General equations for Biomass Properties

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1. Introduction

The problem to be treated is to investigate if general equations can be used to define properties of biomass fuels. The following properties were selected:

- the amount of char (Y_{char})
- the composition of char ($X'_{C,char}$, $X'_{H,char}$, $X'_{O,char}$)
- the heating value of char (H_{char})
- the amount of tar (Y_{tar})
- the composition of tar ($X_{C,tar}$, $X_{H,tar}$, $X_{O,tar}$)
- the heating value of tar (H_{tar})
- the heat of devolatilisation (H_{devol})
- the heating value of volatiles (H_{vol}).

These properties depend of many parameters, such as temperature, particle size, residence time, heating rate and composition. In this work, in order to simplify the problem, only the temperature dependence, considered to be the main parameter, has been taken in account. So, empirical correlations have to be found between these properties and the input data which are:

- the temperature of devolatilisation reactor (T)
- the heating value of biomass (H_{wood})
- the ash content in biomass (Y_{ash})

As small particles are considered, the temperature expressed in this report in Kelvin is the temperature of the reactor, assumed to be almost the same as the temperature of devolatilisation and the temperature of the particle during pyrolysis.

These empirical correlations are found by curve fitting (see appendix). Different equations (linear, quadratic, cubic, quadric, or nth-degree equation) and a regression model were tested. The results are presented in this paper.

2. Method

Curve fitting was used to find empirical correlations. The real problem is to decide how the data points should be represented. Individual judgment can often be used, the freehand method of curve fitting. This method has the disadvantage that different observers can obtain different curves and equations. A more scientific approach is the use of the least square method. However, for the quantitative analysis of data, nothing can replace experience, and the qualitative knowledge of the phenomenon representing data. Special attention should be given to the fact that the regression found is often valid between the limits (or near to them) of the data analysed. In this report, both methods will be used. Some of the equations have been made using the freehand method of fitting curve, some with the least square method [1].

3. Definitions

In this report, the biomass is supposed to be pyrolysed in a temperature range of 573 K -1173 K. Pyrolysis is a thermal decomposition of a product without any oxygen at high temperature (more than 473 K). It gives volatile gases, char and tar. Devolatilisation, the first stage after drying, is the release of gases and tars when a solid fuel is heated. Tar is a complex mixture of condensable hydrocarbons with a molecular mass larger than benzene (C_6H_6). Char is the carbon-rich remaining after the volatile content of a solid fuel has been driven-off by heating.

4. Data sources

Measured data were used to find most of the equations. In order to make a general study, the data were chosen to represent the largest variety of biomass possible. But, before using data found in literature, the data sources have to be checked to see if these empirical data can be used together and compared or not. Indeed if the experiments have not been done under the same conditions, the results can be influenced.

The experimental conditions of the data found for tar are collected in Table 1. These data were measured after the same type of reaction, flash pyrolysis. This type of reaction yields higher amount of tar than slow pyrolysis. In [2], secondary reaction, tar cracking, is important; it leads to a lower amount of tar. The type of reactor is not the same in all cases; a fluidised bed reactor was used for [4], [5] and [6]. The temperature range used is quite similar, 600-900 K. For all the data except for [6], gas residence time is small. Particle size is small for all the species tested. Different forms of poplar-aspen were tested, so, actually, these data concern few species. The real difference is in the analysis conditions. The samples from [4] and [5] were not measured from dry basis.

Table 1: data source for tar

References	[2]	[3]	[4]	[5]	[6]
species	wood, coconut shell, straw	gum hardwood	aspen poplar wood, aspen poplar-bark, bagasse, wheat straw, corn stover, iotech cellulose, sugar maple	hybrid - aspen poplar sawdust	IEA standard poplar-aspen, hybrid poplar-aspen
Type of reaction	pyrolysis, thermal cracking	rapid pyrolysis	flash pyrolysis	flash pyrolysis	flash pyrolysis
Type of reactor	quartz tube heated by a cylindrical oven	electrical screen heater reactor	fluidized bed reactor	fluidized bed reactor	fluidized bed reactor
fluidising gas	n.g.*	helium	nitrogen	nitrogen	nitrogen
Pressure	atmospheric	5 psig	atmospheric	atmospheric	atmospheric
Type of temperature	temperature of reactor	temperature of reactor	temperature of reactor	temperature of reactor	temperature of reactor
temperature range	600-1300K	600-1400K	673-923K	818-828K	673-900K
gas residence time	0-4 s	0.1 s	0.44 s	0.38-1.07s	10s
time of run	n.g.	n.g.	n.g.	30 min	n.g.
heating rate	500 -1000 °C /min	1000 K/s	n.g.	n.g.	n.g.
particle size	3- 5 mm	0.045- 0.088 mm	0.1- 0.25 mm	0.1- 0.25 mm	0.6 mm
analysis conditions	moisture free	moisture free, ash free	non-moisture free, non-ash free	non-moisture free, ash free	moisture free, non-ash free, oxygen found by difference

* n.g. : not given

The experimental conditions of the data found for char are collected in Table 2. The type of reactions are different: generally, flash pyrolysis leads to lower amount of char compared to slow pyrolysis [14] and secondary reaction (tar cracking) in [2] leads to higher amount of char. The data were measured in a temperature range of 600-1300K. The gas residence time is small in general for these samples except for [6]. The heating rates are in the same order, except for [2] which is higher, 500-1000 K/min. Particle size is small for all the species tested. There are differences in the analysis conditions: for 16 species out of 34, the amount of char was measured from dry wood.

Table 2: data source for char (1)

References	[2]	[4]	[6]	[7]	[8]	[9]
species	wood, coconut shell, straw, hybrid poplar aspen, white spruce	aspen poplar wood, aspen poplar-bark, bagasse, wheat straw, corn stover, iotech cellulose, sugar maple	IEA standard poplar-aspen, hybrid poplar-aspen, wheat straw, maple	eucalyptus wood	wood chips	almond shells, sawdust, straw, rice husks, olives stones, grapes stones, compost
type of reaction	pyrolysis, thermal cracking	flash pyrolysis	flash pyrolysis	carbonisation	pyrolysis	flash pyrolysis
type of reactor	quartz tube heated by a cylindrical oven	fluidized bed reactor	fluidized bed reactor	horizontal tube furnace	radiant furnace	fluidized bed reactor
fluidising gas	n.g.*	nitrogen	nitrogen	N_2	nitrogen	nitrogen
Pressure	atmospheric	atmospheric	atmospheric	n.g.	n.g.	atmospheric
type of temperature	temperature of reactor	temperature of reactor	temperature of reactor	temperature of reactor	bed temperature	temperature of reactor
temperature range	600-1300K	673-923K	673-900K	673-1073K	650-1000K	873-1173K
gas residence time	0 -4 s	0.44 s	10 s	n.g.	n.g.	n.g.
time of run	n.g.	n.g.	n.g.	n.g.	n.g.	n.g.
heating rate	500-1000 °C/min	n.g.	n.g.	10K/min	25K/min	n.g.
particle size	3- 5 mm	0.1-0.25 mm	0.6 mm	0.5- 0.8mm	0.2- 3mm	0.15-0.5mm
analysis conditions	moisture free	non-moisture free, non-ash free	moisture free, non-ash free, oxygen found by difference	moisture free, ash free	moisture free	non-moisture free, ash free

*n.g.: not given

Table 2: data source for char (2)

References	[10]	[11]	[12]	[13]	[14]	[15]
species	Brocville poplar, white spruce, red maple, IEA poplar	holm-oak wood sawdust	mixed wood waste	pine wood	oil palm shell (biomass)	cellulosa
type of reaction	flash pyrolysis	pyrolysis	flash pyrolysis	slow pyrolysis	pyrolysis	pyrolysis
type of reactor	fluidized bed reactor	cylindrical stainless steel reactor	fluidized bed reactor	static batch reactor	fluidized bed reactor	n.g.*
fluidising gas	n.g.	n.g.	nitrogen	nitrogen	nitrogen	n.g.
Pressure	n.g.	atmospheric	n.g.	n.g.	n.g.	n.g.
type of temperature	temperature of reactor	temperature of reactor	temperature of reactor	pyrolysis temperature	temperature of reactor	temperature of reactor
temperature range	720-820K	573-1173K	673-823K	573-1000K	673-873K	573-773K
gas residence time	0.7s	n.g.	2.5s	n.g.	1.48s at 773 K	n.g.
time of run	n.g.	30 min	n.g.	2 h	n.g.	5 min
heating rate	n.g.	n.g.	n.g.	5-80 K/min	n.g.	n.g.
particle size	1mm diameter	0.65-1mm	n.g.	$1cm^3$ cubes	0.2-0.4 mm	n.g.
analysis conditions	moisture free	non-moisture free, non-ash free	non-moisture free, non-ash free, oxygen by difference	non-moisture free, non-ash free	moisture free	non-moisture free, ash free

*n.g.: not given

The experimental conditions of the data found for the composition of char, after pyrolysis, are collected in Table 3. The data were measured in a range of temperature of 623-1123K. The heating rates are in the same order, about 10K/min. Particle size is small for all the species tested. The time of a run is different; it varies from 5 minutes to 1 hour for certain species. But, the main difference is in the analysis conditions: the composition of char was measured from moisture and ash-free basis for 4 species.

Table 3: data source for char composition

References	[7]	[15]	[16]	[17]	[18]	[19]
species	eucalyptus wood	cellulosa	straw and stalk of rapeseed plant	Argentinean hardwood species	almond shells, hazelnut shells, beech wood	olive stones
type of reaction	carbonisation	pyrolysis	pyrolysis	pyrolysis	pyrolysis	pyrolysis
type of reactor	horizontal tube furnace	n.g.*	stainless steel tubular reactor	fixed bed reactor	n.g.	n.g.
fluidising gas	N_2	n.g.	nitrogen	nitrogen	nitrogen	nitrogen
pressure	n.g.	n.g.	n.g.	n.g.	n.g.	n.g.
type of temperature	temperature of reactor	n.g.	n.g.	temperature of reactor	final pyrolysis temperature	final pyrolysis temperature
temperature range	673-1073 K	573-773 K	673-1173 K	623 K or 1123 K	573-1123 K	623-1123 K
gas residence time	n.g.	n.g.	n.g.	n.g.	n.g.	n.g.
time of run	n.g.	5min	30 min	3h or 1h	n.g.	1h
heating rate	10 K/min	n.g.	5 C/min	5 K/min	20 C/min	10 K/min
particle size	0.5- 0.8 mm	n.g.	1 mm	1.2- 1.4 mm	0.91 mm	0.04-0.045 mm
analysis conditions	moisture free, ash free	non-moisture free, ash free	non-moisture free, non-ash free	moisture free, ash free	non-moisture free, non-ash free	moisture free, ash free, oxygen by difference

*n.g.: not given

Other data for the composition of char are collected in Table 4. They were used to check the general equations found from the data of Table 3. The type of reaction of this sample is not the same: flash pyrolysis for [4], [6], [12], pyrolysis and thermal cracking of tar for [2], pyrolysis for [7], [15] and carbonisation for [11]. The data were measured for a maximal temperature range of 573-1300K. The residence time for [6] is quite long: 10s. The two heating rates mentioned are different. Particle size is small for all the species tested. There are differences in the analysis conditions, as the composition of char was measured from moisture free basis for 6 species out of 11.

Table 4: data source for the checking of the amount of char

References	[2]	[4]	[6]	[7]	[11]	[12]	[15]
species	wood, coconut shell, straw,	Poplar aspen with lime added	standard poplar-aspen, hybrid poplar-aspen, wheat straw,	Gum hardwood	holm-oak wood	mixed wood waste	cellulosa
type of reaction	pyrolysis, thermal cracking	flash pyrolysis	flash pyrolysis	carbonisation	pyrolysis	flash pyrolysis	pyrolysis
type of reactor	quartz tube heated by a cylindrical oven	fluidized bed reactor	fluidized bed reactor	horizontal tube furnace	cylindrical stainless steel reactor	fluidized bed reactor	n.g.
fluidising gas	n.g.*	nitrogen	nitrogen	N_2	n.g.	nitrogen	n.g.
pressure	atm*	atm	atm	n.g.	atm	n.g.	n.g.
type of temperature	temp of reactor	temp of reactor	temp of reactor	temp of reactor	temp of reactor	temp of reactor	n.g.
temperature range	600-1300K	673-923 K	673-900K	673-1073K	573-1173K	673-823 K	573-773 K
gas residence time	0 -4 s	0.44 s	10 s	n.g.	n.g.	2.5s	n.g.
time of run	n.g.	n.g.	n.g.	n.g.	30 min	n.g.	5min
heating rate	500-1000 °C/min	n.g.	n.g.	10K/min	n.g.	n.g.	n.g.
particle size	3- 5 mm	0.1-0.25 mm	0.6 mm	0.5- 0.8mm	0.65-1mm	n.g.	n.g.
analysis conditions	moisture free, non-ash free	non-moisture free, non-ash free	moisture free, non-ash free, oxygen by difference	moisture free, ash free	non-moisture free, non-ash free	non-moisture free, non-ash free, oxygen by difference	non-moisture free, ash free

*n.g.: not given
* atm: atmospheric pressure

5. Results

Empirical correlations have been established based on the data found in literature. For some properties, the lack of data prevents from producing an accurate regression model. So, in such cases, equations were taken directly from literature. Some of the data are collected in Tables 5 and 6, the reference of the others are quoted in the Figures 2, 3, 4, 6, 7 and 8.

5.1 *Composition of tar*

For the amount of tar (Y_{tar}), a sample of 14 species with 4 or 5 points each time was found (see Table 5). Figure 1 shows that the amount of tar increases with temperature until 773 K and then starts to decrease. It was difficult to establish an equation which fits the data. Samolada and Vasalos [2] proposed an empirical equation. This correlation has the same shape but seems to correspond to higher amount of tar. However, the conditions of measurements of this sample are not exactly the same (see Table 1). Species measured from non-moisture free basis, [4] and [5], seem to lead to higher amount of tar in Figure 1. Not the same reactions occur; flash pyrolysis in [3], [4], [5] and [6] leads to high amount of tar, whereas thermal tar cracking in [2] leads to lower amount of tar. The type of reactor can also influence the results as for [4], [5] and [6], a fluidised bed was used. So, the correlation of Samolada and Vasalos [2] can be used if flash pyrolysis in a fluidised bed reactor is considered:

$$Y_{tar} = 55.19 - 11.5\ T^* - 21.69\ T^{*\,2} \tag{1}$$
$$T^* = (T\text{-}833)\ /\ 160$$

where T^* is a dimensionless temperature and T the temperature of the reactor in Kelvin.
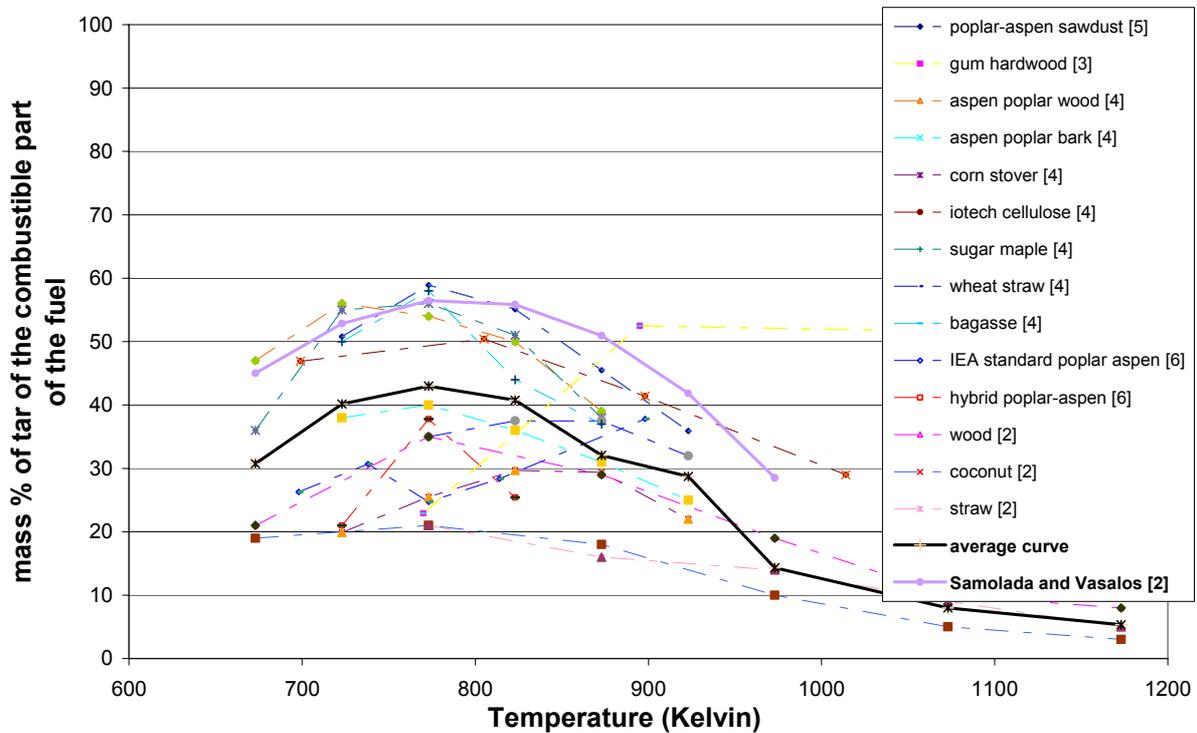
Figure 1: Mass % of tar of the combustible part of the fuel related to temperature

For the tar composition, not enough data were found to establish a relationship with temperature. The carbon, hydrogen and oxygen contents in tar don't seem to vary with temperature (see Figures 2, 3 and 4), but only a sample of four species with just few points was available as a support for this judgement. The mass percentage of carbon in tar remains approximately at 54.5 %, the percentage of hydrogen at 6.5 % and the percentage of oxygen was about 39 %.

$$X_{C,tar} = 54.5 \tag{2}$$
$$X_{H,tar} = 6.5 \tag{3}$$
$$X_{O,tar} = 39 \tag{4}$$
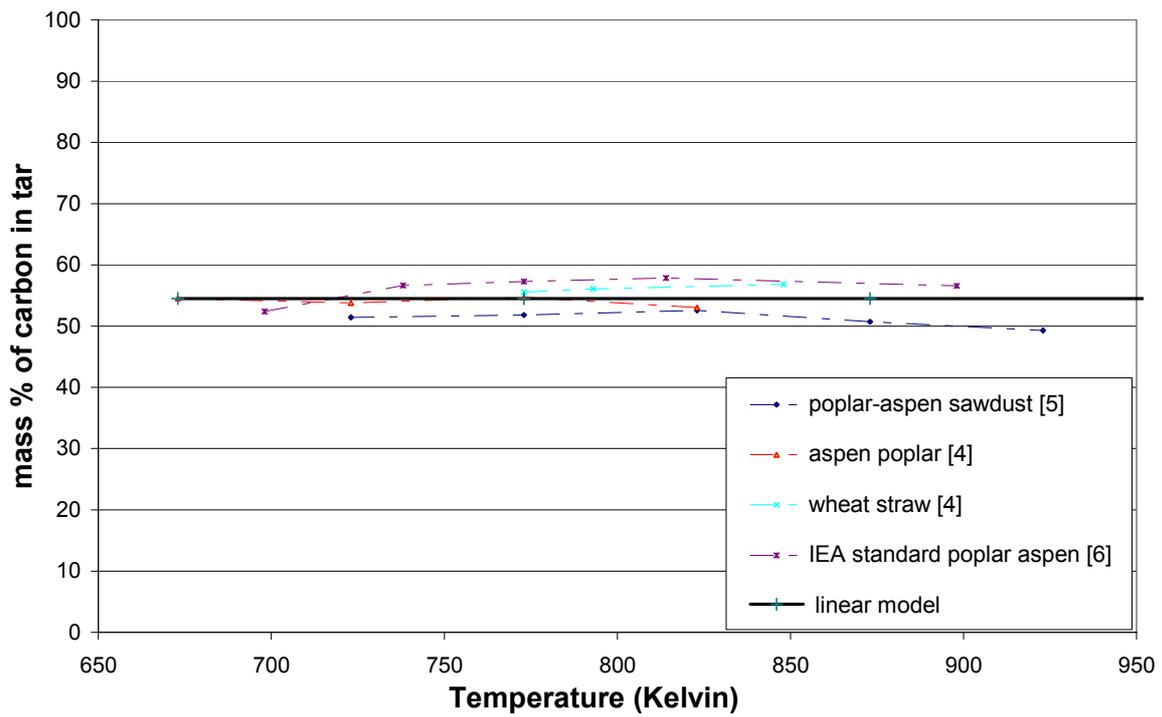
Figure 2 : Mass % of carbon in tar related to temperature
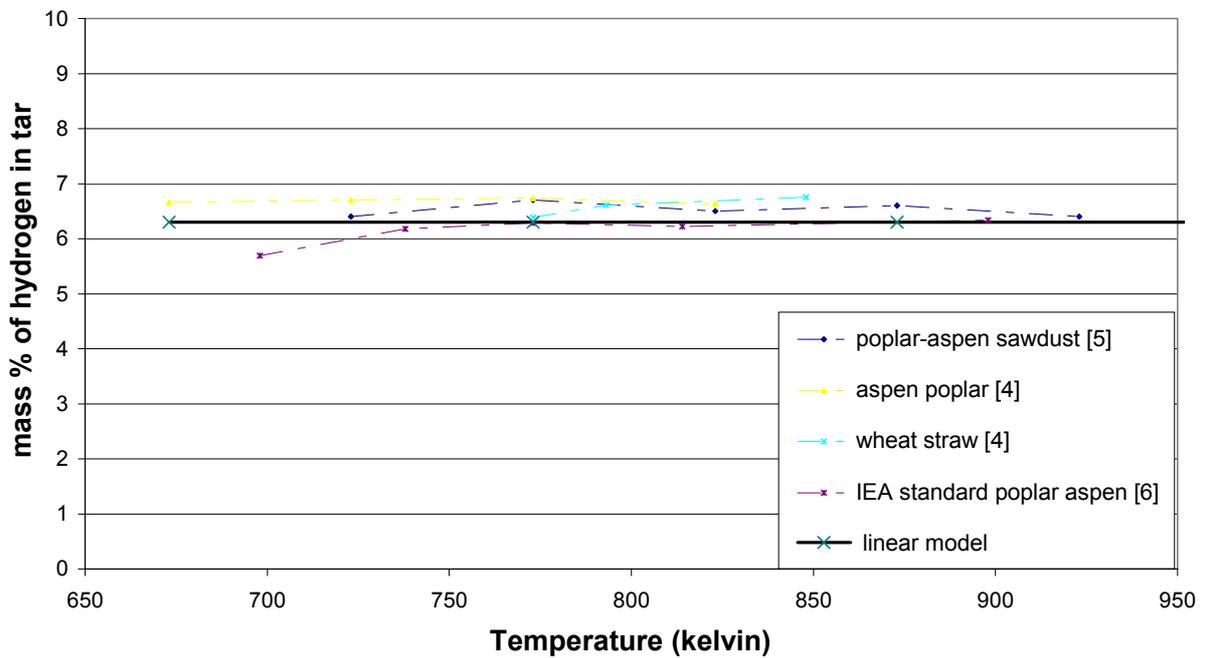
Figure 3: Mass % of hydrogen in tar related to temperature
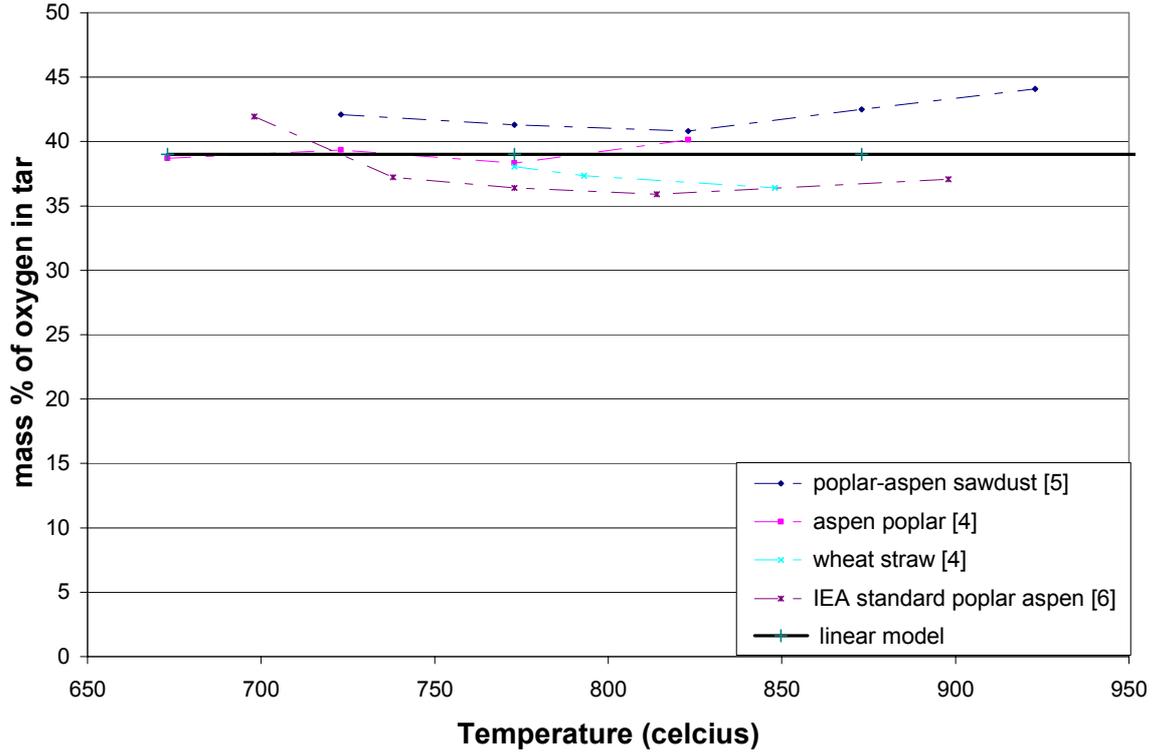
Figure 4: Mass % of oxygen in tar related to temperature

These values can be considered as approximations of carbon, hydrogen and oxygen contents in tar.

5.2 *Heating value of tar*

A general assumption [20] for the heating value of tar is that the composition of tar is close to that of wood between 673 K and 923 K, so the heating value of tar is between 22 and 26 MJ/kg (combustible substance), and between 973 K and 1273 K, the composition is close to that of lumped hydrocarbons, whose heating value is about 40 MJ/kg. However, no further data were found to make a model. So, initially, it was thought that the heating value of tar could be determined from the heating value of its components, but the different substances present in tar and their amount were too difficult to find. Finally, a general correlation of Mason and Gandhi [3] was adopted:

$$HHV = 146.58 \ X_{C,tar} + 568.78 \ X_{H,tar} - 51.53 \ X_{O,tar} \tag{5}$$

where HHV, the high heating value, is expressed in Btu/lb. As 1 Btu/lb = 2.326 kJ/kg, it becomes in kJ/kg:

$$HHV = 340.95 \ X_{C,tar} + 1322.98 \ X_{H,tar} - 119.86 \ X_{O,tar} \tag{6}$$

5.3 *Composition of char*

More data are available for char (see Table 6). The amount of char formed during pyrolysis seems to decrease exponentially when the surrounding temperature increases (see Figure 5).
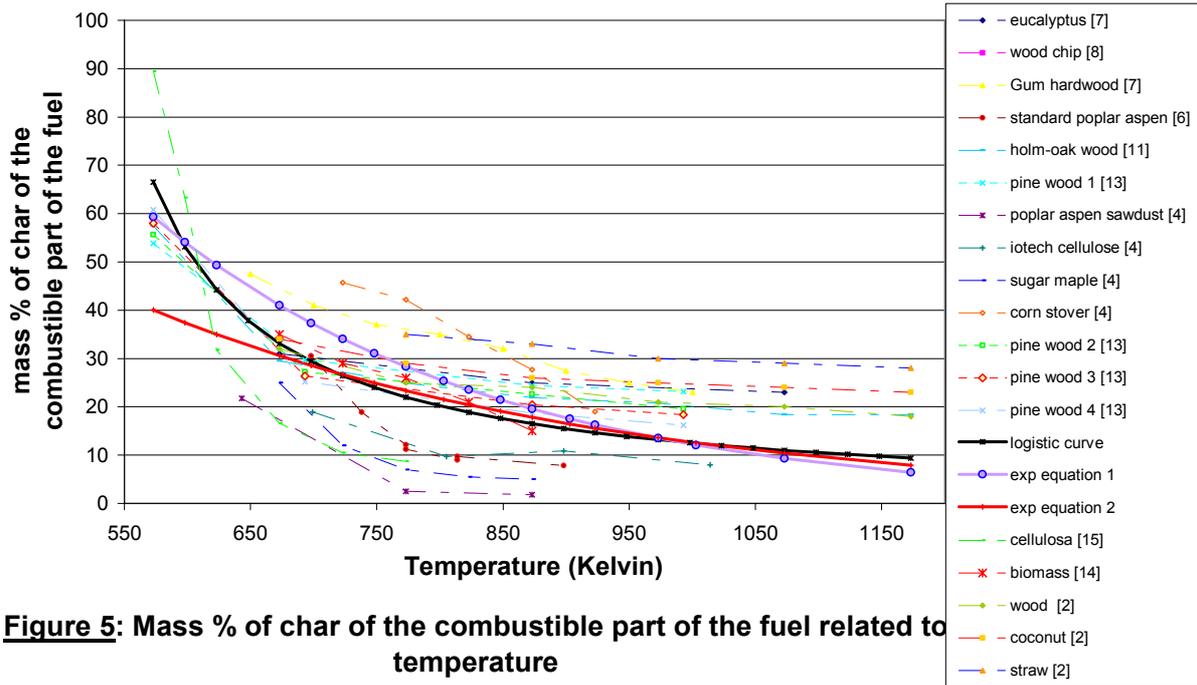
Figure 5: Mass % of char of the combustible part of the fuel related to temperature

The reaction conditions are not always the same (see Table 2). Flash pyrolysis leads to lower amount of char compared to slow pyrolysis [13] that is why there are lower values for [4] and [6]. Secondary reaction (tar cracking) in [2] and carbonisation in [7] lead to higher amount of char.

Three correlations were established from a sample of 16 species (see Table 4):

model 1: $Y_{char} = 180 \times \exp[-0.0037 \times (T-273)]$ (7.a)
model 2: $Y_{char} = 90 \times \exp[-0.0027 \times (T-273)]$ (7.b)
model 3: $Y_{char} = 5 / (1 - 1.25 \times \exp[-5 \times 0.0002 \times (T-273)])$ (7.c)

where T, temperature of the reactor, is in Kelvin.
Equations 1 and 2 are both exponential. The general trend line of the first correlation seems to be closer to the data (especially for pine wood [13], biomass [14], eucalyptus [7] and holm-oak wood [11]) for a temperature range between 573 K and 1173 K (see Figure 5). The shape of the logistic curve seems to be the one that fits best the data, as there are high values of char content for low temperature like in [13], [14] and [11], and then a fast decay followed by a lower decay from 873 K. This logistic curve was calculated using a special program for curves fitting and forecast [1] (see appendix).

Empirical data of 12 species constituting the composition of char were collected. The molar percentage of carbon in char increases with temperature, while the molar percentages of hydrogen and oxygen decrease (see Figures 6, 7 and 8). Almond shells and hazelnut shells have higher amount of carbon and lower amount of hydrogen and oxygen, whereas Brazil nutshell and cellulose [15] have lower amount of carbon and higher amount of hydrogen and oxygen compared to the other data, maybe because Brazil nutshell and cellulose [15] were measured from ash-free basis (see Table 3).

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Once again, three models fitting the empirical data for carbon content were found:

model 1: $X'_{C,char} = 0.069 \times (T\text{-}273) + 28.38$ (8.a)

model 2: $X'_{C,char} = 98 \times (1\text{-} 0.7 \times \exp[\text{-} 0.0018 \times (T\text{-}273)])$ (8.b)

model 3: $X'_{C,char} = 98 / (1+ \exp[\text{-}98 \times 0.00035 \times (T\text{-}273)])$ (8.c)

where T, the temperature of the reactor, is in Kelvin.
The first model is linear, it fits the data correctly (see Figure 6), but it doesn't correspond to reality, the carbon content can't be higher than 100 %. The second model is exponential, it seems better than the linear one as the growth slows down at high temperatures, but it doesn't follow exactly the general shape of the data, this equation represents too high values. The third model seems to be the best one; it was made with the same program as for the amount of char [1-4], it fits correctly the data and has a mathematical asymptote at 100%.
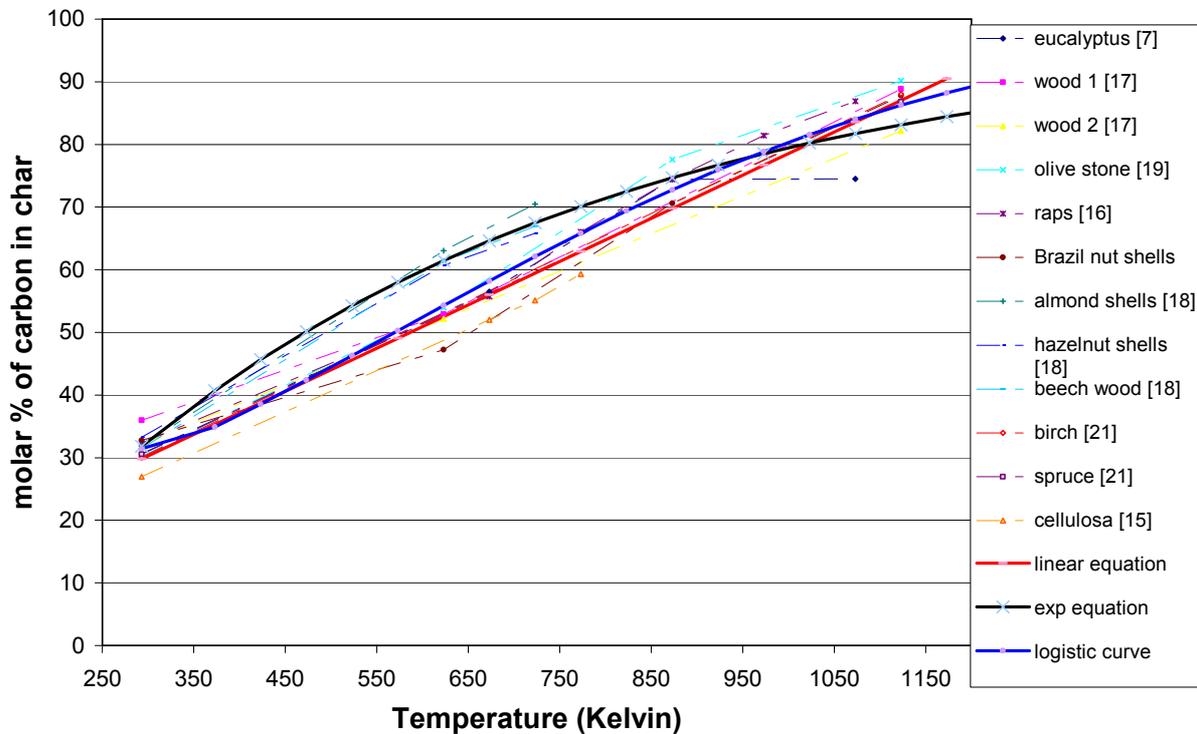
Figure 6: Molar % of carbon in char related to temperature

For the hydrogen content, two relations have been established (T is in kelvin):

model 1: $X'_{H,char} = \text{-} 0.048 \times (T\text{-}273) + 50$ (9.a)

model 2: $X'_{H,char} = 53 \times \exp[\text{-} 0.00177 \times (T\text{-}273)]$ (9.b)

Even if model 1 fits correctly the data, it doesn't correspond to reality as it gives negative values for temperatures higher than 1173 K (see Figure 7). The second, which is exponential, also fits the data correctly, but it decreases slowly at high temperatures, so it is better.
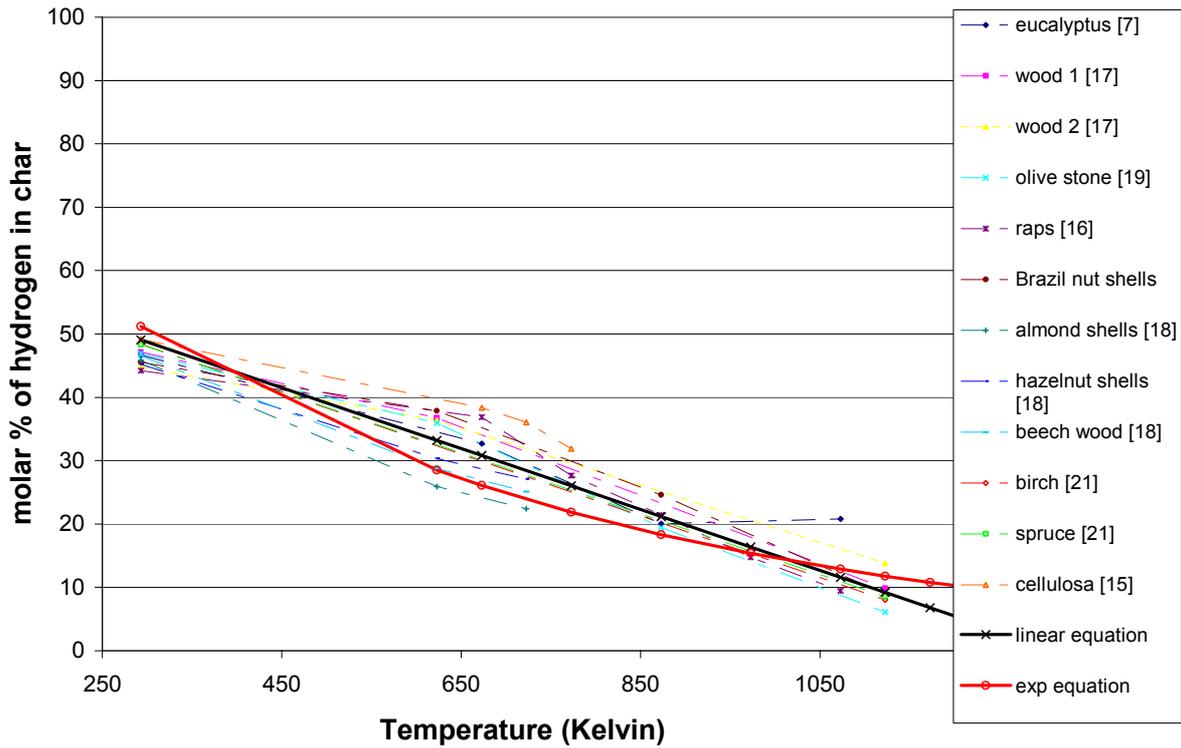
Figure 7: **Molar % of hydrogen in char related to temperature**

For the oxygen content, only an exponential model, closer to reality, was studied (see Figure 8):

$$\text{model}: X'_{O,char} = 25 \times \exp[-0.0027 \times (T-273)] \tag{10}$$

From the Figure 8, it is seen that spruce and birch [21] represent higher molar percentage of oxygen, but only two points were available, one at 273 K and one at 1173 K that is why it is represented by a linear relationship.
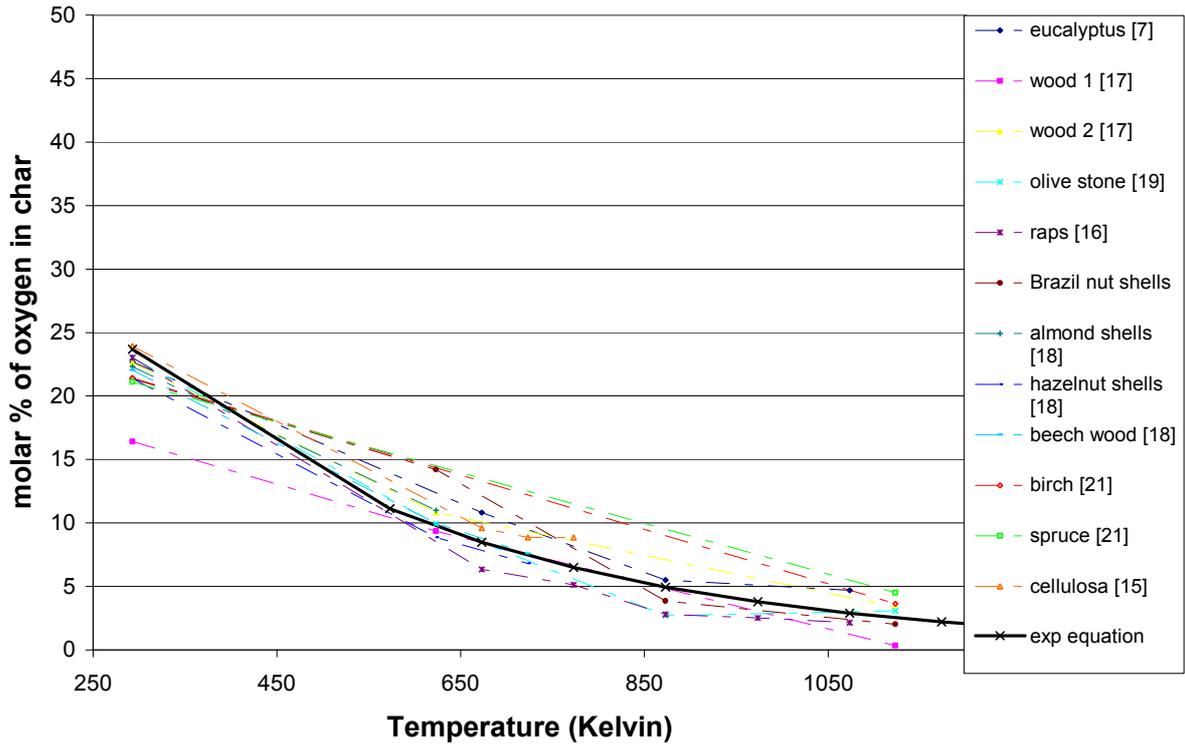
Figure 8: Molar % of oxygen in char related to temperature

5.4 *Heating value of char*

No empirical data on char heating value were found, so models from the literature were chosen. The first one relates the heating value to the amount of char [20]:

$$H_{char} = 16700 + 2930 / Y_{char} \qquad \text{for} \quad Y_{char} > 0.7 \qquad (11.a)$$
$$H_{char} = 34\,000 \qquad \text{for} \quad Y_{char} < 0.7 \qquad (11.b)$$

This expression is not very convenient, since if one of the relations found for the amount of char (7) is used; from a temperature of 973 K, the heating value of char remains constant at 34 MJ/kg. So, another one from literature, which is related with the composition of char, was used [22]:

$$HHV = 318.1\, X_{C,char} + 142.3\; X_{H,char} + 154\; X_{O,char} \qquad (12)$$

This equation shows the advantage of using other general equations (8.c), (9.b) and (10) which are quite reliable.

5.5 *Heat of devolatilisation*

The heat of devolatilisation (H_{devol}) is generally taken to be equal to -200 kJ/kg at the temperature of devolatilisation. Devolatilisation occurs in the temperature range 700- 900 K [20]. The literature values are generally given at the temperature of devolatilisation but it can be interesting to calculate the heating value of devolatilisation related to the reference temperature (273 K):

$$H^{\circ}_{devol} = H_{devol} + \int_{Tref}^{Tdev} (c_{p,wood} - (Y_{char} + Y_{ash}) \times c_{p,char} - c_{p,vol})\, dT \qquad (13)$$

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To calculate this heating value, the amount of ash (Y_{ash}), char (Y_{char}) and the specific heat of wood ($c_{p,wood}$), char ($c_{p,char}$), and volatiles ($c_{p,vol}$) are necessary. The amount of ash is known as it is an input data and the amount of char is calculated with equation (7.c). For the specific heat of wood, one of these three relations [20], which give nearly the same result, can be used:

$$c_{p,wood} = 4.206\ T - 37.7 \tag{14.a}$$
$$c_{p,wood} = 4.607\ T - 132.8 \tag{14.b}$$
$$c_{p,wood} = 3.867\ T + 103.1 \tag{14.c}$$

For char, one of these two can be chosen, as they also give the same trend line:

[20] $$c_{p,char} = -334 + 4.41\ T - 3160.10^{-6}\ T^2 + 1010.10^{-9}\ T^3 - 119.10^{-12}\ T^4 \tag{15.a}$$
[23] $$c_{p,char} = 420 + 2.09\ T - 6.85.10^{-4}\ T^2 \tag{15.b}$$

For the volatile gases, the specific heat is estimated from the composition of the volatile gases given in literature [20]:

$$c_{p,vol} = \Sigma\ \gamma_i\ c_{p,i} \qquad \text{where } \Sigma\ \gamma_i = 1 \tag{16}$$

if the volatile gases are assumed to be composed of light hydrocarbons, carbon monoxide, carbon dioxide, vapour of water, hydrogen and lumped hydrocarbons.

5.6 *Heating value of volatile gases*

The heating value of wood can be divided into two parts: one belonging to the char, on to the volatiles (including the heat of devolatilisation) [20]:

$$H_{wood} = Y_{char} \times H_{char} + (\ Y_{vol}\ H_{vol} - H^{\circ}_{devol}) \tag{17}$$

Consequently, the heating value of volatiles can be deduced easily:

$$H_{vol} = (\ H_{wood} - Y_{char} \times H_{char} + H^{\circ}_{devol}\ )\ /\ (1 - Y_{char}) \tag{18}$$

The heating value of wood (H_{wood}) is an input value. The amount of char (Y_{char}) can be calculated with the equation (7.c). The heating value of char is given by equation (12) and the heat of devolatilisation by equation (13).

6. Discussion

In this part, the purpose is to check the equations found, in order to determine their validity for a large variety of biomass materials.

6.1 C*omposition of tar*

Apparently, the composition of tar doesn't vary with the temperature, so these values can be compared with others from literature. In literature [20], the composition of lumped hydrocarbons is given as $C_6H_{6.2-8}O_{0.1-1}$. From the mass percentages found in the present work, $C_{4.5}H_{6.5}O_{2.4}$ is obtained for tar. These compositions are quite similar, except for oxygen; the value found seems twice as high as the one we are supposed to find, but this value concerns

wood and not biomass in general. Thus, the mass percentages found just give an idea of the composition of tar.

However, the composition of tar cannot be expressed only as a function of temperature. The residence time and the heating rate of devolatilisation are also parameters that influence the tar composition. The best assumption that can be made is to consider the tar composition to be the same as that of wood for low temperature of devolatilisation, and the same as that of lumped hydrocarbons for high temperature of devolatilisation.

6.2 *Heating value of tar*

If the values of carbon, hydrogen and oxygen in tar determined above are used (equations 2, 3 and 4), a constant tar heating value of 21MJ/kg is obtained. This value is lower than that for lumped hydrocarbons (26MJ/kg – 40MJ/kg) [20]. However, there is not a great difference considering the approximation made for the mass percentages of tar composition; the amount is nearly the same. So, the correlation of Mason and Gandhi found in literature can be retained.

6.3 *Composition of char*

Once the equations (8), (9) and (10) for char composition were found, data concerning the composition of other types of biomass can be found in literature (see Table 4). On the Figures 9, 10 and 11, the data of Table 7 are represented together with the general equation found for char composition (equations 8.c, 9.b and 10). The equations established just fit correctly a part of the data ([2] and [11]). Flash pyrolysis in [4], [6] and [12] lead to lower amount of char, so it may explain why these values have such a low carbon molar percentage and so high hydrogen and oxygen molar percentage. Furthermore, the data of [7] and [15] were measured from ash-free basis. However, some of the data may be not very significant, as only few points are available in a narrow temperature range 673- 823 K. Thus, the equations (8.c, 9.b and 10) can be considered to be correct for a large variety of biomass.
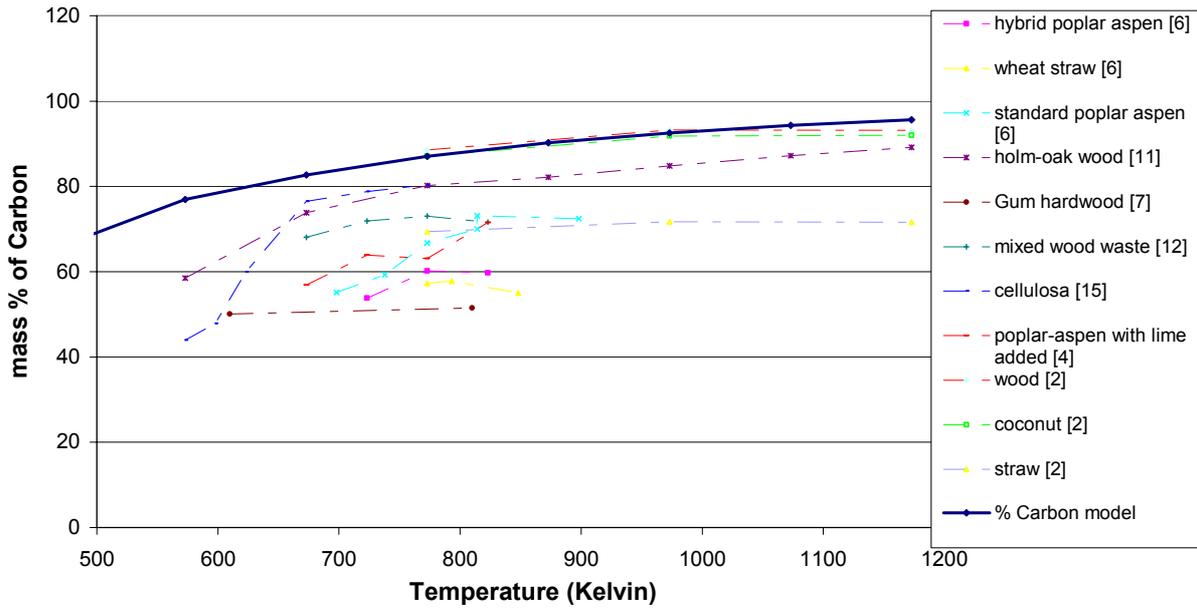
Figure 9: Comparison with the equation found for the mass % of carbon in char
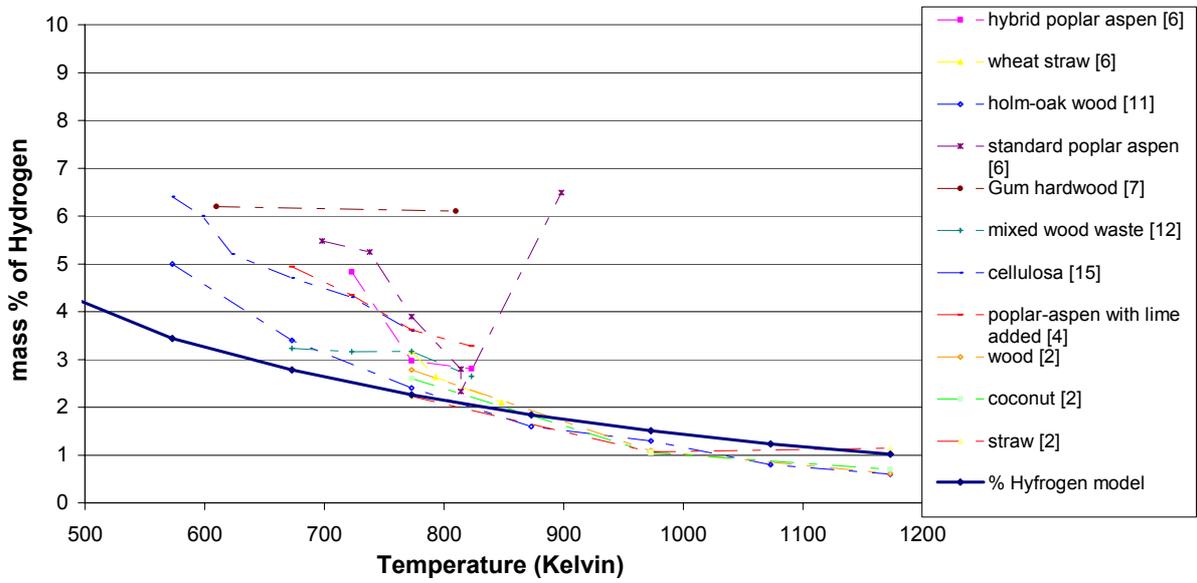
Figure 10: Comparison with the equation found for the mass % of Hydrogen in char

17
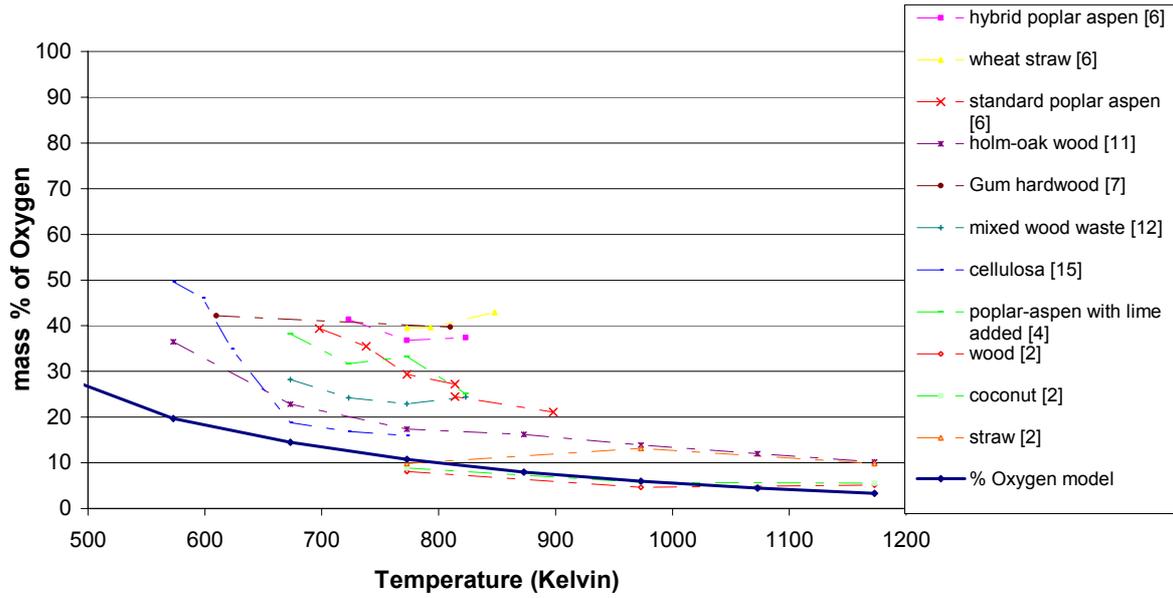
Figure 11: Comparison with the equation found for the mass % of Oxygen in char

Another manner to check the validity is to work with the molar ratios of carbon to hydrogen and carbon to oxygen, as usually it is another manner to work. A sufficient range of species of biomass is available for the composition of char (Table 3). So, equations which relate these two ratios with the temperature can be found. The correlations established are (see Figures 12 and 13):

$$\frac{X'_{C,char}}{X'_{H,char}} = 0.55 \times \exp\left[\,0.0032 \times (\text{T-273})\right] \tag{19}$$

$$\frac{X'_{C,char}}{X'_{O,char}} = 1.7 \times \exp\left[\,0.0035 \times (\text{T-273})\right] \tag{20}$$

The relations found by making the quotient of equations (8.c) and (9.b), and the quotient of equations (8.c) and (10) can be graphically compared with curves drawn from the relationships (19) and (20). The comparisons are found in the Figures 12 and 13. For some species, not enough points (sometimes just two for birch and spruce [21]) were available, that is why some results seem not to follow the general trend line. However, the two curves are nearly similar; so the correlations established (8.c, 9.b and 10) are once again validated.
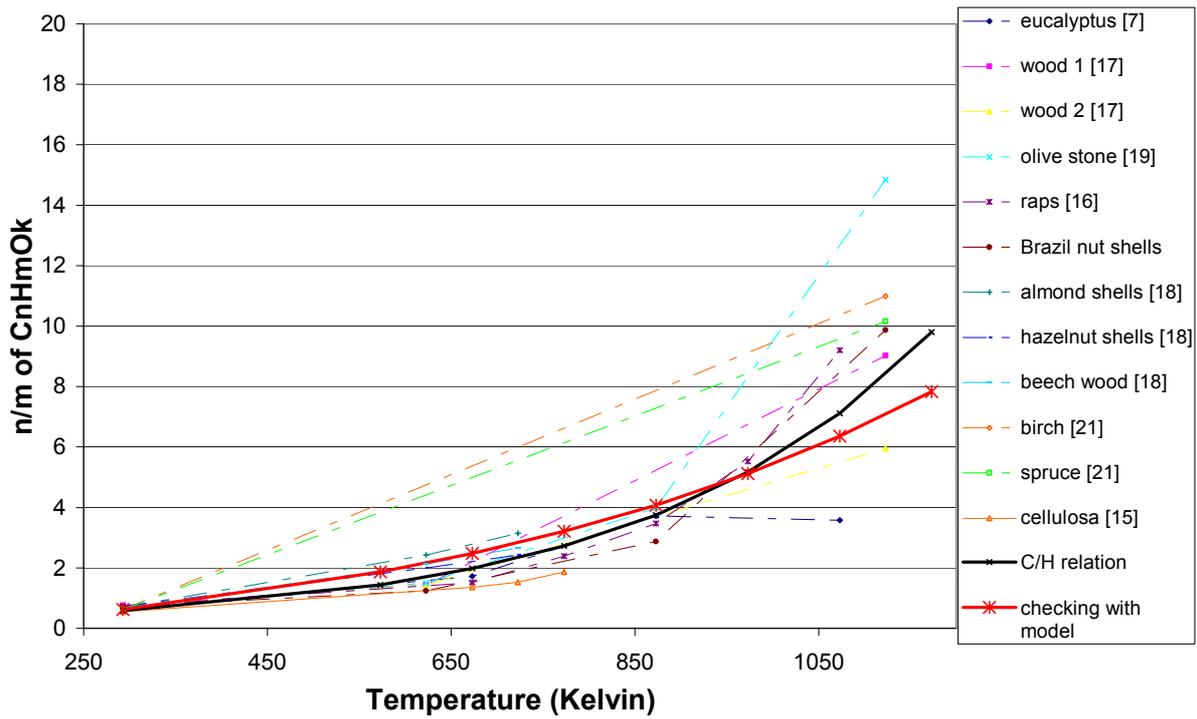
Figure 12: Ratio n/m for CnHmOk related to temperature
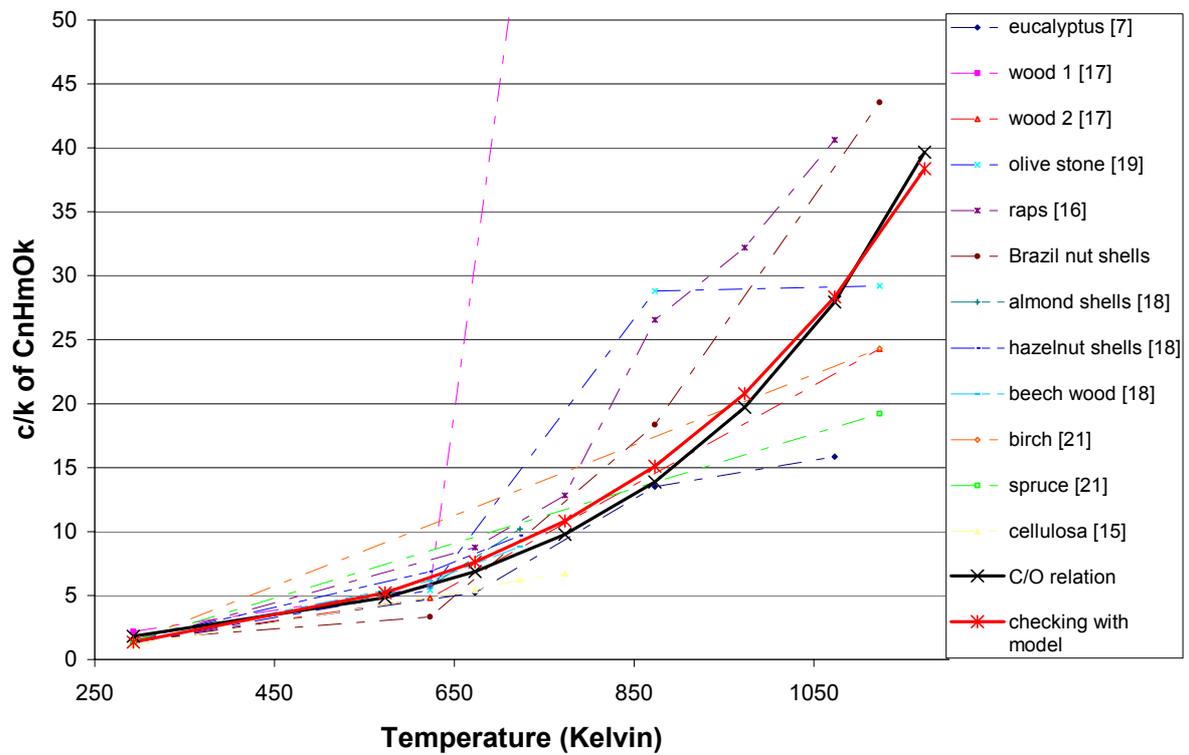
Figure 13: Ratio n/k of CnHmOk related to temperature

6.4 *Heating value of char*

It is difficult to find directly empirical values for the heating value of char. One was found for biomass *Cynara cardunculus L.* [24]. The heating value varies from 17.4 MJ/kg at 573 K to 32 MJ/kg at 1073 K. If equations (8.c), (9.b) and (10) inserted in equation (12) are used, the heating value of char varies from 25.2 MJ/kg at 573 K to 28 MJ/kg at 1073 K (see Figure 14). The amount is correct, but more data would be required to know if the small difference of the model compared to the one found in literature is significant or not.
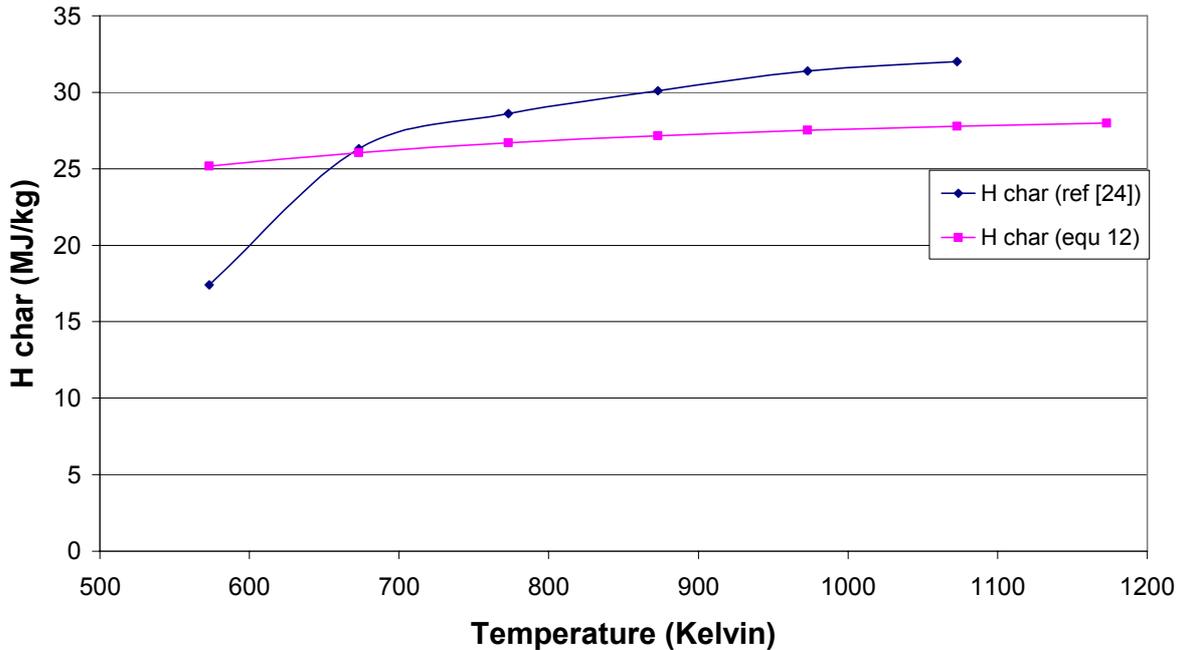
Figure 14: Heating value of char related to temperature

6.5 *Heat of devolatilisation*

A value of the heat of devolatilisation can be calculated, if equations (14.c), (15.a) and (16) from [20] are used for the specific heats:

$\gamma_{CiHj} = 0.18$ $\qquad\qquad$ $\gamma_{H2O} = 0.19$
$\gamma_{CO} = 0.42$ $\qquad\qquad$ $\gamma_{H2} = 0.006$
$\gamma_{CO2} = 0.13$ $\qquad\qquad$ $\gamma_{CnHmOk} = 0.07$

The specific heat of volatiles is obtained using the specific heats of all these species taken from [20]. The equation found is:

$$c_{p,vol} = 1036 + 1.495\ T - 312.495\ 10^{-6}\ T^2 - 45.569\ 10^{-9}\ T^3 + 28.936\ 10^{-12}\ T^4 \qquad (21)$$

where T is in Kelvin.
This value seems correct and corresponds to usual data found in literature [25].
Then, H°_{devol} can be deduced using the equation (13) (see Figure 15).
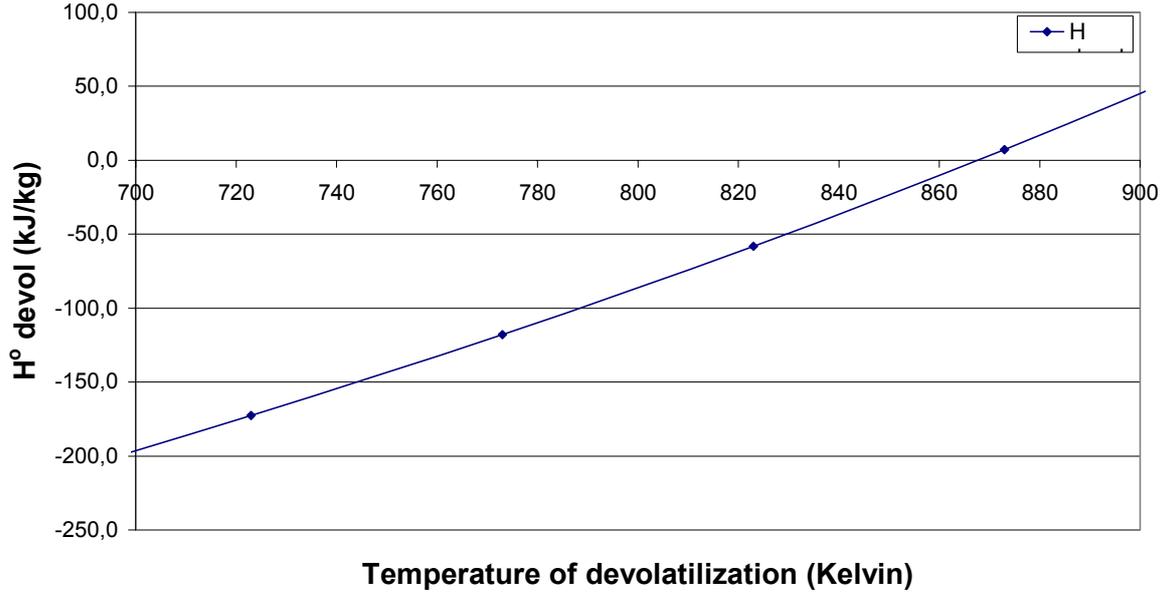
Figure 15: Heat of devolatilization at 273 K (T ref) considering different temperature of devolatilization

If devolatilisation is considered to occur between 700 and 900 K and if the heat (H_{devol}) keeps a constant value in this temperature range, the heat of devolatilisation at the reference temperature (H°_{devol}) increases from -186 kJ/kg at 700 K to 59.5 kJ/kg at 900 K. These results seem strange in first sight, as usually H°_{devol} is not so far from H_{devol}.

6.6 *Heating value of volatiles*

Using the models established in this report for Y_{char} (7.c), H_{char} (12) and H°_{devol} (13), the heating value of volatiles can be determined using the equation (18). It varies from 13.8 MJ/kg at 673 K to 18.6MkJ/kg at 973 K (see Figure 16). These values can be compared with those of literature. The gas mixture generated by the pyrolysis of *Cynara cardunculus L*. [24] has a medium-low heating value between 6.91 MJ/m^3_n at 673 K and 12.57 MJ/m^3_n at 973 K. To compare these two values, the units should be the same. The density of volatiles can be calculated using the mass ratios γ_i in [20] and the density of each gas, ρi:

$$\rho_{vol} = \Sigma\, \rho_i \times \gamma_i \tag{22}$$
$$\rho_i = M_i\, /\, V_m \tag{23}$$
$$V_m = V_o \times T\, /\, T_o \tag{24}$$

where M_i is the molar mass of the component and V_m is the molar volume calculated with the equation (24) according to the gas temperature T in Kelvin [20]. This gives a heating value of gas for *Cynara cardunculus L*. [24], which varies between 11.1 MJ/kg at 673 K and 20.3 MJ/kg at 973 K. So, the values found using the equations (18) of this report are correct.
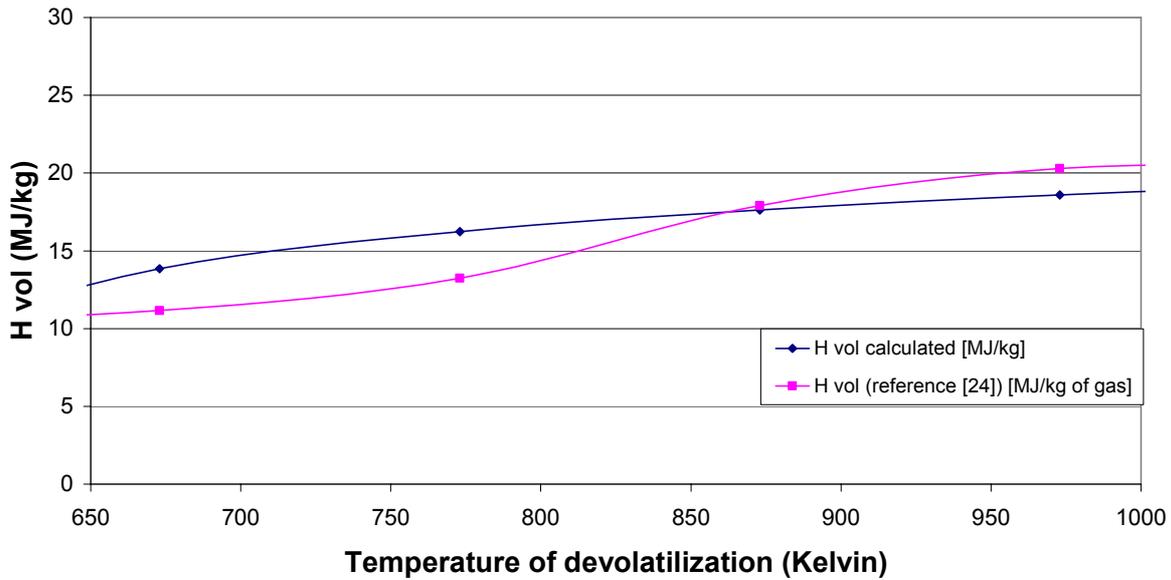
Figure 16: Heating value of volatiles related to the temperature of devolatilization

7. Conclusion

The purpose of this work is to find general equations expressing biomass properties. Only temperature dependence has been taken in account. A large amount of empirical data were collected, and curve fitting was used to find these equations. The equations found for the amount of tar (1), the heating value of tar (5), the amount of char (7.c), the composition of char (8.c), (9.b), (10) and the heating value of char (12) can be considered as reliable and have been checked in Section 4 as being valid for a large variety of biomass. However, more information would have been necessary to determine if the values obtained with the equation (13) for heat of devolatilisation and (17) for heating value of volatiles are in accordance with the reality or not. At last, the lack of data found for the composition of tar prevents from finding accurate models, equations (2), (3) and (4) which show a relationship with temperature.

In a future work, it could be interesting to try to improve some of these models finding more empirical data for the composition of tar related to the temperature, and to establish general equations from empirical data for the heating values of char and tar. It should be a good thing too, to study the influence of other parameters such as the size of the particle, the heating rate and the type of wood or biomass on these properties, to see if the temperature remains the main parameter. Thus, new models which include not only the temperature dependence could be built.

Nomenclature:

c_p [J/kg.K]: specific heat (related to subscript)
H [kJ/kg]: lower heating value (related to subscript)
HHV [kJ/kg]: high heating value (related to subscript)
M [kg/mol]: molar mass
m^3_n [-]: normal m^3 (at 273 K and 101325 Pa)
T [K]: temperature
T* [-]: dimensionless temperature
T_o [K]: reference temperature (273 K)
V_o [m^3/mol]: molar volume at To (0.0224 m^3/mol)
V_m [m^3/mol]: molar volume at T
X [-]: mass fraction based on ash-free substance
X' [-]: molar fraction based on ash-free substance
Y [-]: mass fraction based on dry ash-free wood

Greek
Ω [-]: mass ratio of two gas species in the volatiles gases
γ_i [-]: mass fraction in the volatile gases

Subscript
C, H, O: carbon, hydrogen, oxygen
C_iH_j: light hydrocarbons
$C_nH_mO_k$: lumped hydrocarbons
ash: ash
char: char
dev: devolatilisation
i: species
vol: volatiles
wood: dry wood

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<u>Appendix:</u>

1. Curve fitting

Curve fitting expresses the relationship that exists between two (or more) variables in a mathematical form. To determine an equation that connects the variables, the first step is to plot the values on a rectangular coordinate system. The resulting set of values, often called a scatter diagram, is visualized in a smooth curve that approximates the data - the approximate curve. The resulting curve is called a regression curve of Y on X, since Y is estimated from X.

2. program for curves fitting and forecast [4]

This program is a combination of regression – for the curve fitting - and a Fibonacci search for forecasting to the equation below. The structure of the part of the program for regression is very flexible and permits to be used with any type of data. In this application, only this part of the program was used. The function is defined by a differential equation; there are two cases according to the growth or the decay of the experimental data:

$$\frac{1}{Y_{char}} \cdot \frac{dY_{char}}{dT} = b \times (Y_{char} - a) \qquad a{>}Y_{char} \qquad\qquad (9.a)$$

$$\frac{1}{Y_{char}} \cdot \frac{dY_{char}}{dT} = b \times (a - Y_{char}) \qquad a{<}Y_{char} \qquad\qquad (9.b)$$

where *a* is the minimum or the maximum value of the sample, and *b* is a constant, proportional to the quotient of the variation of the amount of char and of the difference between the constant *a* and the temperature at the same point. If these equations are integrated, two solutions are obtained:

$$Y_{char} = \frac{a}{1 + A \cdot \exp(-baT)} \qquad a{>}Y_{char} \qquad\qquad (10.a)$$

$$Y_{char} = \frac{a}{1 - A \cdot \exp(-baT)} \qquad a{<}Y_{char} \qquad\qquad (10.b)$$

where A is the constant of the integration. These results can be written as:

$$\ln\left(\frac{a}{Y_{char}} - 1\right) = \ln A - baT \qquad a{>}Y_{char} \qquad\qquad (11.a)$$

$$\ln\left(1 - \frac{a}{Y_{char}}\right) = \ln A - baT \qquad a{<}Y_{char} \qquad\qquad (11.b)$$

For each empirical value (T, Y_{char}), this program creates the corresponding point (T_i, $Y_{char\ i}$), calculating $\left\{T_i, \ln\left(\frac{a}{Y_{char}} - 1\right)\right\}$ or $\left\{T_i, \ln\left(1 - \frac{a}{Y_{char}}\right)\right\}$.

Table 5: mass percentage of tar for different species of biomass

name	poplar-aspen sawdust	gum hardwood	aspen poplar wood	aspen poplar bark	corn stover	iotech cellulose	sugar maple	wheat straw	bagasse	IEA standard poplar aspen	hybrid poplar-aspen	wood	coconut	straw	average	standard deviation
ref	[5]	[3]	[4]	[4]	[4]	[4]	[4]	[4]	[4]	[6]	[6]	[2]	[2]	[2]		
number of points	5	3	5	5	5	4	5	4	4	5	3	6	6	5		
T (Kelvin)																
673			47				36					21	19		30.75	13.23
698	50.8	22.9				46.9				26.3					36.6	14.57
723	58.9		56	38	19.9		55		50	30.69	20.97				40.17	14.9
773	55.1		54	40	25.5		56	35	58	24.72	37.79	35	21	21	37.68	14.65
823	55.1		50	36	29.7	50.4	51	42	44	28.36	25.41				41.2	10.71
873	45.5		39	31	29.4		38	42	37			29	18	16	32.49	9.77
898		52.5				41.4				37.8					43.9	7.66
923	35.9			25	22			32							28.73	6.36
973												19	10	14	14.33	4.51
1014						29									29	0
1073												10	5	9	8	2.65
1173												8	3	5	5.33	1.41
1355		50.2													50.2	0

Table 6: Mass percentage of char for different species of biomass (1)

name	eucalyptus	wood chip	Gum hardwood	holm-oak wood	standard poplar aspen	sugar maple	corn stover	pine wood 1	pine wood 2	pine wood 3	pine wood 4	poplar aspen sawdust	iotech cellulose
reference	[7]	[8]	[7]	[11]	[6]	[4]	[4]	[13]	[13]	[13]	[13]	[4]	[4]
number of points	3	6	8	7	5	5	5	5	4	4	4	3	4
T (Kelvin)													
573		58		57.4				53.8	55.6	58	60,8		
598													
623		40	47.5									21.77	
673	31	25		29.5		25							
698			41		30.51			29.7	27.2	26.4	25,2		18.9
723						12	45.7						
748			37		18.88								
773				24.9	11.67	7	42.2	7				2.5	
803			35										9,7
823		21			9.35	5.5	34.5						
848			32										
873	25			21.9		5	27.7	24.4	22.6	20.4	18,7	1.82	
898			27.5		7.81								10.9
923		20					19						
973			25	20.7									
1003			23					23.2	19.6	18.4	16.2		8
1073	23	20		18.4									
1173				18.4									

Table 6: Mass percentage of char for different species of biomass (2)

name	brockville poplar	red maple	hybrid poplar aspen	white spruce	iea poplar	maple 1	maple 2	mixed wood waste	wheat straw	wheat straw 2	grape stones	olives stones	rice husks
reference	[10]	[10]	[6]	[10]	[10]	[6]	[6]	[12]	[6]	[4]	[9]	[9]	[9]
nunber of points	2	2	3	3	1	1	3	4	4	4	4	4	4
T (Kelvin)													
573													
598													
623													
673								24.1					
698													
723			25.46					21.4					
748				16.3			16.65						
773	15.45	12.9	13.21	12.2	10.53		10.92	18.9	22.13	37			
803		9		12.3		13,8	9.57		20.51				
823	10.6		10,64					17.03	19.13	23			
848									17.3				
873										18	24	25	12.5
898													
923										15			
973											22.5	17.5	11
1003													
1073											18	11	8
1173											11	7	3

Table 6: Mass percentage of char for different species of biomass (3)

name	compost	almond shells	straw	sawdust	biomass	cellulosa	wood	coconut	straw	average	standard deviation
reference	[9]	[9]	[9]	[9]	[16]	[15]	[2]	[2]	[2]		
nuber of points	4	4	4	4	5	6	6	6	5		
T (Kelvin)										average	standard deviation
573						89.4				61.9	12.3
598						63.3				63.3	0
623						31.8				39.8	7.9
673					35	16.6	32	34		28	5.9
698										28.4	6.7
723					29	10.5				24	12.9
748										22.2	9.9
773					26	8.7	25	29	35	19.5	10.7
803										15.7	9.4
823					21					17.2	8.5
848										24.7	10.4
873	17.3	21	19	12.5	15		24	26	33	20.7	6.3
898										15.4	10.6
923										18	2.6
973	17	18	7	12			21	25	30	18.9	6.6
1003										18.1	5.6
1073	7.5	9	4	2.5			20	24	29	15	8,4
1173	3.3	8	2	2			18	23	28	10,3	9,2

Table 7: Mass percentage of char components for different species of biomass (1)

name	Gum hardwood			mixed wood waste			standard poplar aspen			holm-oak wood			hybrid poplar aspen			cellulosa		
number of points	2			4			5			7			3			6		
ref	[7]			[7]			[6]			[11]			[6]			[15]		
mass % of components — T (kelvin)	C %	H %	O %	C %	H %	O %	C %	H %	O %	C %	H %	O %	C %	H %	O %	C %	H %	O %
573										58.5	5	36.5				44	6.4	49.6
598																47.9	6	46.1
610	50.1	6.2	42.2															
623																		
673				68.1	3.23	28.2				73.8	3.4	22.8				59.9	5.2	34.9
698							55.13	5.48	39.39							76.5	4.7	18.8
723				71.9	3.16	24.2							53.84	4.83	41.33	78.8	4.3	16.9
738							59.28	5.25	35.47									
773				73	3.17	22.9	66.77	3.9	29.33	80.2	2.4	17.4	60.22	2.97	36.81	80.4	3.6	16
793																		
810	51.5	6.1	39.7															
814				71.6	2.65	24.,4	69.99	2.8	27.21									
823																		
848																		
873										82.2	1.6	16.2	59.77	2.81	37.42			
898							72.45	6.49	21.06									
973										84.8	1.3	13.9						
1073										87.2	0.8	12						
1173										89.2	0.6	10.2						

Table 7: Mass percentage of char components for different species of biomass (2)

name	poplar-aspen with lime added			wheat straw			wood			coconut			straw		
number of points	4			3			3			3			3		
ref	[4]			[6]			[2]			[2]			[2]		
mass % of components	C %	H %	O %	C %	H %	O %	C %	H %	O %	C %	H %	O %	C %	H %	O %
T (kelvin)															
573															
598															
610															
623															
673	56.87	4.94	38.19												
698															
723	63.93	4.35	31.72												
738															
773	63.1	3.62	33.28	57.26	3.17	39.57	88.51	2.78	8.12	87.09	2.6	8.88	69.38	2.23	9.82
793				57.77	2.63	39.6									
810															
814															
823	71.56	3.28	25.16												
848				55.01	2.1	42.89									
873															
898															
973							93.22	1.09	4.6	9.83	1.05	5.71	71.7	1.07	13.12
1073															
1173							93.18	0.62	5.1	92.02	0.7	5.55	71.63	1.15	9.86