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Comparison of Devolatilization/Char Oxidation and Direct Oxidation of Solid Fuels at Low Heating Rate

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Fundamental information can be obtained by comparing the behavior of different classes of solid fuels (low- and high-volatile matter coals, biomass fuels, residues, wastes, and plastics) in oxidizing and inert thermogravimetric runs. Different mechanisms can be recognized and attributed to devolatilization, char oxidation, and direct oxidation. The direct oxidation of the fuel can be favored with respect to the traditional devolatilization/char oxidation scheme depending on the conditions used and the characteristics of the fuel. Oxygen enhances the thermal devolatilization of the fuel and the reactivity of the produced char. The reactivity of all fuels are quantified by defining characteristic temperatures of each mechanism and providing kinetics for all steps. Also, the effect of the operating conditions are evaluated. Results obtained in this work represent a significant set of data on very different solid fuels, useful for modeling purposes, for practical system handling (grate furnaces or fixed-bed combustors, operating in conditions similar to this study), for safety of fuel stockpiles, and for investigations on ignition and char reactivity.

1. Introduction

The direct combustion of alternative fuels (biomass, wastes, and low quality coals) is limited at present because of techno-logical and economical problems, depending on the sources (seasonal availability, heterogeneous nature), the characteristics (low heating value, high moisture or ash content), and the behavior (problematic ignition, agglomeration, slagging, fouling and corrosion phenomena in the combustor) of these materials.[1] However, the current interest in the use of these fuels is the result of important advantages: they represent a renewable energy source, biomass can be considered CO_2 neutral fuels, pollutant emissions (SO_2, NOx, heavy metals) are generally lower than for coals, and wastes can be exploited for their energy content instead of destined to landfill.[2] Finally, the use of low quality coals would allow the use of a large quantity of energy sources.

Data on the properties and behavior of alternative fuels are not so abundant as for coals because of their limited use and the extreme variety of their nature and origin. Moreover, the characteristics of a fuel depend strongly on the experimental equipment and the conditions used.[3,4] A detailed characterization is required to evaluate the possibility of and the conditions for using these fuels in a process (direct combustion, cocombustion, pyrolysis, gasification).

Global combustion is traditionally schematized in a first devolatilization step (essentially promoted by thermal mecha-nisms), followed by a char oxidation step, each step acting independently. However, the direct oxidation of the fuel is expected to occur and could be competitive. Oxygen breaks chemical bonds in the fuel contributing to the formation of lighter species, thus enhancing the thermal devolatilization. However, oxygen-related reactions are heterogeneous and require diffusion to the reactive surface, which can be compro-mised by the conditions used.

Devolatilization is favored over direct oxidation by the rapid heating rate (HR) of the sample, the high resistance to oxygen diffusion, and the high reactivity of the fuel. These conditions can be verified in large-scale combustors (for instance, pulver-ized furnaces and fluidized-bed reactors), where the effective HR of the fuel is much faster than the oxygen diffusion. Furthermore, the release of volatiles from a large amount of fuel during the feeding (especially for high-VM content fuels) can create a cloud which prevents oxygen to diffuse toward the solid material, which experiences practically inert conditions and is transformed into the char product. A flame is formed by the combustion of volatile compounds, which consumes oxygen in a homogeneous reaction and increases the temperature of the chamber. Once the devolatilization is completed, the oxygen can attach to the solid residue, and this process is considered the controlling step during the combustion.

On a laboratory scale, the small amount of the sample, the low heating rate, and the continuous feeding of carrier gas (in thermogravimetric experiments, for instance), allow the effects of both paths to be separated and distinguished, so that the reactivity of different fuels can be evaluated. Nevertheless, these conditions are similar to those encountered in large-scale plants, as grate furnaces or fixed-bed reactors, commonly used for biomass and waste fuels, so that results obtained in this work can be applied to these cases. However, they can be used for other applications only for a qualitative evaluation because operating conditions have a strong influence on both devola-tilization and char oxidation processes.[4−6]

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Table 1. Ultimate and Proximate Analyses and Heating Value of Fuels

fuel	ultimate analysis (% daf)				proximate analysis (% dry)			HV (MJ/kg)
	C	H	N	S	VM	FC	ash	
Qiyi coal	75.2	3.6	1.3	0.2	12.8	70.4	16.8	30
Tower coal	87.3	3.6	1.3	0.2	8.9	85.8	5.3	34
Kema coal	71.4	4.5	1.1	0.8	30.4	55.8	13.8	28.7
US coal	81.0	5.5	1.3	1.0	33.3	59.2	7.5	29
wood pellets	49.4	6.1	1.0	0.7	76.9	20.8	2.3	19
pine wood	53	6	0.2	0.08	80.6	17.7	1.7	18.1
olive residue	51.2	6.7	0.8	0.05	78.4	20.4	1.2	20.1
cacao residue	47	6	2.6	0.2	71.8	20.5	7.7	17.9
sewage sludge	52	8	6	1.2	47.8	6.6	45.6	11
PE	84.3	15.4			98.5	0	1.5	43
PET	62	4.2			85.3	13.6	1.1	22

In this work, a laboratory procedure is applied to different classes of solid fuels to evaluate the reactivity of the fuel and its char in inert and oxidizing conditions. Low heating rates and temperatures up to 900 °C are used. The behavior of fuels is quantified by defining temperatures characteristic of each mechanism (direct oxidation, inert devolatilization, char oxidation) and providing reactivity parameters for all steps and isolated substeps. Results obtained in this work represent a significant set of data on very different solid fuels, useful for modeling purposes,[7] for practical system handling, as for grate furnaces[8] or fixed-bed combustors (operating in conditions similar to this study), for safety of fuel stockpiles,[9] and for investigations on ignition[10,11] and char reactivity.[12]

2. Experimental Section

2.1. Materials. The ultimate and proximate analyses and the heating value of two low-volatile matter (VM) coals (coal Qiyi and Tower), two high-VM coals (coal Kema and US), lignin-cellulosic materials (namely, wood pellets, pine wood, olive residue, cacao residue), a sewage sludge, and two different plastics (PE and PET) are listed in Table 1. All fuels are crushed and sieved, and the 0.125−0.300 mm fraction is used in this work.

2.2. Experimental Procedure. A thermogravimetric balance (TG Q500 V6.1 of TA Instruments) is used to perform runs in both inert and oxidizing environments with a constant gas-flow rate (100 mL/min) of pure nitrogen or air, respectively. A sample of 5 mg is inserted into an alumina crucible, dried at 110 °C to reach a constant weight, and then the thermal history is programmed according to one of the following procedures.

• The raw fuel is used as the starting material in the "direct oxidation" procedure (in air flow). The maximum temperature is programmed where no further weight loss is detected (approximately 700 °C for biomass fuels, 800−900 °C for coals). The reference heating rate is 20 °C/min, so that the behavior of different classes of fuels can be compared.

• The raw fuel is used as the starting material in the "devolatilization" procedure (in nitrogen flow). The maximum temperature is 800 °C for biomass fuels and 900 °C for coals, after the main weight loss step. For some materials the effect of the HR is

evaluated in the range of 5−100 °C/min, the reference conditions being 20 °C/min. This procedure is also applied to produce the char for the next procedure.

• The char produced according to the previous procedure is oxidized in air. The maximum temperature is programmed where no further weight loss is detected. A constant HR run at the reference conditions of 20 °C/min is carried out to compare the reactivity of chars produced in different conditions.

Preliminary thermogravimetric runs are performed with the HR varying in the range of 5−100 °C/min. This allows the optimal experimental conditions to be individuated, for a comparison of the behavior of different classes of fuels. The devolatilization of solid fuels depends strongly on the conditions used.[3,4] In general, the higher the HR, the higher the temperature required for the devolatilization, the wider the temperature range for the respective weight loss, and consequently, the flatter the peak in the derivative weight loss (dtg) curve. In low-HR oxidation runs, the different weight loss steps are well distinguished but too close, so that, for some fuels (coals, for instance), the individuation of both steps is impossible. Vice versa, at high HR, the separation of peaks in the dtg curve can be easier, but the flatness of the second peak can lead to ambiguous parameters as for reactivity and characteristic temperatures. This is the reason an intermediate HR (20 °C/min) is adopted as a reference condition, thereby avoiding superimposition of weight loss steps and obtaining well-defined dtg peaks. However, the effects of the HR will be discussed in the section 4.4, most results being actually focused on the reference conditions.

3. Results

On the basis of the results obtained in this work, the fuels are grouped in four classes, namely, lignin-cellulosic materials (wood pellets, pine wood, olive residue, and cacao residue), plastics (PE and PET), sludges (sewage sludge), and coals. Qualitatively, all fuels in each group behave similarly, in both inert and oxidizing conditions. So that, the results for the representative material of each group can be compared as in Figure 1, where the weight loss curves of devolatilization and oxidation for wood pellets, sewage sludge, PE, and Kema coal are reported. For some fuels, the derivative weight loss curve is also reported to show the different steps of decomposition.

Detailed results are reported for all fuels in the following paragraphs, defining the temperature ranges for the devolatilization, the char oxidation, and the direct oxidation.

3.1. Devolatilization. The temperature for the devolatilization of lignin-cellulosic materials is relatively low, in the range of 200−400 °C (namely, 237−395 °C for the main devolatilization step of wood pellets, 234−393 °C for pine wood, 218−362 °C for olive residue, and 178−384 °C for cacao residue). A multicomponent decomposition is observed in the devolatilization of all lignin-cellulosic materials (see the dtg curve of wood in Figure 1a) and attributed to the different reactivities of

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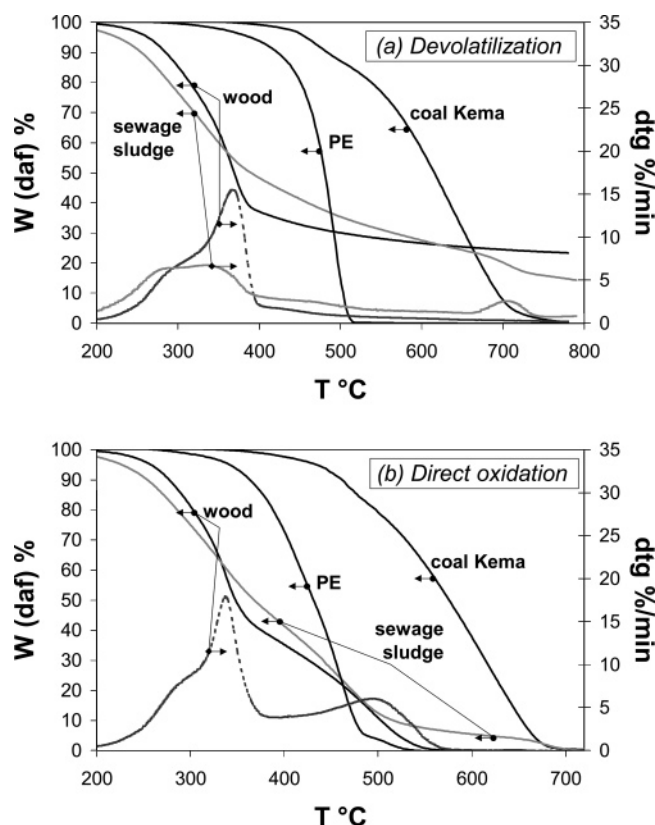
Figure 1. Comparison of the weight loss curves for (a) devolatilization (in nitrogen) and (b) direct oxidation (in air) of different classes of fuels. The derivative weight loss curve (dtg) of some materials is also reported on the secondary axis.

chemical components, namely, cellulose, hemicellulose, and lignin.[13–15] Depending on the chemical composition, the substeps are different and can be isolated from the global weight loss curve. In particular, the respective temperatures of the substeps for wooden biomasses (wood pellets and pine wood) are very close, whereas the decomposition substeps for olive and cacao residues are more differentiated, and the respective temperatures are lower compared to those of wooden fuels (322 and 332 °C for the maximum devolatilization rate of cacao and olive residues, respectively; 368 and 372 °C for wood pellets and pine wood, respectively).

Sewage sludge exhibits a multicomponent devolatilization similar to that of lignin-cellulosic materials: it begins at 233 °C and ends at 521 °C, with a main weight-loss step in the same range as that of lignin-cellulosic fuels and a long tail at higher temperatures, attributable to less reactive organic compounds. Furthermore, the decomposition of inorganic matter (carbonates) can be observed at very high temperatures, 668–739 °C (see the dtg curve in Figure 1a). This was also verified in the case of paper sludge, studied in a previous work.[16]

Plastics show a very pronounced devolatilization step, in a quite narrow temperature range, and this is attributable to the more uniform chemical composition of these polymeric materials compared to more heterogeneous materials, as biomasses and coals. The interval of decomposition is at quite high

temperatures (441–516 °C for PE and 429–472 °C for PET). This is caused by the stronger nature of chemical bonds in plastic fuels with respect to lignin-cellulosic fuels. Unlike PET, PE produces no char after a complete devolatilization.

The devolatilization of coals is actually more complex and requires higher temperatures, especially for low-volatile coals. An important long tail in the weight loss following the main weight-loss step can be noticed in all cases studied. The devolatilization of the high-volatile coals starts above 400 °C and ends at 750–800 °C (considering the long tail in the devolatilization), namely, 432–772 °C for Kema coal and 412–775 °C for US coal. The devolatilization of the low-volatile coals requires higher temperatures (470 and 477 °C for Qiyi coal and Tower coal, respectively), and while it cannot be actually considered complete even at 900 °C, that is the maximum temperature reached in the experimental run.

3.2. Char Oxidation. The oxidation of chars produced after devolatilization is carried out in air imposing the reference HR of 20 °C/min to compare the reactivity of different materials. Chars obtained in reference conditions from lignin-cellulosic materials show a single step of weight loss in the range 400–600 °C (namely, 402–642 °C for wood pellets, 408–590 °C for pine wood, 389–600 °C for olive residue, 411–630 °C for cacao residue) that is at higher temperature than the correspondent devolatilization.

The char of sewage sludge is somewhat more reactive than other biomass chars, considering the temperature range for the oxidation (361–580 °C). PE is a noncharring material. Oxidation of PET char requires relatively high temperatures, that is 564–655 °C.

Although they have different behaviors during devolatilization, as discussed above, only minor differences are noticed for the oxidation of chars from different rank coals (502–719 °C for Kema coal, 511–754 °C for US coal, 535–740 °C for Qiyi coal, and 531–778 °C for Tower coal).

3.3. Direct Oxidation. The direct oxidation of the representative materials for all groups of fuels is compared in Figure 1b. For lignin-cellulosic materials, two apparent macrosteps can be distinguished in the weight loss: the former at relatively low temperature is attributed to the devolatilization process, and the latter at high temperature is the result of the oxidation of the solid residue.[6,8,15,17] Qualitatively, the first weight loss reveals a multicomponent decomposition similar to that in inert conditions. The temperature ranges are actually shifted toward lower values compared to the separated steps of devolatilization and char oxidation. Also, for PET and sewage sludge, the different weight-loss steps are evident, whereas for PE a complex weight-loss step is noticed. The high temperature required for the devolatilization of coals (especially for low-volatile coals) makes the analysis of the different steps during direct oxidation more difficult. In fact, in some cases, the weight loss steps are partially or even completely superimposed so that the immediate discussion of raw data is hardly feasible. As a matter of fact, a more accurate elaboration of the experimental results and the definition of characteristic temperatures are required to quantify the difference between direct oxidation and the separated steps of devolatilization/char oxidation. This is the object of the following section.

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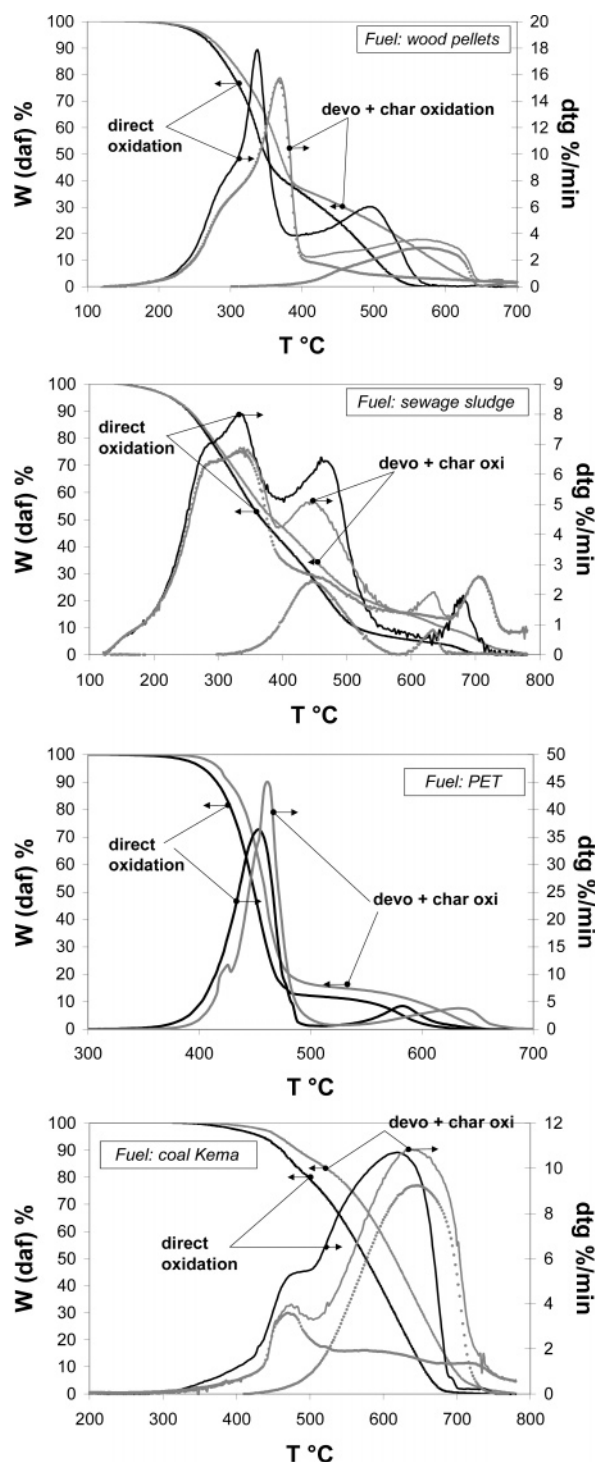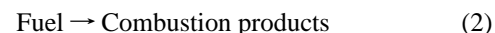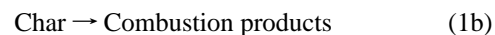
Figure 2. Weight loss and derivative (dtg) curves for direct oxidation (black curves), separate steps of devolatilization and char oxidation (dotted gray curves), and the weighted sum of separated steps (continuous gray curves).

4. Discussion

4.1. Comparison of Direct Oxidation and Devolatilization/Char Oxidation.

The experimental results obtained in the direct oxidation and separated steps of devolatilization/char oxidation are compared in Figure 2, where the weight loss and the dtg curves are reported for most fuels. In particular, the separated step runs of devolatilization and char oxidation are summed according to the weight fraction of each step to obtain the "devo + char oxi" curve (summing mechanisms 1a and 1b). The comparison of this curve with the "direct oxidation" curve (path

2) makes more evident the difference between path 1 and path 2 during the global combustion.

$$\text{Fuel} \rightarrow \text{Char} + \text{Volatiles} \qquad (1a)$$

$$\text{Char} \rightarrow \text{Combustion products} \qquad (1b)$$

$$\text{Fuel} \rightarrow \text{Combustion products} \qquad (2)$$

In path 1, separate steps give primarily char and volatile products, which successively burn heterogeneously and homogeneously, respectively, giving combustion products. Reaction 1a is a thermal mechanism, requires no oxygen and releases volatile compounds, which can subsequently burn in the presence of oxygen if the temperature is high enough for the combustion reaction. However, no further weight loss can be detected from thermogravimetric analysis so the oxidation of volatile compounds is not considered in the present work. The solid char formed after devolatilization is oxidized in the presence of oxygen according to reaction 1b so the char can be considered as an intermediate compound in global reaction 1. The direct oxidation of the fuel leads to combustion products in path 2 with no formation of intermediates. Oxygen is supposed to react directly on the solid fuel to give the final compounds.

Qualitatively, oxidizing conditions favor the reactivity of all fuels and the produced char when the temperature ranges for the correspondent weight-loss steps are compared. As a matter of fact, a quantitative analysis needs the individuation of methodical parameters for every step. Characteristic temperatures are defined and discussed in the following section, and the reactivity analysis in section 4.3 allows the fuel and char reactivity to be evaluated in both the direct oxidation and separated steps of devolatilization and char oxidation.

4.2. Definition of the Characteristic Temperatures.

Characteristic temperatures for all materials are defined and listed in Table 2 to quantitatively compare direct oxidation and the separate steps of devolatilization/char oxidation for all fuels. They will be discussed in the following paragraphs for all classes of fuels at the reference conditions. The effect of the operating conditions on these parameters will be also discussed, for some materials, in section 4.4.

T_{de} and T_{ox} are defined as the temperatures for the maximum in the dtg curve of the devolatilization run and the correspondent peak in the direct oxidation curve, respectively. T_{de} is higher than T_{ox} for all lignin-cellulosic materials (10−30 °C). T_{ox} and T_{de} have similar values in sewage sludge. PE exhibits very different T_{de} and T_{ox} values (and a very different dtg shape, too), while the difference is less marked for PET. As noticed above, the superimposition of dtg peaks and the low-volatile matter content make the definition of T_{ox} for the low-volatile coals Qiyi and Tower ambiguous. A more defined shoulder in the dtg curve for Kema coal and US coal revealed that T_{ox} and T_{de} are very close, even if a higher reactivity can be recognized during the direct oxidation with respect to the inert devolatilization.

The temperature at the separation of the weight-loss curves in oxidizing and inert conditions, T_d, is another interesting parameter, depending on the operating conditions used but useful in the comparison of different fuels under the same conditions. In this context, T_d is the minimum temperature required to detect the effects of oxygen on the first steps of the decomposition of a material compared to that of the inert decomposition. The thermal breakage of chemical bonds of the solid matrix leading to lighter compounds is strongly enhanced by the presence of oxygen. Also, the exothermic nature of oxygen-related reactions

Table 2. Characteristic Temperatures in Reference Conditions (HR 20 °C/min)[a]

	VM/FC	H/C	T_d (°C)	T_{de} (°C)	T_{ox} (°C)	T_{cs} (°C)	T_{co} (°C)
Qiyi coal	0.18	0.048	384	662		665	599
Tower coal	0.10	0.041	425	664		671	634
US coal	0.56	0.068	378	465	457	655	630
Kema coal	0.55	0.063	360	476	480	646	618
wood pellets	3.7	0.123	220	368	338	568	496
pine wood	4.6	0.113	257	372	344	547	502
olive residue	3.8	0.131	223	332	290	554	493
cacao residue	3.5	0.128	280	322	312	530	489
sewage sludge	7.2	0.154	266	334	335	444	470
PE	not defined	0.183	254	493	461		
PET	6.3	0.068	333	460	452	633	581

[a] T_d is the temperature of separation between the weight-loss curves of direct oxidation and devolatilization; T_{de} is the temperature for the maximum of the dtg curve during the single step of devolatilization; T_{ox} is the temperature for the maximum of the dtg peak attributed to the devolatilization in the dtg curve of the direct oxidation; T_{cs} is the temperature for the maximum of the dtg curve during the single step of char oxidation; T_{co} is the temperature for the maximum of the dtg peak attributed to the char oxidation in the dtg curve of the direct oxidation.

increases the temperature of the sample and makes the process faster compared to inert conditions. This is the reason that T_d has been used to characterize the ignition of fuels in past works.[10,11] This topic is behind the object of the present work, so that only the comparison of T_d for different classes of fuels is noticed and discussed. The complexity of ignition issues should be actually studied with further investigations (e.g., optical diagnostics or gas analysis), evaluating the effects of the operating conditions and the experimental techniques.[10,11,18,19] Nevertheless, data presented here can be used for a preliminary study concerning the ignition of different fuels and the safety of stockpiles.

In the reference condition (HR 20 °C/min), T_d is between 220 and 280 °C for the biomass fuels studied in this work (Table 2). The T_d for PE and sewage sludge is in the temperature range of the biomass fuels (254 and 266 °C, respectively), while it is higher for PET (333 °C). T_d is even higher for coals, between 360 °C for Kema coal and 425 °C for the low-VM coal Tower. When all groups of fuels studied are considered, a trend of T_d decreasing with the H/C ratio is verified in Table 2 (a similar relationship can be found for coals).[20] However, this schematization is hardly suitable for plastic materials; therefore, they are separated in the graph, the value for PET being very close to that of the coals and that of PE being beyond biomass fuels. As a matter of fact, the VM/FC ratio would be even less representative, even though coals and biomass fuels can be related.[8]

Finally, two temperatures are defined to characterize the char oxidation, namely, T_{cs} for the separate char oxidation step and T_{co} for the char oxidation during direct oxidation. Mostly, T_{cs} is higher than T_{co}, that is the char formed during the direct oxidation is more reactive than that produced after a single-step devolatilization. This is particularly the case for biomass fuels, which show T_{cs} in the range of 530−570 °C, which is 40−70 °C higher than the respective T_{co} values. The characteristic temperatures of PET char differ by more than 50 °C. T_{cs} is much higher for coals (640−670 °C) and is 30 °C higher than the respective T_{co}. T_{cs} is lower than T_{co} only for sewage sludge (444 °C and 470 °C, respectively). The peaks noticed at temperature between 600 and 700 °C for this material are attributed to the decomposition of inorganic compounds (carbonates) and are not investigated here.[16]

4.3. Evaluation of the Reactivity. Reactivity parameters are calculated for a single first-order reaction (SFOR) model. This

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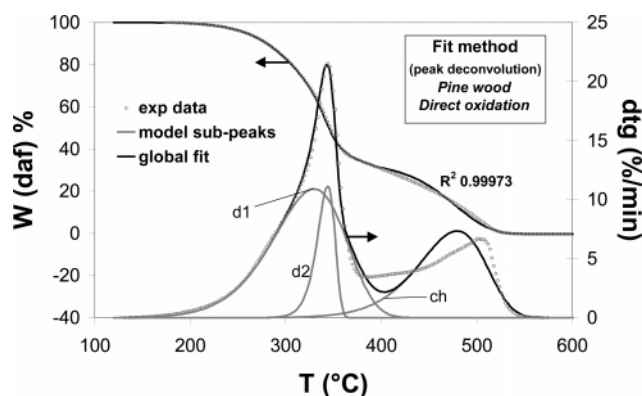(20) Furimsky, E. *Fuel Process. Technol.* **1988**, *19*, 203−210.

Figure 3. Example of peak deconvolution (nomenclature of subpeaks is listed in Table 3) and fitting procedure with SFOR approximations. Comparison of experimental data (symbols) and model results (continuous curves). *R* is the Pearson coefficient.

can be obtained from the mass balance on volatile species, V, considering the Arrhenius law for the constant rate

$$dV/dt = k(V - V_\infty) \qquad k = A \exp(-E/RT) \qquad (3)$$

As a matter of fact, this model is not suitable for either multicomponent materials (biomass and wastes) or separated-step runs. However, the simplicity and the small number of parameters of the SFOR model allow the direct comparison of very different fuels to provide preliminary parameters for further and more accurate modeling, and it can be used to fit isolated steps after the analysis of multiple dtg peaks. So, the procedure adopted in this work is as follows: the analysis of the global run (direct oxidation or devolatilization/char oxidation), the deconvolution of the dtg curve in the lowest number of SFOR substeps, and the optimization of all parameters to fit the weight-loss curve.

An example of the fit result is illustrated in Figure 3, where the analysis of the direct oxidation of pine wood is carried out. It is worth noting that the fit is not optimized on the subpeaks of the dtg curve but on the global weight loss curve. A global R^2 (with *R* being the Pearson's coefficient) higher than 0.999 is achieved in all cases comparing the curve obtained from the separated SFOR substeps and the experimental results.

The reactivity parameters of all fuels are listed in Table 3. Also, the respective fraction of each substep is indicated. Biomass fuels generally requires two SFOR models for the devolatilization step (d1 and d2) and one for the char oxidation (ch). Only for the direct oxidation of olive residue is one SFOR model sufficient to fit the devolatilization step. Sewage sludge requires two SFOR models for devolatilization, one for char

Table 3. Fraction (*x*) and Reactivity Parameters (*E*, *A*) for SFOR Substeps[a]

fuel	peak	direct oxidation			devolatilization and char oxidation		
		x (%)	*E* (MJ/kmol)	*A* (min^{-1})	*x* (%)	*E* (MJ/kmol)	*A* (min^{-1})
Qiyi coal	gs	100	128.2	1.48×10^7	100	140.7	2.40×10^7
Tower coal	gs	100	121.7	2.74×10^6	100	127.8	3.22×10^6
Kema coal	d	35	102.1	2.71×10^6	27	91.6	2.95×10^5
Kema coal	ch	65	144.7	1.20×10^8	73	144.8	6.00×10^7
US coal	d	19	218.9	4.38×10^{15}	18	137.6	2.60×10^9
US coal	ch	79	101.8	2.79×10^5	79	119.5	1.63×10^6
wood pellets	d1	46	69.4	6.70×10^5	38	71.1	7.90×10^5
wood pellets	d2	11.5	346	6.96×10^{29}	20.5	259	1.52×10^{21}
wood pellets	ch	39.5	107	1.32×10^7	37	75	2.02×10^4
pine wood	d1	52	75	1.62×10^6	48	75.3	1.45×10^6
pine wood	d2	13.5	344	2.90×10^{29}	17	300.5	4.47×10^{24}
pine wood	ch	33	129	5.05×10^8	31	99.5	1.45×10^6
olive residue	d1	52.5	68.2	8.07×10^5	31.5	73.2	3.45×10^6
olive residue	d2				11.5	278	1.35×10^{24}
olive residue	ch	44.5	110.8	2.27×10^7	50	50	6.92×10^2
cacao residue	d1	4	146.4	7.33×10^{15}	24	66.9	3.09×10^6
cacao residue	d2	53	51	1.80×10^4	29.5	82.6	1.09×10^7
cacao residue	ch	39	120	9.20×10^7	40.5	59.2	2.32×10^3
sewage sludge	d1	26	34	2.02×10^2	45	39.6	1.06×10^3
sewage sludge	d2	33	55.2	2.99×10^4	3.5	152	8.03×10^{12}
sewage sludge	ch	26.5	118.2	1.20×10^8	30	78.5	1.81×10^5
sewage sludge	cd	7	275	1.15×10^{15}	5	543.5	1.18×10^{29}
PE	d1	81	99.5	1.10×10^7	46	190.5	2.66×10^{13}
PE	d2	18	408	7.67×10^{28}	54	398.1	1.61×10^{27}
PET	d	88	237.5	1.37×10^{17}	83	289	5.09×10^{20}
PET	ch	12	253	2.66×10^{15}	17	189	7.14×10^{10}

[a] gs, global SFOR fit; d, SFOR fit for the devolatilization macrostep; d1, d2, SFOR fit for devolatilization substeps; ch, SFOR fit for the oxidation of char; cd, SFOR fit for the decomposition of carbonates.

oxidation, and another for the decomposition of carbonates at high temperature (cd). As for plastic materials, both the devolatilization and direct oxidation of PE are schematized using two SFOR models. PET requires one SFOR for the devolatilization macrostep and one for the oxidation of char. Similarly, high-volatile coals require one SFOR for the devolatilization and one for the oxidation of char in both direct oxidation and the separated steps. Finally, one SFOR model is sufficient to fit the decomposition of low-volatile coals in both cases.

The values obtained in this work are comparable to the literature data for pyrolysis, char oxidation, and combustion of similar fuels.[17,21-25] Generally, every fuel exhibits an exponential factor *E* lower for the direct oxidation than for the corresponding step performed separately (Table 3). This denotes a higher reactivity of steps during the direct oxidation than during the separated steps. In some cases, the values of preexponential factor *A* are completely different so the direct comparison of kinetics is difficult.

To compare the reactivity of different classes of fuels and to remark the effect of oxygen in the first step of the decomposition, the Arrhenius plot for the first peak is studied in both inert and oxidizing runs. Figure 4 shows ln k_{de} and ln k_{ox} (that is, the constant rate in inert and oxidizing conditions, respectively) as function of 1/*T* for the first step of different classes of fuels. In this graph, the higher the distance of curves for the same fuel, the more marked the effects of oxygen on the initial devolatilization during direct oxidation. In fact, at the same temperature, the constant rate is larger for oxidizing than for inert conditions for most fuels. Only sewage sludge exhibits a similar rate in both cases. Furthermore, the order of reactivity of different fuels
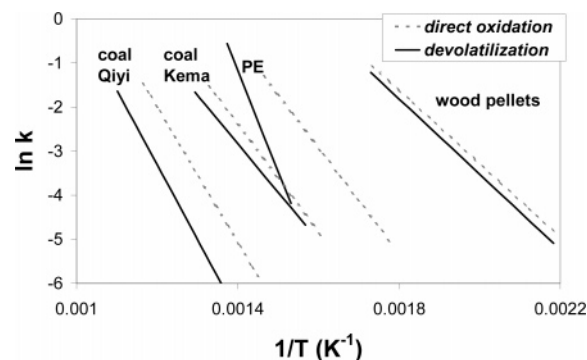
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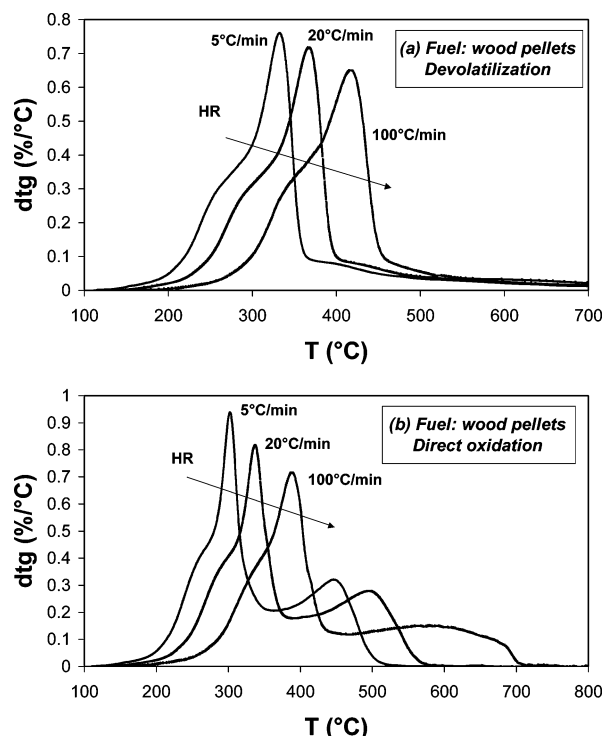

Figure 4. Arrhenius plot for the first step in devolatilization and oxidizing conditions.

can be easily recognized passing from the less-reactive coal Qiyi, to coal Kema, PE, and the more reactive wood pellets.

4.4. Effect of the Operating Conditions. The effect of the operating conditions on the characteristic temperatures is also studied for direct oxidation and the separated steps of devolatilization/char oxidation. The results for wood pellets are reported in the graph in Figure 5. The characteristic temperatures for different runs with a heating rate in the range of 5−100 °C/min are listed in Table 4 for some fuels of different classes. In general, higher HR values lead to higher T_{de} and T_{ox} values. However, a general trend in the difference between T_{de} and T_{ox} can hardly be seen, even for fuels of the same class. For instance, it remains practically constant as the HR increases (wood pellets) or, in some cases, decreases (olive residue and PE).

The variation of T_d with the HR is significant for all fuels studied. Higher HRs lead to higher T_d values, as shown in Table 4. When the entire HR range used (from 5 to 100 °C/min) is considered, variations of 50−60 °C are observed for lignin-cellulosic materials, of 95 °C for PE and, even 110 °C for Kema coal. Variations so impressive should be taken into account when using these data for ignition investigations. Clearly, the ignition temperature is not a characteristic of the fuel because it depends

Figure 5. Derivative (dtg) weight loss curves for (a) devolatilization and (b) direct oxidation of wood pellets at different HRs.

Table 4. Characteristic Temperatures in Different Operating Conditions

	HR (°C/min)	T_d (°C)	T_{de} (°C)	T_{ox} (°C)	T_{co} (°C)
Kema coal	5	320	433		512
	20	360	476	480	618
	60			494	680
	100	430	510	498	655
wood pellets	5	206	333	302	446
	20	220	368	338	496
	60	250	395	371	539
	100	243	417	388	579
olive residue	5	206	300	264	439
	20	223	332	290	493
	60	254	355	322	542
	100	256	365	340	606
sewage sludge	5	216	308	299	392
	20	266	334	335	470
	100	270	388	375	597
PE	5	204	464	415	
	20	242	493	461	
	60	287	527	505	
	100	299	548	525	

strongly on the experimental technique and the operating conditions, as demonstrated in Table 4. However, a trend of T_d with the HR can be recognized to define an onset temperature for each fuel. For instance, when T_d is referred to the HR on a logarithmic scale, the onset temperature can be defined by considering the asymptotic fit for HR tending to be zero. When this method was Applied, the onset temperatures were found to be 303 °C for coal Kema, 195 and 196 °C for wood pellets and olive residue, respectively, and 186 °C for PE.

As for the characteristic temperatures of chars, T_{co} strongly increases during the direct oxidation in the entire range of HR (5−100 °C/min). For lignin-cellulosic materials it passes from approximately 440 °C to 580−600 °C. A similar increase can be noticed for the T_{co} of Kema coal, but it is delayed at higher temperature. The increase is even higher for sewage sludge: T_{co} passes from 392 °C at 5 °C/min to 597 °C at 100 °C/min. Also, the higher the HR, the wider the temperature range for the char oxidation.

Finally, the temperature for the maximum rate of char oxidation T_{cs} is used to compare the reactivity of chars from the same fuel obtained at different HRs. T_{cs} is obtained under reference conditions (HR 20 °C/min). The reactivity of chars from wood pellets varies negligibly in the entire range of HR during the devolatilization. The peaks of the dtg curves are very close. T_{cs} is 558, 568, and 570 °C for chars obtained after devolatilization runs at 5, 20, and 100 °C/min, respectively. These values are very close. Small differences are also noticed for chars from olive residue. The difference in the reactivity of Kema coal and Qiyi coal are even less marked. So, the conclusion is that no significant effect on the char reactivity can be attributed to the HR during the devolatilization, at least in the limited range of conditions studied in this work. As a matter of fact, the operating conditions are known to strongly influence the properties of char, as reported in refs 5 and 26. However, in these cases, a very wide range of HR has been considered, covering several orders of magnitude, even using different experimental apparatuses.

5. Conclusions

Important information can be determined by comparing the behaviors of different classes of solid fuels under oxidizing and inert conditions. Different mechanisms can be recognized and contributed to devolatilization, char oxidation, and direct oxidation of the raw material. The direct oxidation of the fuel can be favored compared to the traditional devolatilization/char oxidation scheme depending on the conditions used and the characteristics of the fuel. Oxygen enhances the devolatilization and the reactivity of the produced char.

In this work, lignin-cellulosic materials (wood pellets and agricultural residues), a sewage sludge, plastics (PE and PET), and low- and high-volatile coals have been studied using constant heating rate thermogravimetric runs. The devolatilization of the parent material was carried out in nitrogen, and the direct oxidation was performed in air, as was the oxidation of char produced after the devolatilization.

The reactivity of these fuels have been quantified by defining characteristic temperatures of the process and providing kinetics for all steps and isolated substeps. Also, the effect of the operating conditions have been evaluated for each classes of fuels, varying the heating rate in the range of 5−100 °C/min. Kinetics obtained in the presence of oxygen differed significantly from those obtained considering each single step performed separately. In all cases, the process attributed to devolatilization during the direct oxidation is favored compared to the devolatilization performed in inert conditions. Also, chars obtained during the direct oxidation exhibited a higher reactivity than chars from the same fuel obtained in a separated devolatilization step, especially for biomass materials.

Results obtained in this work represent a significant set of data on very different solid fuels, useful for modeling purposes, for practical system handling (grate furnaces or fixed-bed combustors, operating in conditions similar to this study), for the safety of fuel stockpiles, and for investigations on ignition and char reactivity.

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