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# Evolution of Aromatic Tar Composition in Relation to Methane and Ethylene from Biomass Pyrolysis-Gasification

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**ABSTRACT:** Tar reduction and monitoring is the major stake for gasification processes. Pyrolysis is the precursor mechanism of the gasification of solid fuels and tar production. The evolution of gas and tar composition produced from wood chips pyrolysis was investigated in a tubular reactor as a function of its wall temperature (700–1000 °C, with gas mean residence times of 1.1–2.7 s). High thermal severities lead to the “gasification” regime, promoting gas production from tar conversion. Tar (benzene, toluene, *o*- and *m*-xylenes, phenol, indene, *o*-, *m*-, and *p*-cresols, naphthalene, 1- and 2-methylnaphthalenes, acenaphthylene, and phenanthrene) were quantified by gas chromatography/mass spectrometry (GC/MS) analysis using deuterated internal standards. Closed mass balances were obtained. A simplified chemical scheme of secondary tar conversion is proposed. Under the investigated range of thermal severity, CH<sub>4</sub> production is mainly controlled by aromatic tar demethylation. Linear relations were observed between the molar production of benzene and CH<sub>4</sub> and between all quantified tars and C<sub>2</sub>H<sub>4</sub> (ethene). CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> could thus be analyzed by direct online methods and used as indicators of the tar content and speciation for gasifier monitoring. The validity of these relations depends upon the thermal conditions of reactors and biomass composition. These relations could be suitable for dual-fluidized-bed gasifiers because H<sub>2</sub>O has very few chemical effects on hydrocarbon thermal conversion.

## 1. INTRODUCTION

The increase of the greenhouse effect and the decline of fossil resources combined with an increased demand for fuels compel researchers to develop renewable alternative routes for energy production with low emissions of greenhouse gases. Biomass gasification is identified as a promising route for the production of combined heat and power, substitute natural gas, hydrogen, or Fischer–Tropsch diesel.<sup>1</sup> The tar content in the product gas is the major cumbersome and problematic parameter in the gasification processes.<sup>2</sup> Tars lead to fouling, coke deposit, and catalyst deactivation. Hence, tar conversion or removal is one of the main challenges for the successful development of commercial gasification technologies and is extensively studied.<sup>3–5</sup>

Pyrolysis is the precursor mechanism of the gasification of solid fuels and tar production. In this paper, “pyrolysis” is defined as the global set of reactions, including biomass primary pyrolysis and tar thermal conversion. The “pyrolysis” regime (char, bio-oil, and/or gas production) depends upon the reactor thermal conditions. High thermal severity in pyrolysis reactors promotes the formation of gases from the conversion of tar. In a “gasification” reactor, pyrolysis (primary and secondary reactions) occurs among other reactions, such as water–gas shift reaction and char oxidation (by O<sub>2</sub>, H<sub>2</sub>O, and/or CO<sub>2</sub>). Dependent upon the thermal severity (gas temperature and residence time) of the vapor-phase conversion in reactors, tars of different compositions and reactivities are produced. Three major product classes can be identified: (i) primary compounds (oxygenates produced at low thermal severity), (ii) secondary (phenolics and olefins produced between 500 and 800 °C, with the temperature range depending upon the gas residence time), and (iii) tertiary tar [benzene and polycyclic aromatic hydrocarbons (PAHs)].<sup>6</sup>

One of the first key steps prior to tar upgrading is the development of tar analysis methods. Tar sampling and analysis strategies were reviewed in a previous paper.<sup>7</sup> Most of the time, tar quantification requires off-line methods and long-time analysis (about 40 min for the gas chromatography method) unsuitable for process monitoring as a function of the tar content in the gas stream. Direct tar online quantification methods based on a flame ionization detector<sup>8</sup> were developed. However, the chemical nature of tar cannot be determined by this method. Some tar compounds, such as naphthalene, could also be monitored by Fourier transform infrared (FTIR) spectroscopy.<sup>9,10</sup> A molecular beam mass spectrometer (MBMS) can be used to improve quantitative, continuous, real-time monitoring of gasifier tar<sup>11</sup> and remains the most advanced method for tar online quantification. Nevertheless, although fragmentation can be minimized, the mass spectra of a complex tar matrix are difficult to interpret because some observed peaks (mass/abundance) can result from different compounds.<sup>11</sup>

Molar correlations between permanent gases (such as C<sub>2</sub> species and CH<sub>4</sub>), which can be easily analyzed online, and tars could exhibit an interesting potential application for indirect online monitoring of tars. For instance, CH<sub>4</sub> and/or C<sub>2</sub> species could be analyzed online by FTIR spectroscopy to give a first assessment of the thermal history and the tar content and composition. Moreover, such molar correlations could be useful to understand the complex series of reactions involved in tar formation and conversion.

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**Table 1. Elementary Composition of the Wood Chips (wt %, on a Dry and Ash-Free Basis)**

C	48.0
O	45.6
H	6.2
N	0.2

To date, only a few studies<sup>12–15</sup> reported some relationships among the ratios of the major gas-phase products (CO, CH<sub>4</sub>, CO<sub>2</sub>, and C<sub>2</sub> hydrocarbons), which are useful to understand the main possible reactions of permanent gas formation during pyrolysis. Nevertheless, these studies did not consider aromatic tar formation mechanisms. The main contributions on the mechanisms of aromatic tar formation from biomass come from the National Renewable Energy Laboratory (NREL) on model tar compounds<sup>16–20</sup> and biomass pyrolysis in fluidized-bed<sup>21,22</sup> and entrained flow reactors<sup>23</sup> using MBMS and multivariate analysis.

To the authors' knowledge, only Brage et al.<sup>24</sup> determined relations between "total tar", chemical distribution of principal tar constituents, and the three C<sub>2</sub> compounds (ethane, ethene, and ethyne), namely, (i) indene to naphthalene, (ii) phenols to aromatics, and (iii) saturated to unsaturated C<sub>2</sub> compounds. These relations were established for gases produced from wood pyrolysis in a fixed-bed reactor between 700 and 900 °C. They are specific to each reactor and mainly depend upon reactor thermal conditions and the selectivity of catalysts (if any).

In a given range of thermal severity, tertiary aromatic tar and methane are mainly produced by demethylation of secondary tar.<sup>25</sup> For instance, the thermal conversion of toluene produces benzene (and PAH) and methane.<sup>25</sup> Hence, molar correlations between some aromatic compounds and methane may be expected because these compounds are produced from the same precursors in a given range of thermal severity. Nevertheless, such correlations would only exist in the absence of consecutive conversion of the products (CH<sub>4</sub> and tertiary tar). As previously reported, the conversion of tertiary tar (benzene and non-substituted PAH)<sup>25</sup> and CH<sub>4</sub><sup>26</sup> is negligible for gas-phase treatment below 1000 °C in a syngas (for residence times less than 1 s, without O<sub>2</sub>). Consequently, CH<sub>4</sub> could be an interesting indicator of the tar content whether a relation between CH<sub>4</sub> and tar is evidenced under a given range of thermal severity.

To the authors' knowledge and despite the numerous studies on wood pyrolysis, no relation between aromatic tar and methane has been previously established. Moreover, there is still a lack of knowledge on aromatic tar quantification for well-defined pyrolysis experiments (closed mass balances and well-defined thermal conditions).

This paper first presents the thermally induced evolution of gas and tar compositions produced from wood pyrolysis in a tubular reactor. The temperature induced interrelations (i) between some permanent gases and (ii) between permanent gases and tar are then investigated and discussed. Linear relations between tars, CH<sub>4</sub>, and C<sub>2</sub>H<sub>4</sub> are evidenced. Direct online analysis of CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> could be used for indirect online tar monitoring under the investigated range of pyrolysis conditions, as previously proposed by Brage et al.<sup>24</sup> for C<sub>2</sub> species on another pyrolysis reactor.

## 2. MATERIALS AND METHODS

Materials and methods were previously described.<sup>7,27</sup> Only the salient points are specified in this paper.

The elementary composition of wood (spruce) samples is presented in Table 1. The moisture content was 7 wt % (on a wet basis).

Wood chips (0.5 g) with an average thickness of approximately 1.5 mm and sieved between 2 and 5 mm meshes were introduced with a sample boat into the center of a quartz tubular reactor (35 mm internal diameter and 600 mm length). The reactor was preheated by electrical resistances up to the set temperature and flushed by N<sub>2</sub> (1 L/min at 20 °C and 1 atm). The volume of the gas conversion zone was kept constant for all experiments (288 cm<sup>3</sup>, 35 mm internal diameter, and 300 mm length). The gas mean residence time was not kept constant for each temperature (by adjusting the carrier gas flow rate). Indeed, the purpose of this work was not a detailed kinetic study of tar conversion because it remains very difficult to study the tar conversion kinetics without decoupling the primary pyrolysis and the tar conversion in two different reactors as in refs 6 and 12. Gas-phase temperature profiles were previously presented as a function of the reactor temperature.<sup>27</sup> The measuring of the average particle heating rate was also extensively presented in this previous paper.<sup>27</sup> The external heat-transfer coefficient that is a better parameter than the particle heating rate was determined as a function of reactor temperatures.<sup>27</sup>

At the outlet of the reactor, the sampling lines were heated at 350 °C. Permanent gases (N<sub>2</sub>, H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>) were collected in a collapsible Tedlar bag and then injected into a gas chromatography/thermal conductivity detector (GC/TCD) 3800 (Varian, Palo Alto, CA). The GC/TCD apparatus is composed of a 250  $\mu$ L loop and two columns (Poraplot Q and molecular sieve 5 A, Varian) according to an inject/backflush and serial/bypass-specific setup.<sup>28</sup> Tars were sampled by solid-phase adsorbent (SPA) tubes (Carbotrap 300, Sigma Aldrich) and impingers filled with methanol. Calibration, sampling conditions, and analytical methods were previously described elsewhere.<sup>7</sup> The choice of the quantified compounds and the deuterated internal standards (see Table 2) was justified in previous publications.<sup>7,27</sup> Benzene is considered as an aromatic tar because it is one of the major and more stable aromatic compounds in pyrolysis/gasification gas and it may cause problems for further advanced applications, such as catalytic gas conversions. A typical chromatogram is presented in Figure 1.

Table 3 summarizes the investigated pyrolysis conditions (see ref 27 for more details about the definitions and the methods of calculation).

The average heating rates of particles (Table 3) obtained in our experimental conditions (1.5 mm particle thickness) were defined at the center of the particles and until a temperature half that of the reactor wall temperature<sup>27,29</sup> was reached. They are similar to those obtained in a fluidized bed with particles of 5 mm thickness.<sup>29</sup> Moreover, the product distribution obtained under our pyrolysis conditions was shown to be close to those reported for the Battelle dual-fluidized-bed gasifier.<sup>30</sup>

Mass balances are satisfactory (see Table 3) for an individual quantification of such a large range of compounds. Its evolution was previously discussed.<sup>27</sup> The gravimetric method was not accurate enough to quantify the low mass of condensable compounds (i.e., water and tars) produced in our conditions.

## 3. RESULTS AND DISCUSSION

**3.1. Evolution of Permanent Gas Composition.** The evolution of gas composition (Figure 2) is in accordance with refs 31–34 with CO as the major permanent gas for all investigated reactor temperatures. H<sub>2</sub> molar fraction increases from 12 vol % (700 °C) to 32 vol % (1000 °C). The evolutions of molar yields differ from molar fraction evolutions because the total gas volume increases from 0.5 to 0.75 N m<sup>3</sup> kg<sup>−1</sup> dry wood for the reactor wall temperature evolving from 700 to 1000 °C. CH<sub>4</sub> yields range from 0.081 to 0.110 N m<sup>3</sup> kg<sup>−1</sup>, and C<sub>2</sub>H<sub>4</sub> yields range from 0.015 to 0.035 N m<sup>3</sup> kg<sup>−1</sup>. CO<sub>2</sub> and H<sub>2</sub>O yields are

Table 2. Quantified Tar and Internal Deuterated Standards

peak number	name	elementary composition	molecular weight (g/mol)	mass spectrum (NIST) [mass (abundance)]
1	benzene	C <sub>6</sub> H <sub>6</sub>	78	78 (999), 77 (283), 51 (221)
2	toluene- <i>d</i> <sub>8</sub>	C <sub>7</sub> D <sub>8</sub>	100	98 (999), 100 (616), 42 (216)
3	toluene	C <sub>7</sub> H <sub>8</sub>	92	91 (999), 92 (621), 65 (85)
4	<i>m</i> -xylene	C <sub>8</sub> H <sub>10</sub>	106	91 (999), 106 (430), 105 (177)
5	<i>o</i> -xylene	C <sub>8</sub> H <sub>10</sub>	106	
6	phenol- <i>d</i> <sub>6</sub>	C <sub>6</sub> D <sub>6</sub> O	100	99 (999), 71 (482), 42 (334)
7	phenol	C <sub>6</sub> H <sub>6</sub> O	94	94 (999), 66 (387), 65 (266)
8	indene	C <sub>9</sub> H <sub>8</sub>	116	116 (999), 115 (800), 63 (170)
9	<i>o</i> -cresol	C <sub>7</sub> H <sub>8</sub> O	108	108 (999), 107 (919), 79 (442)
10	<i>m</i> - and <i>p</i> -cresol	C <sub>7</sub> H <sub>8</sub> O	108	
11	naphthalene- <i>d</i> <sub>8</sub>	C <sub>10</sub> D <sub>8</sub>	136	136 (999), 108 (116), 137 (103)
12	naphthalene	C <sub>10</sub> H <sub>8</sub>	128	128 (999), 127 (193), 102 (122)
13	2-methylnaphthalene	C <sub>11</sub> H <sub>10</sub>	142	142 (999), 141 (657), 115 (245)
14	1-methylnaphthalene	C <sub>11</sub> H <sub>10</sub>	142	142 (999), 141 (700), 115 (320)
15	acenaphthylene	C <sub>12</sub> H <sub>8</sub>	152	152 (999), 151 (196), 76 (173)
16	phenanthrene	C <sub>14</sub> H <sub>10</sub>	178	178 (999), 176 (202), 179 (150)

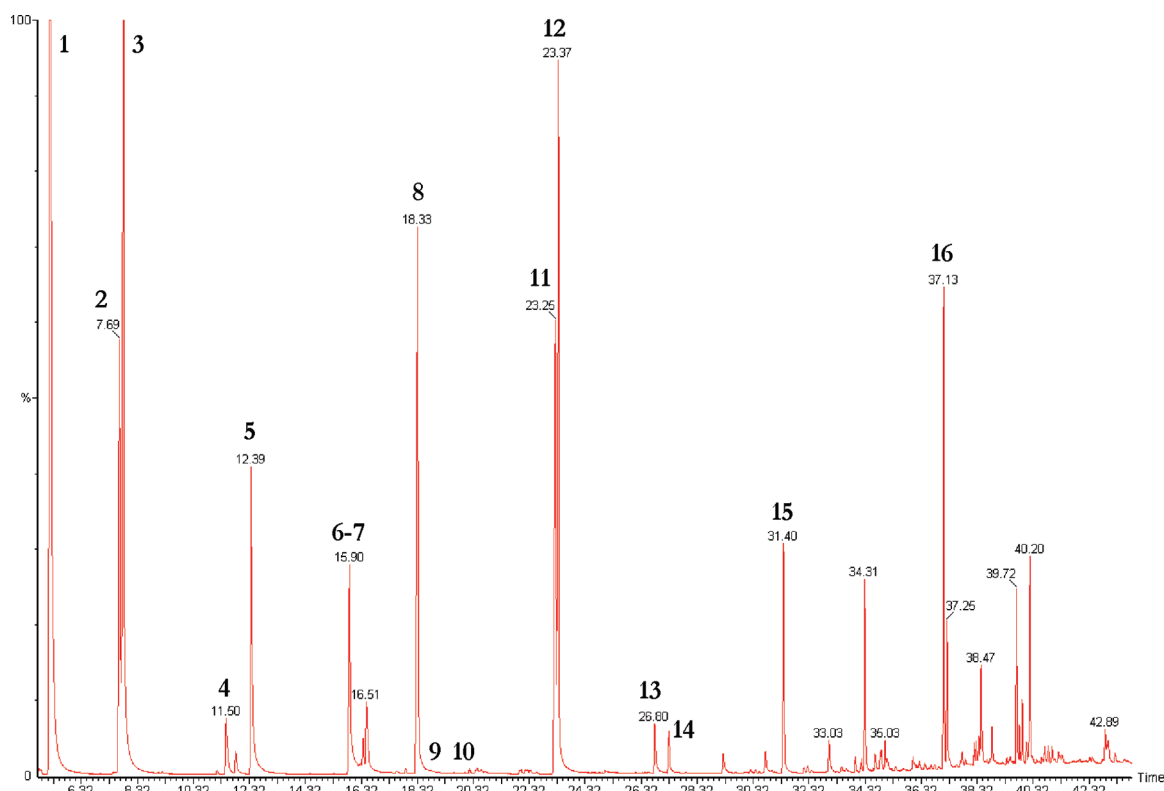


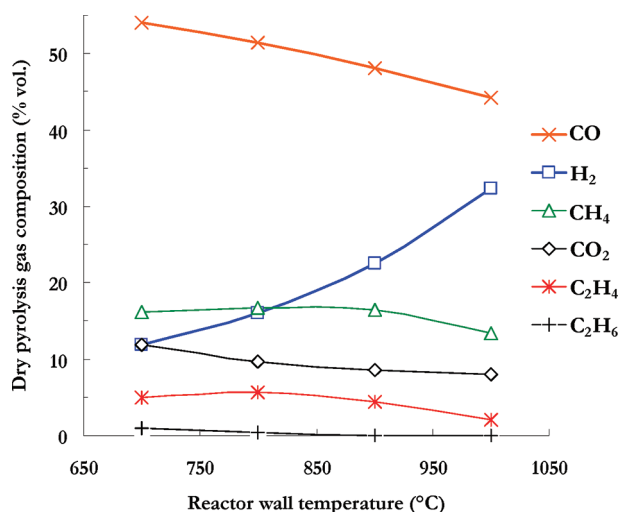
Figure 1. Total ionic current chromatogram of tar with internal standards. The pyrolysis reactor is set at 800 °C.

Table 3. Pyrolysis Conditions Investigated in This Work

reactor wall temperature (°C)	700	800	900	1000
mean gas residence time (s)	2.7	2.0	1.5	1.1
average wood chips heating rate (°C s <sup>-1</sup> ) (see the text for the definition)	20	25	33	42
mass balance of the experiments (%)	92.1	101.8	99.4	97.8

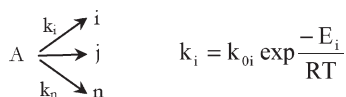
constant under the range of reactor temperatures in agreement with Authier.<sup>35</sup>

**3.2. Thermally Induced Interrelations between Permanent Gases.** To discuss permanent gas and tar evolution, a



**Figure 2.** Evolution of permanent gas composition (without N<sub>2</sub> carrier gas). See Table 3 for pyrolysis conditions.

simplified kinetic scheme with parallel reactions can be considered following the same approach as in refs 12, 14, and 15.



A precursor “A”, which could be either wood, cellulose, a primary (levoglucosan, methoxy-phenols, etc.) or secondary (toluene, etc.) tar, could form  $n$  compounds (the stoichiometric coefficients can be neglected for the following approach). Global rate equations for the conversion of  $n_A$  moles of compound A and the formation of  $n_i$  moles of compound  $i$  are assumed to be of the form<sup>12</sup>

$$\frac{dn_A}{dt} = -(\sum k_i)n_A \quad (1)$$

$$\frac{dn_i}{dt} = k_i n_A \quad (2)$$

where the rate constant,  $k_i$ , is assumed to follow an Arrhenius law, with  $k_{0i}$  and  $E_i$  being the pre-exponential factor and the activation energy, respectively, for the reaction producing a compound  $i$ .

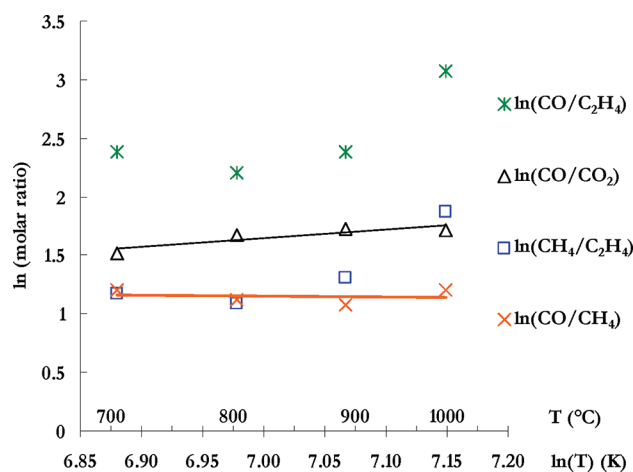
Assuming reactions within the gas-phase section of the reactor and a constant gas-phase temperature (as presented in ref 27), the solution of eq 2 gives<sup>12</sup>

$$n_i = \frac{k_i n_{A0}}{\sum k_i} \left( 1 - \exp \left( -\frac{\sum k_i}{t} \right) \right) \quad (3)$$

The logarithm of the molar ratio of products  $i$  and  $j$  leads to

$$\ln \left( \frac{n_i}{n_j} \right) = \ln \left( \frac{k_i}{k_j} \right) = \ln \left( \frac{k_{0i}}{k_{0j}} \right) - \frac{E_i - E_j}{RT} \quad (4)$$

The plot of  $\ln(n_i/n_j)$  as a function of  $1/T$  [or  $\ln(T)$ ] could give interesting information about the reactions of pyrolysis product formation. (i) If  $\ln(n_i/n_j) = B$  (with  $B$  being a constant), the rate constants of the formation of products  $i$  and  $j$  exhibit the same activation energy. (ii) If  $\ln(n_i/n_j) = B + C/T$  (with  $C$  being a constant), products  $i$  and  $j$  are formed in the range of



**Figure 3.** Logarithm of the molar ratio of some permanent gases on the dependence of the logarithm of the temperature.

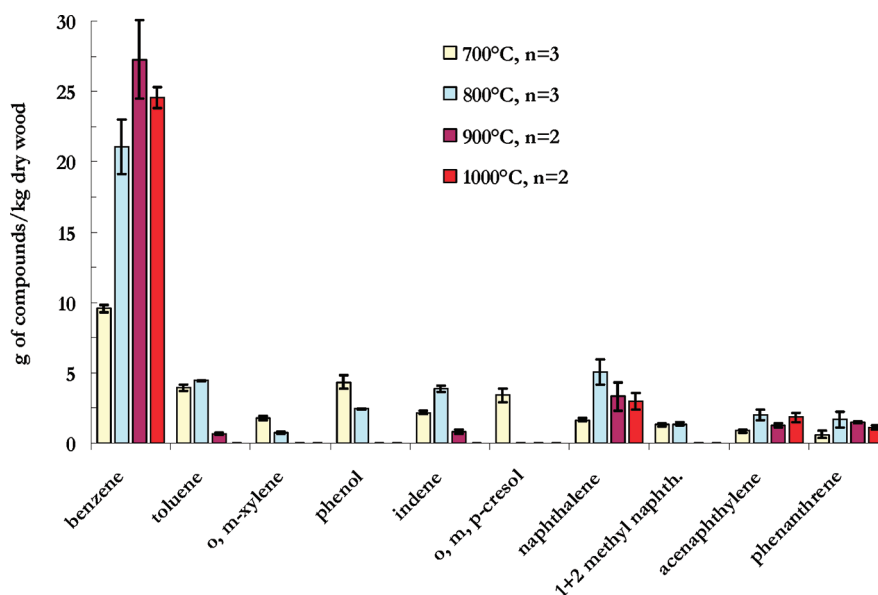
temperatures with a constant difference in the activation energies. (iii) If  $\ln(n_i/n_j) = f(1/T)$  exhibits a nonlinear evolution in the temperature range, a modification of the kinetic scheme takes place from parallel to consecutive (chain) reactions.

We are aware that true reactions are far more complex, involving many radicals and intermediate species.<sup>26,36</sup> This method is just a first simplified approach to assess the main reactions. It was previously used to study the evolutions of the logarithm of the ratio of yields of CO over C<sub>2</sub>H<sub>4</sub> (between 500 and 750 °C,<sup>12</sup> between 500 and 800 °C,<sup>14</sup> and between 377 and 727 °C<sup>15</sup>), CO over CH<sub>4</sub>,<sup>12,14</sup> CO over CO<sub>2</sub>,<sup>15</sup> and CH<sub>4</sub> over C<sub>2</sub>H<sub>4</sub><sup>12</sup> on the logarithm of the temperature<sup>14,15</sup> or the inverse of the temperature.<sup>12</sup> A linear evolution of the logarithm of (CO/CO<sub>2</sub>),<sup>15</sup> (CO/C<sub>2</sub>H<sub>4</sub>),<sup>14,15</sup> and (CO/CH<sub>4</sub>)<sup>14</sup> was observed and showed that these “compounds present comparable apparent kinetics (especially activation energy), which include primary and secondary reactions”<sup>15</sup> for the cited temperature conditions. These linear dependencies would be established for a large range of heating rates, from fast pyrolysis in a fluidized bed<sup>14</sup> to slow pyrolysis in a packed bed,<sup>15</sup> and for different types of biomasses.<sup>15</sup> The evolutions of these logarithm ratios have never been studied for reactor temperatures higher than 800 °C.

Few variations of the logarithm of (CO/CO<sub>2</sub>) and (CO/CH<sub>4</sub>) (see Figure 3) are observed for the range of studied thermal severities, in agreement with refs 14 and 15. A small increase in the CO/CO<sub>2</sub> ratio is achieved between 700 and 800 °C. CO is still produced between 700 and 800 °C from tar (precursor) conversion, whereas no CO<sub>2</sub> and H<sub>2</sub>O yield evolution can be observed between 700 and 1000 °C.<sup>27</sup> The water–gas shift reaction is thus not significant under our conditions (N<sub>2</sub> carrier gas). CO is probably mainly formed between 700 and 800 °C by the hydroxyl function of phenols decomposition to give cyclopentadienyl and tertiary tar.<sup>20,37</sup> Among other reactions, H<sub>2</sub>O is produced from the dehydration of cellulose<sup>38</sup> and CO<sub>2</sub> is produced from transglycosylation of active cellulose<sup>39</sup> at reactor temperatures lower than 700 °C. H<sub>2</sub>O and CO<sub>2</sub> formation mechanisms are thus beyond the scope of the present paper because these reactions occur at reactor temperatures lower than those investigated.

A modification of the evolution of  $\ln(\text{CO}/\text{C}_2\text{H}_4)$  and  $\ln(\text{CH}_4/\text{C}_2\text{H}_4)$  as a function of  $\ln(T)$  can be observed at 800 °C (Figure 3). When the temperature increases up to 800 °C, the





**Figure 4.** Evolution (average value and relative standard deviation for a number of experiments,  $n$ ) of aromatic tar yields as a function of the reactor temperature.

molar ratios of  $\text{CH}_4/\text{C}_2\text{H}_4$  and  $\text{CO}/\text{C}_2\text{H}_4$  increase because of  $\text{C}_2\text{H}_4$  conversion.

Only traces of primary tar were detected at 800 °C. The end of primary tar conversion at 800 °C leads to a modification in the kinetic scheme. Below 800 °C (under our residence time conditions), gas production rates are mainly controlled by primary tar conversion.<sup>12</sup> From 800 °C, gas yield evolution is then mainly controlled by secondary, alkyl tertiary products and  $\text{C}_2\text{H}_4$  conversions. Antal et al.<sup>40</sup> and Walawender et al.<sup>41</sup> reported that the conversion rates of the product gases exhibited a “break” at about 680 °C. This “break temperature” (800 °C in our case) depends upon reactor severity and more precisely the completion of primary tar conversion.

**3.3. Evolution of Aromatic Tar Composition.** The aim of this section is to describe the quantified tar evolution produced from wood chips pyrolysis with a constant reactor volume for thermal conversion as a function of the reactor temperature. A detailed kinetic study of tar conversion is beyond the scope of the present paper.

Figure 4 displays the evolution (average value and relative standard deviation for a number of experiments,  $n$ ) of the mass yields of aromatic tars as a function of the reactor temperature. Note that the reactor wall temperature evolution leads to a modification of primary (occurring inside the particles) and gas-phase secondary reactions (see Table 3).

The tar mass yields (Figure 4) were about 4 times higher than those mentioned by Brage et al.<sup>24</sup> This discrepancy could be explained by a lower heating rate and a higher tar cracking over char<sup>4,42,43</sup> in the fixed-bed reactor used by Brage et al.<sup>24</sup> To our knowledge, tar quantification in similar conditions to ours has not been reported in the literature.

The qualitative evolution of quantified aromatic tar between 700 and 900 °C is in good agreement with refs 23, 24, 44, and 45.

From 700 to 800 °C and for a mean gas residence time of 2 s, cresols are converted into toluene and phenol in agreement with ref 45 but with a higher conversion in our case because of a higher gas residence time. Phenol is mainly decomposed to benzene, indene, and naphthalene via cyclopentadienyl radicals

(not analyzed)<sup>20,46–48</sup> and then to higher unsubstituted aromatic compounds.<sup>49–52</sup> Phenol conversion is one of the key reactions for refractory tar and soot formation from biomass pyrolysis, in agreement with Fitzpatrick et al.<sup>50</sup> Other routes for PAH formation could also be possible at higher temperatures and/or under  $\text{O}_2$  oxidation conditions, for instance, from molecular-weight growth reactions of  $\text{C}_2$ – $\text{C}_5$  radicals.<sup>19,20,23</sup> Toluene is competitively formed from cresols and converted to benzene and methane by demethylation.<sup>25,45</sup>

Between 800 and 900 °C, phenol, indene, and toluene were almost completely converted into benzene and naphthalene. Considering the kinetic constant given by Jess,<sup>25</sup> the toluene conversion degree of 85% (between 800 and 900 °C) requires a gas residence time of about 4 s, which is higher than our gas residence time (1.5 s). This discrepancy is likely due to radical mechanisms, which could increase tar conversion in the real pyrolysis gas. For instance, the concentration of OH radicals could be increased in a real pyrolysis gas by a high  $\text{CO}_2$  concentration and, thus, could increase hydrocarbon conversion. We previously showed that OH radicals are mainly produced from  $\text{CO}_2$  and not from  $\text{H}_2\text{O}$  during the thermal conversion of a syngas (without  $\text{O}_2$ ).<sup>26</sup> A higher concentration of OH radicals (produced by a  $\text{CO}_2$  concentration higher in a real syngas than in ref 25) leads to a faster oxidation of hydrocarbons. Furthermore, we showed that the presence of  $\text{C}_2\text{H}_4$  (present in a real syngas but not in the model syngas by ref<sup>25</sup>) can involve a larger concentration of H radicals, which could favor the conversion of hydrocarbons.<sup>26</sup>

Methylnaphthalenes would be converted to naphthalene and acenaphthylene between 800 and 900 °C.<sup>45</sup>

Few conversions of unsubstituted aromatic compounds (benzene and PAH) were observed between 900 and 1000 °C, which is in agreement with refs 25 and 48. This point highlights that temperatures higher than 1000 °C with a gas residence time higher than 1 s are required to achieve a significant thermal conversion of these compounds.

These findings lead to the simplified scheme of tar conversion shown in Figure 5. The radical intermediate species are not

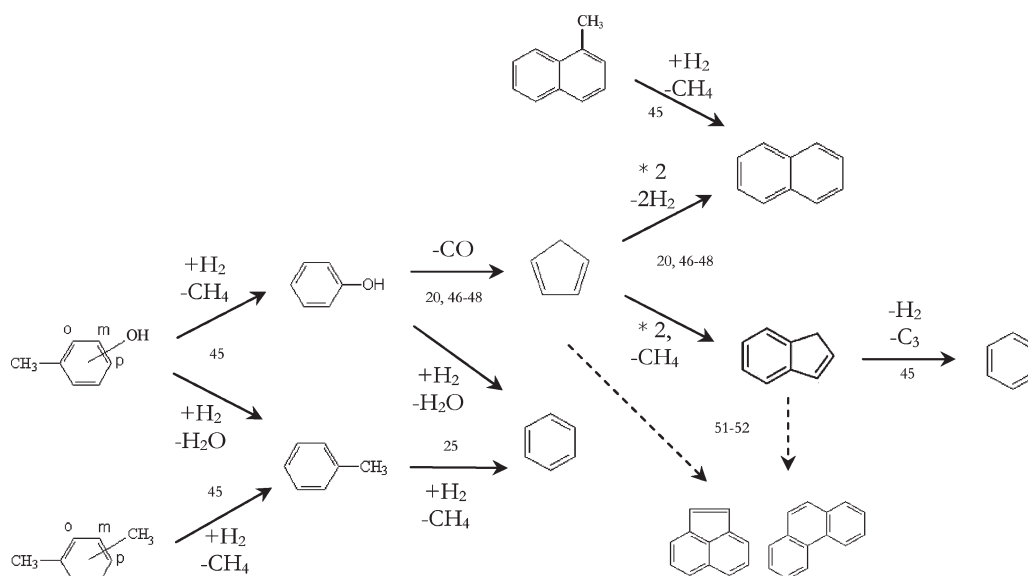


Figure 5. Simplified mechanism of homogeneous thermal conversion of main aromatic tar (secondary/tertiary reactions) in a biomass pyrolysis gas.

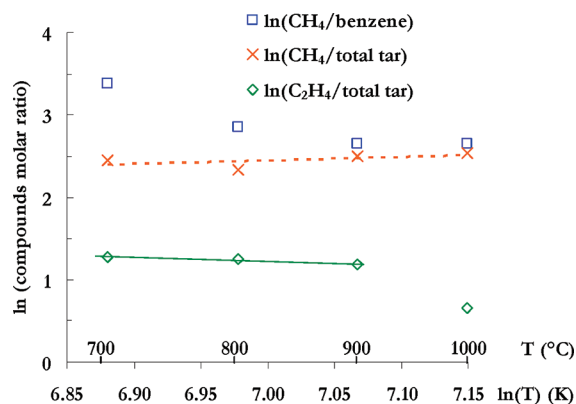


Figure 6. Logarithm of the molar ratio of some permanent gases and quantified tar on the dependence of the logarithm of the reactor wall temperature.

described. The mechanisms of PAH formation, such as acenaphthylene and phenanthrene, in biomass pyrolysis gas are still not clearly known (to the authors' knowledge). PAHs are probably formed from cyclopentadienyl and indenyl radicals.<sup>51,52</sup> Although detailed mechanisms of tar evolution from biomass thermal decomposition are under development,<sup>26,36</sup> the detailed mechanisms of aromatic tar formation and conversion are still not clearly elucidated.

**3.4. Thermally Induced Interrelations between Permanent Gases and Tar.** Brage et al.<sup>24</sup> suggested the use of some molar ratio to estimate online the tar content in product gases for a specific reactor (fixed bed). The relation between naphthalene/indene and total tar is not linear (as found by Brage et al.<sup>24</sup>) in our experimental conditions probably because of different gas thermal severity and "total tar" definition.

CH<sub>4</sub> is produced from methylated tar conversion (Figure 5) and could be an indicator of tar maturation, which is easier to be quantified than tar. Moreover, the evolution of C<sub>2</sub> compounds was correlated with the evolution of tar maturation.<sup>24</sup> Figure 6 presents the logarithm of the molar ratios between CH<sub>4</sub> and

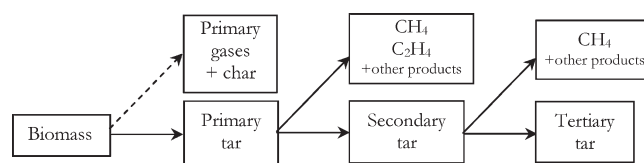


Figure 7. Simplified scheme of CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, and tar formation (adapted from ref 6).

benzene, CH<sub>4</sub> and total quantified tars, and C<sub>2</sub>H<sub>4</sub> and total quantified tars.

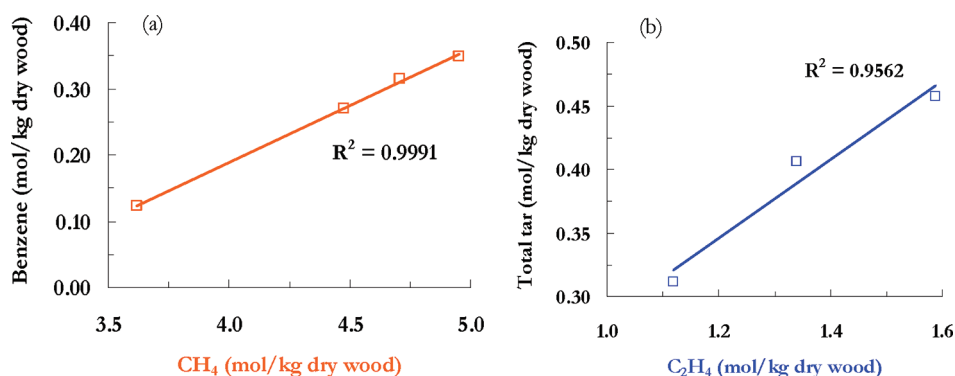
Naphthalene, acenaphthylene, and phenanthrene are assumed to be good indicators of higher PAHs.

The evolution observed in Figure 6 can be explained considering the simplified scheme displayed in Figure 7.

As proposed by Milne et al.,<sup>2</sup> "secondary" CH<sub>4</sub> and "tertiary" CH<sub>4</sub> (Figure 7) can be formed by (1) primary tar conversion and (2) methylated secondary tar conversion (detailed in Figure 5), respectively.

The logarithm of CH<sub>4</sub>/benzene decreases down to 900 °C and becomes constant beyond 900 °C. It shows that CH<sub>4</sub> formation is favored versus benzene formation at 700 and 800 °C. CH<sub>4</sub> is formed from precursors (tar with a methyl function, such as xylenes, cresols, methyl-naphthalenes, etc.), which can lead to (secondary) CH<sub>4</sub> and to other tar than benzene, such as phenol, toluene, etc. (see Figure 5). Considering secondary and tertiary tar ("total tar"), the logarithm of the CH<sub>4</sub> ratio versus total tar is almost constant for our range of thermal severity (Figure 6). It shows that "no competition is observed"<sup>12</sup> between CH<sub>4</sub> and (quantified) aromatic tar formation. These compounds present comparable activation energies of the formation from the same type of precursors (aromatic compounds with methyl or methoxyl functions). In our range of thermal conditions (700–1000 °C), CH<sub>4</sub> formation is mainly controlled by demethylation of aromatic tar, such as toluene, xylene, cresols, etc. (Figure 5). More, little CH<sub>4</sub> and tertiary tar conversions are observed below 1000 °C, in agreement with refs 25 and 26.

The logarithm of C<sub>2</sub>H<sub>4</sub>/total tar is linear between 700 and 900 °C, but from 900 °C and beyond, the kinetic scheme is



**Figure 8.** Linear relations between (a) benzene and CH<sub>4</sub> production (from 700 to 1000 °C) and (b) total quantified tar and C<sub>2</sub>H<sub>4</sub> (from 700 to 900 °C).

modified mainly by C<sub>2</sub>H<sub>4</sub> conversion. This linear relation cannot be explained because the pathways of C<sub>2</sub>H<sub>4</sub> formation in a pyrolysis gas are not well-understood (to our knowledge). The lack of validated detailed kinetic mechanisms does not allow for the determination of the main elementary reactions controlling CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> formation and conversion, as presented in ref 26.

Moreover, the yields of benzene and CH<sub>4</sub> production are clearly correlated in our conditions. A linear relation between the molar production of benzene and CH<sub>4</sub> (700–1000 °C) and a close to linear relation between the total of quantified tars and C<sub>2</sub>H<sub>4</sub> (700–900 °C) were found with a good regression factor, especially for CH<sub>4</sub> (Figure 8).

As a consequence, CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> could be used as indicators of the investigated secondary and tertiary tar production for a reactor under the same range of investigated thermal severity. The linear relations presented in Figure 8 are independent of the reactor temperature. Benzene or “total tar” productions could thus be estimated by a direct online CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> analysis, for instance, by FTIR analysis, without quantifying the thermal severity, which is difficult to estimate on pilot plants because of gas residence time and temperature distributions.

These reactor-specific relations should be checked for other pyrolysis reactors. It could depend upon the biomass initial composition (as methyl function/aromatic ring ratio, mineral catalytic effect, etc.) and the reactor thermal conditions.

Catalysts and O<sub>2</sub> modify the kinetic scheme. These relationships would probably not be suitable for autothermal fluidized-bed gasifiers, in which biomass pyrolysis products are partially oxidized by O<sub>2</sub>.

The determined relations could be suitable for pyrolysis reactors or maybe for dual-fluidized-bed gasifiers. It is known that biomass pyrolysis (including primary and secondary reactions) and water–gas shift are the main reactions occurring in a dual-fluidized-bed reactor<sup>35,53</sup> and that H<sub>2</sub>O has very few chemical effects on secondary and tertiary tar,<sup>25,54</sup> C<sub>2</sub>H<sub>4</sub>, and CH<sub>4</sub> thermal conversion.<sup>26,54</sup> The steam/biomass ratio has consequently very few chemical effects on the CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, and tar yields (in kg of products/kg of biomass).<sup>54</sup> Indeed, it was previously shown that the CH<sub>4</sub> and tar yields obtained under our pyrolysis conditions are close to those reported for the Battelle dual-fluidized-bed gasifier with little bed catalytic effect.<sup>30</sup> The suitability of these relations for the dual-fluidized-bed reactor would thus mainly depend upon the catalytic selectivity of the bed material.

#### 4. CONCLUSION

The evolutions of gas and tar compositions, produced from wood pyrolysis in a tubular reactor, were investigated as a

function of the reactor temperature. Tar (benzene, toluene, *o*- and *m*-xylenes, phenol, indene, *o*-, *m*-, and *p*-cresols, naphthalene, 1- and 2-methylnaphthalenes, acenaphthylene, and phenanthrene) were quantified by gas chromatography/mass spectrometry (GC/MS) analysis and deuterated internal standards. The main mechanisms of gas and tar production under the investigated range of thermal severity are assessed using a simplified method [evolution of the logarithm of the compound ratio versus ln(*T*)]. CH<sub>4</sub> production is mainly controlled by aromatic tar demethylation. A simplified scheme of tar conversion is presented.

A linear relation between benzene and CH<sub>4</sub> yields (between 700 and 1000 °C) and a close to linear relation between the “total tar” and C<sub>2</sub>H<sub>4</sub> yields (between 700 and 900 °C) were established. Consequently, CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> could be used as indicators of tar production and speciation in a gasification reactor, under the range of investigated thermal severity. Benzene or the investigated secondary and tertiary tar productions could be estimated by a direct online CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> analysis, for instance, by FTIR analysis. The suitability of these relations, depending upon the thermal severity of reactors, should be checked on other pyrolysis reactors and dual-fluidized-bed gasifiers. The validation of detailed kinetic mechanisms, such as the one developed recently by Ranzi et al.,<sup>36</sup> and flow rate analysis, using the same methodology as in ref 26, should bring considerable insight into the determination of the main elementary reactions controlling evolutions of tar and gas compositions and the best indicators of tar production. Such a methodological approach was previously developed to study, for instance, the formation of aromatic compounds in methane flames.<sup>55</sup>

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