15].

A previous analysis [15] of the thermal behavior of a loose-packed (wheat) straw beds exposed to a forced

flow of hot air showed that degradation rates become significant for bed temperatures of about 500 K. However, the ignition temperatures are only slightly higher, hence oxidative degradation is a slow process, resulting in maximum conversions of about 50%. Tests were conducted for an air temperature (T_a), of 540 K resulting in maximum bed temperatures of 520 K and the increase in the air flow rates (nominal velocities in the range 0.9–1.8 $m\ s^{-1}$) only caused a reduction in the conversion time [15]. Fig. 7, together with the ash content in straw, also reports the ash content (as percent of the initial dry straw mass) of chars obtained from oxidative degradation as a function of the washing time (solid lines) for two different conversion levels (and air flows). The first point worth of noting is that untreated char ($t_w = 0$, no washing) contains roughly the same ash as straw. Hence, the low temperatures of the conversion process (520 K) do not cause any significant release of alkali metals. Indeed, previous studies [16,19] report that chlorine release starts at 473 K and the process takes place into two steps. In the first, corresponding to temperatures of 473–673 K, about 60% of the total content is lost, whereas the remaining part is released in the temperature range 873–1173 K. Potassium, on the other hand, is released only for temperatures above 973 K. The leaching behavior of char ashes is qualitatively the same as straw ashes. However, the process is slower (maximum variations during the first 20 min, against the 10 min of straw) and water washing is less effective, especially for higher conversion levels (minimum ash contents of 3 and 4% against 2% of straw).

In order to investigate the role of conversion on the leaching process, extraction tests have been carried out for char produced from oxidative degradation for different retention times and thus with different conversion levels. Fig. 8 reports the ash content of the untreated and washed (2 h in hot water) char as a function of the solid mass fraction ($u = 0.9\ M/g$ and $T_a = 540\ K$). As anticipated, the ash content in straw is roughly constant during the conversion process but, as conversion increases, ash extraction through water treatment becomes successively more difficult (especially for conversions between 30 and 50%). Thus the reduction in the ash content varies from a maximum of about 58% (unconverted straw) to 27% (conversion of 50%).

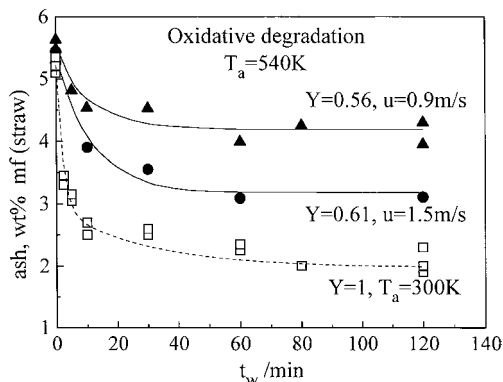


Fig. 7. Ash content (as percent of the initial moisture free (mf) straw mass) as a function of the leaching time for straw and straw chars.

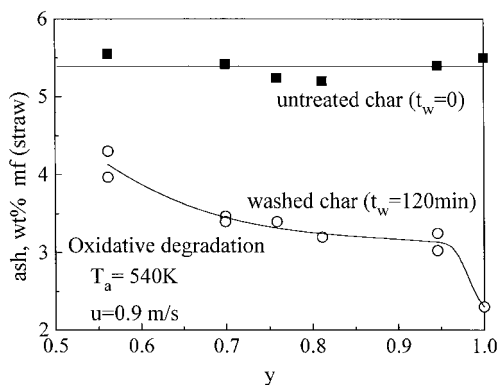


Fig. 8. Ash content (as percent of the initial moisture free (mf) straw mass) for straw chars as a function of the conversion level.

The effects of water treatment have also been investigated for pyrolysis chars obtained for the different heating conditions of Fig. 5. It has been found that the ash content of chars from washed straw is practically independent of the reaction temperature and coincident with the initial value (2–2.3% on a straw basis). Ashes in chars from untreated straw present a region of roughly constant values (about 5.5%) for T_s below 750 K, followed by a slight decrease, possibly due to chlorine release [16,19]. Finally, as already observed for the low-temperature chars of oxidative degradation, water extraction of ashes is less effective for chars than for straw. Indeed, for all the thermal conditions examined, the minimum ash content of washed char is about 3% on a straw basis (against 2%).

The reduced effectiveness of water washing for ash removal, when applied to straw chars, can be due to physicochemical changes which affects the char matrix and to a different mode of occurrence of potassium as soon as degradation begins. In particular, it has been observed [29] that lignin and hemicellulose in straw undergo a phase change during the degradation process, with the formation of a molten-phase intermediate, which traps the ash components, thus making their extraction more difficult as char is formed. Microscopic analysis of straw particles [16] also shows that potassium is bound to the organic matrix. As the temperature is raised above 673 K, potassium is partly released from the original sites and is repositioned in the form of discrete particles (KCl, K_2CO_3) and partly still remains bound in the charred

Table 3

Elemental analysis of pyrolysis chars, expressed as percent of the initial mass, and content of nitrogen (N_c) with respect to the initial value (steady surface temperature of 850 K) for untreated and washed straw

	%C	%H	%N	%O	%S	N_c (%)
Straw char	64.27	2.39	0.48	14.31	0.30	44.67
Washed straw char	73.35	3.22	0.61	14.03	0.08	48.67

organic matrix. It can be understood that the effectiveness of water washing for ash removal increases as the char particles become successively smaller. In particular, particles of about 150 μm have proven sufficient for removing completely alkaline metals [7], although the process is still slower than for straw. Furthermore, for practical application, particle size reduction causes an increase in the pretreatment costs.

Other information on the effects of the straw pretreatment on the char characteristics can be observed from Table 3, where the elemental composition of pyrolysis chars obtained for $T_s = 850$ K is reported for the two straws examined. As expected, the %C and %H increase as the leaching process becomes more effective (lower ash content). Another consideration can be made in relation to the nitrogen content. A comparison with the nitrogen content of unconverted straw shows that the amount retained in the char (N_c) is roughly 50% of the initial value and is independent of the leaching treatment. Therefore, if char is applied in a combustion system (for instance, co-fed with coal), flue gas treatments, following the conversion process, should account for the possible problematic evolution of about 50% of the initial nitrogen content in straw.

4. Conclusions

This study has presented some new data on the effects of water washing on the degradation characteristics of straw together with an analysis of the feasibility of char washing (instead of straw washing). Both cases of straw decomposition in air and inert atmosphere have been examined. Water washing mainly removes potassium (and chlorine), thus reducing both the activity of the low-temperature reaction path leading to char (and gas) formation for degrada-

tion in inert atmosphere and the reactivity of char in air.

For limited heat and mass transfer (slow heating rates and small sample sizes), straw degradation in air consists of a devolatilization stage followed by char combustion. Leaching reduces the conversion range where devolatilization occurs and also results in slightly higher maximum reactivity. However, char combustion reactivity is always lower for washed straw. As a consequence, in the presence of significant effects of process exothermicity, a net separation between the two conversion stages is observed only for washed straw.

For both air and nitrogen, the initial degradation temperature is higher for washed straw. For heating conditions pertinent to fixed-bed reactors and for a wide range of pyrolysis temperatures (660–990 K), water washing increases the liquid yields with a reduction in the char formation (values about 10% higher for liquids and 19% lower for chars with reference to untreated straw, dry and ash free basis). Furthermore, for low conversion levels of the lignin fraction (maximum temperatures below 850 K), given the linked formation of char and gas (essentially CO and CO₂), gas yields are also lower.

Low-temperature (520 K) degradation of untreated straw in air, characterized by conversions of about 50%, allows all the alkali metals to be retained by the solid phase product. However, hot water washing of char particles (0.5–1 mm), which roughly retain the original straw shape, is less effective than straw washing and the process becomes successively more difficult as the conversion level increases. Pyrolysis in inert atmosphere at process temperatures above 750 K causes some part of the chlorine to be released and, again, water washing of the resulting char particles is less effective than straw washing (maximum reductions of about 45 against 58%). This can be attributed partly to the trapping of ash components inside the organic char matrix, following the formation of a molten phase of straw components while degrading, partly to the changes (mode of occurrence) undergone by alkali metals during high-temperature treatments.

Acknowledgements

The research was funded in part by the European Commission in the framework of the Non Nuclear

Energy Programme (Joule III), Contract JOR3-CT97-0138. Thanks are also due to Giuseppe Portoricco and Carlo Di Russo for their contribution to the straw degradation tests carried out by the laboratory.

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