

EMPIRICAL CORRELATIONS FOR BIOMASS PYROLYSIS PREDICTIONS

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ABSTRACT: This work provides literature data on the characteristics of biomass pyrolysis. It is analyzed the behavior of product yields and properties on pyrolysis peak temperature dependence (within 200-1000°C). Empirical relationships are derived from the collected data, which can be used to approximate the elemental composition and heating value of chars, tars and total permanent gas as well as yields of carbon monoxide, hydrogen and light hydrocarbons. Some of these relationships seem valid for almost any biomass and are roughly independent of the pyrolysis conditions. Since pyrolysis is a common stage on the thermo-chemical conversion of solid biomass, the information provided here can be applied in the scope of pyrolysis, gasification and combustion applications.

Keywords: volatiles, char, tar, pyrolysis, gasification, combustion.

1 INTRODUCTION

Thermo-chemical conversion of solid carbonaceous fuels evolves a set of sequential stages that includes drying, pyrolysis (or devolatilization) and gasification or combustion. Drying and pyrolysis are driven by heat transport (i.e. temperature) to the fuel particles causing it to thermal decompose into moisture, pyrolytic volatiles and char. Due to high volatile matter content, pyrolysis is a key stage on the conversion of solid biomass leading to a significant mass loss of the parent fuel particles. The release of volatiles from the solid fuel can be seen as the primary pyrolysis step, to distinguish from the secondary conversion of the primary products. While primary pyrolysis is complete below around 500-600°C, the secondary reactions are only active at higher temperature. Under inert atmosphere (i.e. only by temperature effect), secondary reactions include mainly thermal cracking of selected volatiles but, under O₂, H₂O or CO₂ enriched atmospheres, there is further reforming, combustion and gasification reactions of volatiles and/or char. Knowledge on the quantities and composition of pyrolytic products (i.e., those resulting from the thermal decomposition of parent fuel and including the effect of secondary reactions) is needed for a better understanding of solid biomass thermo-chemical conversion, especially during pyrolysis and gasification applications.

A huge amount of literature data has been produced on the behavior of biomass upon pyrolysis, regarding kinetics, product yields and product properties. The experimental rigs, operating conditions, biomass type, methodologies and measurements have varied widely among investigations. A common feature is that biomass is thermally converted under a sweep of inert carrier gas and the volatiles are rapidly cooled down. Therefore, the resulting experimental data has good deal of usefulness in different situations since the pyrolytic products were not further reacted with O₂, H₂O, CO₂, etc. to a significant extent. Some literature data on the pyrolysis of a variety of solid biomasses has been structured in a database in a previous work [1]. The analysis of the collected data has shown that: (i) general trends exist for product yields and properties as a function of reactor peak temperature, (ii) for a given peak temperature, the heating rate and fuel type (wood vs. non-wood) explains most of variability in data, and (iii) simplified particle models, based on mass and energy balances and empirical relationships, can be

developed to predict the yields of volatiles released from specific biomass under various pyrolysis conditions.

In this work it is presented some literature data on the composition of char, tar and permanent pyrolysis gas. Empirical relationships are derived from the collected data. The information provided has practical use in engineering applications where first estimates of pyrolytic product yields and properties are necessary.

2 METHODS

The database developed consists of a MSExcel® worksheet, where it is structured data collected from 66 investigations [2-67], including a huge number of solid biomasses (woody and non-woody) having particles of a variety of shapes and sizes (between 0.05 to 100mm), and reactor peak temperature within 200-1000°C. For each investigation, the recorded information includes: (i) reactor type (e.g. fixed bed), (ii) reactor scale (industrial, pilot or laboratory), (iii) type of biomass (e.g. spruce, pine), (iv) nature of the biomass, taken wood as reference (wood vs. non-wood), (v) value of the heating rate (e.g. 500°C/min), (vi) classification of heating rate according to "slow" vs. "fast", (vii) fuel properties (ash content, moisture content, elemental composition, particle size and heating value), (viii) the dependence of product yields and properties on peak temperature and (ix) a variety of observations like residence time, catalyst, etc. A description on how the literature data has been implemented in the referred database can be found elsewhere [1]. A simplified description of pyrolytic volatiles has been accomplished by lumping a huge number of individual species into few groups: H₂O, CO₂, CO, H₂, CH₄, non-methane light (non-condensable) hydrocarbons (C_xH_y) and condensable (liquids at ambient conditions) organic compounds (here simply referred as "tars"). Mass product yields have been expressed on a dry ash-free (daf) fuel basis. The distinction between "slow heating rates" and "fast heating rates" is here based on the threshold of 1000°C/min. The selection of regression models was done by a trial-and-error strategy, where the observed trends were taken in account. Models with higher squared correlation coefficient (R²) were selected.

3 RESULTS

3.1 Product property

3.1.1 Elemental composition

The normalized C, H and O composition of parent biomasses and respective chars and tars produced under diverse pyrolysis conditions is presented in Fig. 1. The data has been collected from various investigations [2,4, 6-8,11-13,15,16,18,20,21,24-28,30-32,34,37,39,40,43,44, 47,49,51,52,54,55,58,59,61,63,65,67], regardless of fuel, reactors and pyrolysis conditions. While the composition of parent fuels ranges within roughly 45-65% carbon, 5-10% hydrogen and 25-50% oxygen, the one of tars is within 45-75% carbon, 5-15% hydrogen and 10-50% oxygen, and the one of chars within 50-99% carbon, 0.3-8% hydrogen and 0.5-45% oxygen (mass %, daf basis). The CHO composition of tars is relatively close to the one of parent fuels. However, ultimate analysis of chars varies widely: roughly from the composition of biomass to the one of graphite (i.e. 100% carbon). On a first glance, there appears that the composition of tars is mainly dependent on the composition of parent biomass while the composition of chars is more sensitive to the pyrolysis conditions. In Fig.2 the mass ratios of carbon content of tars and chars to the respective carbon content of parent fuels are plotted against peak temperature. Although there is some scatter in the collected data, it can be observed that at progressively higher temperatures the produced chars are more enriched in carbon than tars. Above 800°C the carbon content of char roughly doubles the one of parent fuel while the collected data for tars is always within 0.92-1.35 kgC/kgC (average of 1.14). A common aspect among chars and tars is that the carbon mass ratios tend to the unity as temperature decreases. Temperature (°C) dependent carbon ratios are expressed here arbitrarily by Eq. 1 and 2, respectively for char and tar.

$$Y_{C, \text{ch}} / Y_{C, F} = 2.051 - 1.594 \cdot \exp(-0.26 \cdot 10^{-2} \cdot T) \quad n=85 \quad R^2=0.58 \quad \text{Eq.1}$$

$$Y_{C, \text{tar}} / Y_{C, F} = 1.047 + 1.9 \cdot 10^{-4} \cdot T \quad n=67 \quad R^2=0.07 \quad \text{Eq.2}$$

General relationships for the O/C and H/C mass ratios of chars and tars as a function of respective carbon contents are presented in Fig.3. For carbon contents below 60%, the H/C and O/C ratios of tars are similar to those of chars. The increase of carbon content of chars with increasing peak temperature (Fig.2) is coupled with a massive loss of hydrogen and oxygen; however, the sharp increase of carbon content of tars is couple with a decrease of oxygen and increase of hydrogen. Anyway, lumped tars are highly oxygenated. Fig.1 to 3 suggests that the primary tars released from solid fuel are progressively converted into more aromatic structures as temperature increases. This can be seen as a conversion towards more thermally stable tars [68]: examples of low temperature tars (<650°C) are guaiacols and phenols while at high temperature (>900°C) it can appear some poly-aromatic hydrocarbons. Better fitting of O/C and H/C mass ratios vs. carbon content of char or tar were achieved by relationships with the form of Eq.3, with coefficients, range of validity and R^2 given in Table I.

$$\frac{Y_{j,i}}{Y_{C,i}} = k1 + \frac{k2 \cdot Y_{C,i}}{k3 + Y_{C,i}} \quad j=H,O \quad i=\text{tar, char} \quad \text{Eq. 3}$$

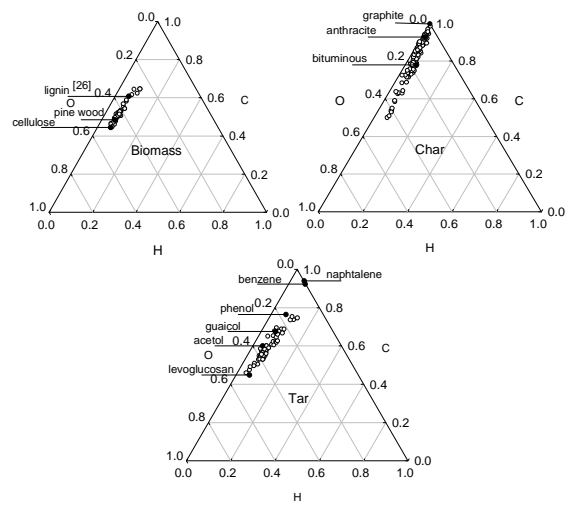


Figure 1: Normalized C,H and O composition of parent biomasses, chars and tars (mass fractions).

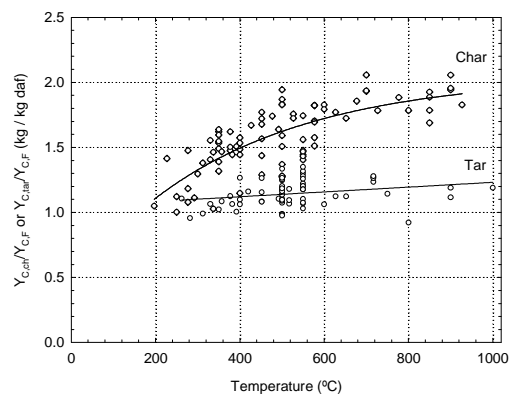


Figure 2: Mass ratios of carbon content in char ($Y_{C, \text{ch}}$) and tar ($Y_{C, \text{tar}}$) to the respective carbon content in parent fuels ($Y_{C, F}$), as a function of pyrolysis peak temperature. Solid lines are given by Eq.1 and 2.

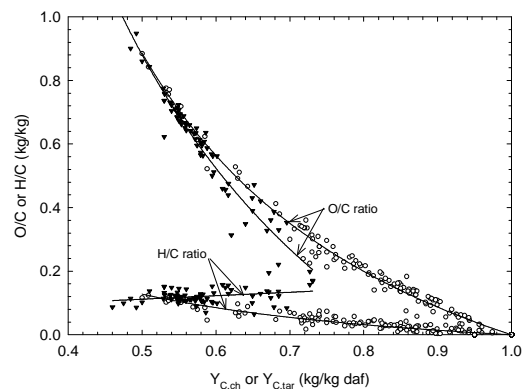


Figure 3: O/C and H/C mass ratios of chars and tars as a function of carbon content of char ($Y_{C, \text{ch}}$) or tar ($Y_{C, \text{tar}}$), respectively [\circ – char, \blacktriangledown – tar]. Solid lines are given by Eq.3 with coefficients according to Table I.

Table I: Coefficients of the non-linear fits to plots of O/C or H/C mass ratios of chars and tars vs. respective carbon contents. [k1, k2 and k3 according to Eq.3. R² is the square of correlation coefficient for the result of curve fitting to n data-points].

i	j	Ratio (kg j/kg C)	k1	k2	k3	Y _{C,i} (kg C/kg i)	n	R ²
Char	O	Y _{O,ch} /Y _{C,ch}	-6.135	5.446	-1.121·10 ⁻¹	0.5 to 0.99	116	0.99
	H	Y _{H,ch} /Y _{C,ch}	-274.822	274.694	-4.646·10 ⁻⁴	0.5 to 0.99	120	0.90
Tar	O	Y _{O,tar} /Y _{C,tar}	-895.258	894.0	-1.192·10 ⁻³	0.5 to 0.73	74	0.94
	H	Y _{H,tar} /Y _{C,tar}	5.718·10 ⁻²	2.152·10 ⁴	1.971·10 ⁵	0.5 to 0.73	74	0.10

3.1.2 Heating value

The collected data on the heating value of chars, tars and total permanent pyrolysis gas [2,4,6,8,11,12,17,18, 21,22,24,25,28,30,32,34,37,39,40,44,47,50,51,54-59,61, 63-65,67] are provided in Fig. 4 to 6, again related to diverse biomasses, reactors and operating conditions. Data for chars and total gas are available over a wide temperature range but data for tars are concentrated within 450-550°C. This is because investigations focus on the characterization of tars at temperatures that yields more bio-oil. The scatter in the collected data is high, namely concerning the data for tars which shows variations up to 20MJ/kg (Fig.5).

Dashed lines in Fig. 4 and 5 are given by an empirical correlation [37] to predict the HHV of fuels from the respective elemental composition. This correlation has been used here with the aim of drawing the trends of the HHV of chars and tars based on data presented in Fig. 2, for which two biomasses with carbon content (denoted Y_{C,F}) of 0.47 kgC/kgF and 0.52 kgC/kgF (daf mass basis) were considered as example. Therefore, Eq. 1 to 3 were used to predict the CHO composition of respective chars and tars as function of peak temperature. Since the nitrogen and sulphur contents are inputs in the quoted correlation for HHV [37], here the nitrogen content was calculated by difference based on the dry ash-free parts of chars and tars and the sulphur content was neglected. The results are in good agreement with the collected data for chars (Fig. 4). It also indicates that the HHV of tars increase with increasing peak temperature (Fig.5), although the collect data do not permit to ascertain this behavior on temperature dependence.

The heating value of chars compares with those of solid fossil fuels, namely above around 600 °C where it is most probably within 30-35 MJ/kg (Fig 4). The drawn dashed lines tend to the HHV of graphite (~33 MJ/kg) as temperatures increases. Concerning tars, data showing heating values above 35MJ/kg refers to pyrolysis of high carbon seeds (>60% carbon, mass % daf basis) [12,55,67] (Fig.5). Conversely, the collected data for wood derived tars is within 18-28 MJ/kg. Therefore, the heating value of tars compares with those of alcohol fuels but, typically, it is lower than those of liquid fossil fuels.

The lower heating value (LHV) of total permanent gas increases with rising pyrolysis peak temperature (Fig. 6). Bellow 400°C it is typically within 2-5 MJ/kg, which compares with a blast furnace gas, but above 800°C it increases to roughly 12-18 MJ/kg. Therefore, at the highest temperatures, the heating value of a pyrolysis gas can approach the one of a carbureted water-gas but it is always much lower than those of gaseous fossil fuels. Moreover, it appears that woody biomasses generate a pyrolysis gas with higher heating value than non-woody biomasses (Fig.6). A temperature-dependent LHV of pyrolysis gas (LHV_G) is here arbitrarily given by Eq. 4.

$$\text{LHV}_G = -6.23 + 0.0247 \cdot T \quad n=98 \quad R^2=0.78 \quad \text{Eq.4}$$

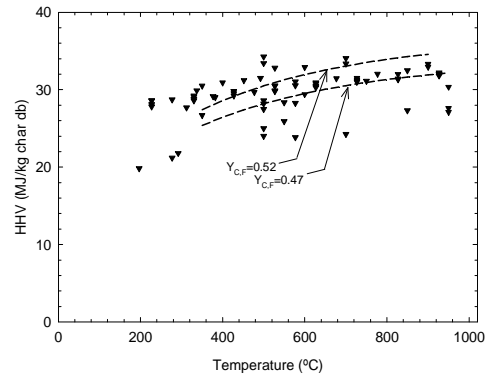


Figure 4: Heating value of chars (dry basis) as a function of pyrolysis peak temperature. Dashed lines are given by an empirical correlation [37], based on the Eq. 1 and 3 for the CHO composition of char.

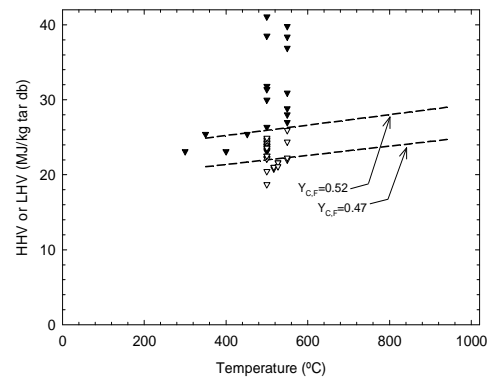


Figure 5: Heating value of tars (dry basis) as a function of pyrolysis peak temperature. Dashed lines are given by an empirical correlation [37], based on the Eq. 2 and 3 for the CHO composition of tar. [▼ - HHV; ▽ - LHV].

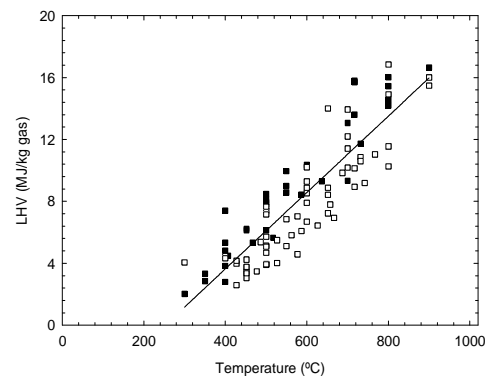


Figure 6: Heating value of total permanent gas as a function of pyrolysis peak temperature. Solid line is given by Eq. 4. [■ - wood; □ - non-wood].

3.2 Yield of main combustible gases

The collected data on the yields of CO, H₂, CH₄ and C_xH_y [4,7,8,17,18,22,24,26,28,29,46] are plotted in Fig. 7 and 9. As before, these data are relative to various biomass fuels, reactors and operating conditions. Apart from CH₄, typically the measurement data on the production of light hydrocarbons are related to a limited number of individual species. The most common is that only some C₂ and C₃ hydrocarbons are measured, although hydrocarbons up to say C₅ can be found in the gas-phase. Thus, the collected data on the yield of C_xH_y can be viewed as a reasonable estimate for the yield of lumped C₂+C₃ fractions but not so good for the whole non-methane light hydrocarbons [1].

Up to around 550-600°C, peak temperature seems of little influence on determining the yields of CO, CH₄ and H₂ (Fig.7). Below this temperature range these yields are typically below, 10%, 1% and 0.1% (mass % of daf fuel), respectively for CO, CH₄ and H₂. However, above 600°C the gas yields become a strong function of pyrolysis peak temperature. Typically, above 800°C gas yields become higher than 20%, 3% and 0.5% (mass % of daf fuel), respectively for CO, CH₄ and H₂. This behavior of gas yields vs. peak temperature resembles the two-step biomass pyrolysis, where the first step is the primary release of volatiles and the second step is its secondary conversion. Literature data show that during pyrolysis, biomass loses most of its original mass up to around 600°C while tars are only appreciably converted above this temperature [1]. Hence, the gas yields below 550-600°C (Fig. 7) are likely a result of the thermal break down of the parent fuel structures, while above 600°C its strong dependence on temperature is an indication of the activity of the secondary reactions of volatiles (mainly tars). Accordingly, both CO and CH₄ are produced during the primary decomposition while H₂ is mostly a product of the secondary reactions of volatiles. This is in good agreement with the experimental data of Funazukuri *et al.* [69] who observed that: (i) up to almost a complete release of volatiles, the gas yields were well correlated with fuel mass loss but independent of peak temperature, and (ii) thereafter, peak temperature was of increasing importance on determining gas yields. Thus, there appears that below around 550-600°C, CO and CH₄ yields depends mainly on the quantity of fuel already decomposed while above that temperature it is mostly driven by peak temperature.

From the collected data, temperature-dependent yields of CO, CH₄ and H₂ (denoted by Y_{i,F}, where i is the ith pyrolytic product and F the daf fuel) are here satisfactorily fitted by Eq.5, with regression coefficients, range of validity, number of data points and R² given in Table II.

$$Y_{i,F} = k_1 + k_2 \cdot (1 - \exp(-k_3 \cdot T))^{k_4} \quad i=\text{CO,CH}_4,\text{H}_2 \quad \text{Eq. 5}$$

A similar behavior for CO, CH₄ and H₂ yields vs. pyrolysis peak temperature suggests correlating the yields of two gases against the yield of the third gas. By using data in Fig. 7, the yields of CH₄ and H₂ were here plotted vs. the respective yields of CO (Fig.8), showing a very similar behavior. These results are also in agreement with previous reviews of literature data on this matter [28,69]. It is worth to point out that Fig. 8 is made of data from investigations where biomass has been heated up to various temperatures (within 300-1000°C); so, in case of experiments above around 600°C, the behavior shown combines the effect of both primary pyrolysis and secondary reactions. It has been found that heating rate,

particle size, degree of parent fuel conversion and peak temperature does not affect this kind of relationships [69], although it depends slightly on the biomass being pyrolysed [28]. Despite of this, good correlation (Table III) was obtained from the collected data, which accounts for pyrolysis of diverse biomasses.

Figure 9 show the yields of CH₄+C_xH_y as a function of respective yields of CH₄. A linear relationship is also obtained. Since here C_xH_y approximates the yield of C₂+C₃ light hydrocarbons, it can be concluded that these hydrocarbon fractions behave as CH₄ on peak temperature dependence. Identical results can also be found in the literature [69]. These results suggests that similar formation/destruction pathways for both CH₄ and C₂+C₃ hydrocarbons.

In this work, the plots of specific gas yields against another gas yield (Fig. 8 and 9) were fitted by linear relationships (Eq.6 and 7), with coefficients, range of validity, number of data-points and R² given in Table III.

$$Y_{i,F} = k_1 + k_2 \cdot Y_{\text{CO},F} \quad i=\text{CH}_4, \text{H}_2 \quad \text{Eq. 6}$$

$$Y_{\text{CH}_4,F} + Y_{\text{C}_x\text{H}_y,F} = k_1 + k_2 \cdot Y_{\text{CH}_4,F} \quad \text{Eq. 7}$$

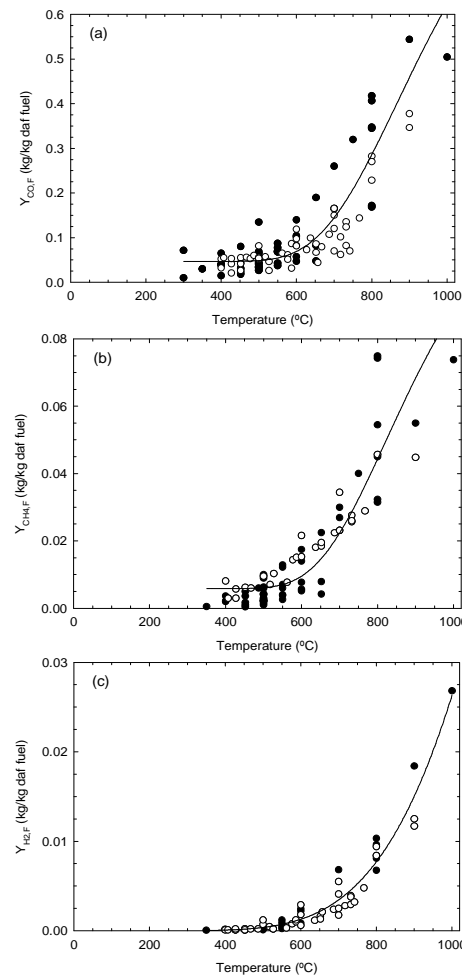


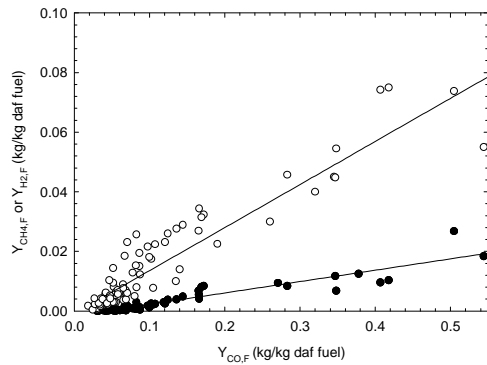
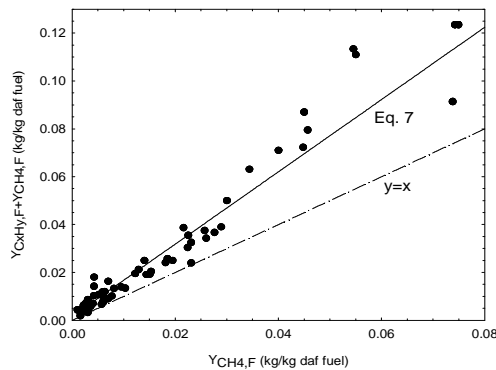
Figure 7: Yields of (a) CO, (b) CH₄ and (c) H₂ as a function of pyrolysis peak temperature. Solid lines are given by Eq.5 with coefficients according to Table II [\circ - slow heating rates; \bullet - fast heating rates].

Table II: Coefficients of the non-linear fits to plots of CO, CH₄ and H₂ yields vs. pyrolysis peak temperature. [k1, k2, k3 and k4 according to Eq.5. T is temperature in °C. R² is the square of correlation coefficient for the result of curve fitting to n data-points].

i	Yield (kg/kg daf fuel)	k1	k2	k3	k4	T (°C)	n	R ²
CO	Y _{CO,F}	0.047	0.975	0.485·10 ⁻²	67.48	300 to 1000	108	0.76
CH ₄	Y _{CH₄,F}	0.58·10 ⁻²	0.120	0.55·10 ⁻²	93.61	350 to 1000	78	0.82
H ₂	Y _{H₂,F}	0.0	1.145	0.11·10 ⁻²	9.38	350 to 1000	65	0.94

Table III: Coefficients of the linear fits to plots of CH₄ and H₂ yields vs. CO yields and CH₄+C_xH_y yields vs. CH₄ yields. [k1 and k2 according to Eq. 6 and 7. R² is the square of correlation coefficient for the result of curve fitting to n data-points].

i	Yield (kg/kg daf fuel)	k1	k2	Y _{CO,F} (kg/kg daf fuel)	Y _{CH₄,F} (kg/kg daf fuel)	n	R ²	
Eq. 6	CH ₄	Y _{CH₄,F}	-8.95·10 ⁻⁴	14.45·10 ⁻²	0.04 to 0.55	--	77	0.89
	H ₂	Y _{H₂,F}	-1.55·10 ⁻³	3.81·10 ⁻²	0.04 to 0.55	--	57	0.87
Eq. 7	--	Y _{CH₄,F} +Y _{C_xH_y,F}	1.60·10 ⁻³	1.51	--	0.001 to 0.075	58	0.94

**Figure 8:** Yields of CH₄ (Y_{CH₄,F}) and H₂ (Y_{H₂,F}) as a function of the respective yield of CO (Y_{CO,F}). Solid lines are given by Eq.6 with coefficients according to Table III. [○ – CH₄; ● – H₂].**Figure 9:** Yields of C_xH_y+CH₄ (Y_{C_xH_y,F}+Y_{CH₄,F}) as a function of the respective yields of CH₄ (Y_{CH₄,F}). Solid line is given by Eq.7 with coefficients according to Table III.

4 CONCLUSIONS

From a database of experimental results on biomass pyrolysis, empirical relationships have been developed to approximate selected properties (elemental composition and heating value) of pyrolytic products and yields of main combustible permanent gases. Despite of the variety of biomass fuels, reactors, operating conditions and methodologies among the analyzed investigations, some

of these relationships can be of very general use.

There is a distinct behavior on the CHO composition of biomass derived chars and tars as a function of pyrolysis peak temperature. The carbon content of char increases rapidly with increasing temperature while the one of tar shows weak temperature dependence. At high temperatures (say, >600°C) chars are very depleted of oxygen and hydrogen but tars are still highly oxygenated. Moreover, in opposition to chars, the hydrogen content of tars increases slightly with peak temperature. In some way the composition of tars resembles the one of parent fuels; this further suggests that biomass undergoes low temperature cleavage (i.e. primary pyrolysis) into smaller organic molecules (i.e. tars) without an extensive modification of the parent chemical structures.

The heating value of chars and total permanent gas increases with pyrolysis peak temperature. In particular, a linear fit of the LHV of gas vs. peak temperature is good over a wide range of temperature. However, the collected data do not permit to draw the respective trend for tars. In an attempt overcome the scarcity of data, the heating value of tars was estimated from the respective elemental composition showing also a weak dependence on peak temperature. Typically, the heating value of chars, tars and permanent gas ranges within roughly 25-35MJ/kg, 20-30MJ/kg and 2-18MJ/kg, respectively.

The yields of the main combustible gases, CO, CH₄ and H₂, show a very similar pattern of change with peak temperature. Below around 550-600°C the release of these gases from solid fuel is more or less independent of peak temperature but thereafter it depends strongly of temperature. CO and CH₄ are products of both primary pyrolysis and secondary reactions while H₂ seems mainly a product of secondary reactions of volatiles. General relationships exist for the yields of CH₄ and H₂ as a function of respective CO yields. Yields of total light hydrocarbons (CH₄+C_xH_y) are also well correlated with yields of CH₄. These relationships are weakly dependent on the biomass under conversion and apply over a wide range of pyrolysis conditions.

5 NOMENCLATURE

T - pyrolysis (reactor) peak temperature (°C)

Y_{i,F} – yield of ith pyrolytic product in a dry ash-free fuel basis (kg i/kg dry ash-free fuel)

Y_{j,F} – mass fraction of jth element in fuel, dry ash-free fuel

basis (kg j/kg dry ash-free fuel)

$Y_{j,i}$ – mass fraction of j^{th} element in i^{th} pyrolytic product (kg j/kg i)

k_1, k_2, k_3, k_4 – regression coefficients

R^2 – square of the correlation coefficient

n – number of data-points

Subscripts

- i = G – total pyrolytic permanent gas
 = ch – dry ash-free char
 = tar – lumped condensable compounds, liquids at ambient conditions
 = C_xH_y – lumped non-methane light hydrocarbons, non-condensable at ambient conditions
 = CO – carbon monoxide
 = CH_4 – methane
 = H_2 – hydrogen
- j = C – carbon element
 = H – hydrogen element
 = O – oxygen element

Abbreviations

db – dry basis

daf – dry ash-free basis

LHV – lower heating value (MJ/kg)

HHV – higher heating value (MJ/kg)

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7 ACKNOWLEDGEMENT

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