Kinetic Modeling of Non-Catalytic Partial Oxidation of Nascent Volatiles Derived from Fast Pyrolysis of Woody Biomass with Detailed Chemistry^{1†}

**Narumon Thimthong^a, Srinivas Appari^b, Ryota Tanaka^b, Keita Iwanaga^a, Shinji
Kudo^b, Jun-ichiro Hayashi^{a,b,c}, Tetsuya Shoji^d, and Koyo Norinaga^{a,b,*}**

^a Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, Kasuga 816-8580, Japan

^b Institute for Materials Chemistry and Engineering, Kyushu University, Kasuga 816-8580, Japan

^c Research and Education Center of Carbon Resources, Kyushu University, Kasuga, 816-8580, Japan

^d Energy Engineering Research Laboratory, Central Research Institute of Electric Power Industry, Yokosuka, 240-0196, Japan

*Corresponding author: Tel.: +81 92 583 7794; fax: +81 92 583 7793

E-mail address: norinaga@cm.kyushu-u.ac.jp

Abstract

The gas-phase partial oxidation (POx) of nascent volatiles (NV) derived from the fast pyrolysis of cedar sawdust at 700 and 800°C was studied both numerically and experimentally. A detailed chemical kinetic model (DCKM) was applied to simulate the POx in a two-stage reactor: the first stage was designed for fast biomass pyrolysis and the second effected the POx of the NV. Analytical pyrolysis experiments were also conducted to approximate the molecular composition of the NV, which is required input for computations using DCKM. The DCKM was modified by an empirical kinetic model for the decomposition of an ill-defined portion of the NV. The kinetic model coupled with a plug-flow reactor model reproduced the observed trends in the product yields with respect

^{1†}Abbreviations: DCKM, detailed chemical kinetic model; NV, nascent volatiles; O/C, oxygen-to-fuel ratio; POx, partial oxidation; TSR, two-stage reactor; UTSR, U-shaped two-stage tubular reactor.

to both temperature and oxygen-to-fuel ratio, for not only the major products, but also minor products such as aromatic hydrocarbons which are typically found in the refractory post-gasification tar.

Keywords

Biomass gasification, Tar, Partial oxidation, Reaction Kinetics, Mechanism

1. Introduction

Biomass is a promising source of renewable energy, and effective and efficient technologies are needed to implement its practical application. As a feedstock comprising both organic and inorganic elements, biomass exhibits a variety of morphologies and physical characteristics. The thermal conversion of biomass through direct combustion suffers from problems of corrosion/erosion and the accumulation of inorganic solids caused by the alkali-containing species in the biomass. Biomass gasification by thermal decomposition followed by the partial combustion of the producer gas is a viable option to not only remove the problems encountered in direct combustion but also to provide cleaner fuel gases suitable for use in gas turbines and engines [1–10]. Biomass gasification products mainly consist of syngas, light hydrocarbons, and trace amounts of H₂S, HCl, NH₃, tar, and solid particles [10,11].

Among the products obtained from biomass gasification, tar is considered to be problematic, as even small amounts can significantly damage downstream equipment and deteriorate gasification efficiency. Therefore, tar control or removal measures are essential for the successful implementation of gasification technology, in terms of producing clean

1 fuel gas as well as easy control and continuous operation [12,13]. Several methods have
2 been reported [14] to remove tar both physically [15,16] and chemically [4,16–21]. Non-
3 catalytic partial oxidation for vapor-phase reforming is a promising technique that can
4 reduce the amount of tar [4,21–24]. Su et al. [21], who found that oxygen significantly
5 impacts the conversion of tar and non-condensable gases, developed a flow reactor to
6 predict tar destruction under partial oxidation conditions. Indeed, Hosokai et al.
7 investigated the gas-phase partial oxidation of nascent volatiles from the rapid pyrolysis of
8 cedar sawdust in two-stage reactor and claimed that the amount of O₂ and the temperature
9 were critical parameters for controlling tar concentrations [4].

10 A deeper understanding of tar formation and consumption behaviors during the vapor phase
11 reactions of biomass nascent volatiles—which consists of hundreds to tens of thousands of
12 chemical reactions—is a key approach for developing the technology to reduce tars. A
13 kinetic model would be useful for understanding those reactions, but limited studies have
14 been reported. Traditional lumping models have been widely used in studies of biomass
15 thermal chemical conversion. However, in the lumping approach, tars are grouped as one or
16 more different lumps and kinetic parameters are determined by numerical fitting [25–29].
17 Therefore, this practical but simplified model is limited with respect to predicting the
18 product gas composition at the molecular level.

19 Detailed chemical kinetic models (DCKM) which comprise thousands of elementary
20 reactions of stable species as well as intermediates (including radical species) for vapor
21 phase reaction of biomass related material have been developed to overcome the
22 disadvantages of the lumping approach [30–33]. With a DCKM, the concentration of each

individual molecule in the gas phase can be directly used as input information without lumping chemical species. Also, the kinetic parameters (frequency factor and activation energy) of individual elementary reactions are provided based on experimental studies and theory. Norinaga et al. developed a DCKM that incorporates more than 8000 elementary reaction steps and more than 500 chemical species which has the potential to predict the vapor-phase cracking of nascent volatiles generated from the fast pyrolysis of cellulose [32,33].

With regard to the kinetic modelling of partial oxidation, no studies have been reported that analyze the partial oxidation of volatiles derived from the primary pyrolysis of biomass by using the DCKM. This is the first attempt to use the DCKM to predict the partial oxidation of nascent volatiles derived from woody biomass (cedar sawdust) fast pyrolysis. The DCKM [32] is used to describe the volatiles' partial oxidation. The initial molecular compositions for DCKM were derived experimentally from the primary pyrolysis of cedar sawdust. There are several missing products which are difficult to identify experimentally that are considered in the simulation by introducing global reactions. The model was critically evaluated by comparing the predicted and experimental results from the secondary vapor-phase partial oxidation of volatile components from cedar sawdust fast pyrolysis [4].

2. Methods

2.1. Experimental

2.1.1. Biomass sample. Japanese cedar sawdust with particle sizes ranging from 350 to 590 μm was dried and then used as the biomass feedstock. Carbon and hydrogen mass fractions were 50.2 and 6.3% on a dry sample basis, respectively.

2.1.2. Gas phase partial oxidation of nascent volatiles. The reported experimental data for the partial oxidation (POx) of nascent volatiles (NV) [4] were used for the critical evaluation of the kinetic model. A tubular and vertical two-stage reactor (TSR) was employed; the first and second stages were designed for fast pyrolysis of the biomass sample and the thermal cracking/POx of the NV, respectively. The sample was fed continuously into the first stage of the TSR at a rate of 0.09–0.21 g/min for 15 min. The temperature of the first stage was held at 700 or 800°C, at which the sawdust was rapidly pyrolyzed to char and volatiles. The char was retained on the quartz frit at the reactor bottom, while the volatiles were swept through the frit under a forced flow of primary nitrogen. The volatiles were then introduced into the second stage of the tubular reactor after dilution with secondary nitrogen or an oxygen/nitrogen mixture with a flow rate of either 1.6 L STP/min and 700°C or 1.4 L STP/min and 800°C. Both the flow rates were fixed so that the residence time of the volatiles in the isothermal zone of the second stage was 3.0 s. The O/C ratio was used as the parameter to describe the composition of the mixture entering the second stage of the TSR; it is defined as the ratio of the number of oxygen atoms in the supplied O_2 gas to the total number of carbon atoms in the NV, and varies between 0 and 1.1. The temperature of the second stage of the tubular reactor was the same as that of the first. All the products passing through the reactor outlet were recovered

by a mist filter, two cold traps, and a gas bag, and analyzed off-line. Detailed descriptions of the POx experimental set-up as well as the product analysis are given elsewhere [4].

2.1.3. Pyrolysis gas chromatography. Analytical pyrolysis experiments were conducted with an originally designed setup [32] to approximate the molecular composition of the NV, and to monitor the secondary gas-phase cracking of the NV. A U-shaped two-stage tubular reactor (UTSR), divided into two zones by a quartz wool filter (one side for the fast pyrolysis of cedar sawdust and the other for the cracking of the nascent volatiles), was used as a pyrolyzer. Approximately 1.0 mg of the sample was wrapped with a sheet of stainless wire mesh (SUS316, 15 mm $\times$ 15 mm) with a mesh opening of 45 μ m and dried under vacuum at room temperature overnight. The wrapped sample was weighed immediately after drying to determine the exact dry mass of the sample, which was subsequently fixed at the upper part of the UTSR. The UTSR was connected to the streamline of a gas chromatograph (GC). After stabilizing the heated section of the UTSR at the desired temperature (700 or 800°C), the sample was dropped into the bottom of the first zone where it underwent fast pyrolysis. The nascent volatiles formed by pyrolysis were swept into the second zone. The residence times of the volatiles in the second zone were varied from 0.2 to 4.1 s by adjusting the volume of the second reactor. The detailed experimental procedure and product analysis are given elsewhere [32].

2.2. Modeling approach

2.2.1. Plug-flow reactor model for TSR. The POx of the NV in the second stage of the TSR (length = 0.7 m) shown in Fig. 1 was numerically simulated with the PLUG code in the DETCHEM program package (DETCHEM^{PLUG}) [34]. DETCHEM^{PLUG} is designed for

the modelling of a non-dispersive one-dimensional flow of a chemically reacting ideal gas mixture under steady-state conditions. The reaction mechanism and boundary conditions (such as the composition and velocity of the feed gas at the inlet of the second stage, the pressure, and the temperature profile along the flow direction) are required for the computations and are summarized in Table 1. The computations were performed for temperatures of 700 and 800°C, and at O/C = 0 as well as O/C from 0.1 to 1.1 with constant intervals of 0.2. A detailed description of the plug-flow computations can also be found elsewhere [35].

2.2.2. Batch reactor model for UTSR. The vapor-phase cracking of the NV in the UTSR was numerically simulated with the BATCH code in the DETCHEM program package (DETCHEM^{BATCH}) [34]. DETCHEM^{BATCH} was designed for the computational analysis of time-dependent homogeneous reaction systems. Calculations were performed under isobaric and isothermal conditions. The composition of the NV, temperature, and pressure are the boundary conditions required for the computations and are also summarized in Table 1. A detailed description of the batch reactor computations can be found elsewhere [34].

2.2.3. Reaction mechanism. A detailed chemical kinetic model (DCKM) for predicting biomass secondary gas-phase reactions was developed. The reaction mechanisms and thermodynamic data are provided as Supplemental Information. The DCKM consists of 548 species and 8159 elementary reaction steps, and the model has been critically evaluated for the secondary vapor-phase reactions of cellulose [32,33] and coffee extraction residues [31]. A global reaction was added to the DCKM to account for the decomposition of the

gas-chromatographically inseparable components included in the NV. The rate constants of the global reactions at both 700 and 800°C were estimated empirically.

3. Results and discussion

3.1. Approximation of the molecular composition of NV derived from cedar sawdust fast pyrolysis

The molecular composition of the NV is one of the required inputs for conducting numerical simulations with the DCKM. Thus, analytical pyrolysis experiments using a UTSR that was directly connected to GC instruments were performed to provide experimental data on the product distributions in the fast pyrolysis of the biomass sample.

Table 2 lists the yields of the products at pyrolysis temperatures of 700 and 800°C and a vapor phase residence time of 0.2 s. Exhaustive analysis with three different GC instrumental configurations enabled the identification and quantification of 52 pyrolysates. The total mass fractional amounts of the identified products including char accounted for 77 and 89% of the sample fed at 700 and 800°C, respectively; the lost 23 and 11% mass fractions are unexplained at this time. The missing materials likely correspond to products which condense at the inner wall of the line between the UTSR and the GC and/or are not separated chromatographically due to their high molecular mass. Based on the elemental balances among the feed and products, the C:H:O atomic ratios were estimated to be 2:3:1 and 6:5:1 for the missing products at 700 and 800°C, respectively.

3.2. Global reactions for reactions of missing components included in NV

1 The DCKM employed here showed an acceptably fine capability for predicting the
2 concentration profiles of major products such as hydrogen, carbon monoxide, carbon
3 dioxide, and methane in the vapor-phase cracking of cellulose at 700 and 800°C [32]. The
4 molecular composition of the volatiles derived from the fast pyrolysis of cellulose fine
5 particles could be almost perfectly defined experimentally, since most of the products were
6 gas-chromatographically separable. This suggests that, as long as the molecular
7 composition of the pyrolysis products are properly defined, the DCKM can provide fair
8 predictions of the major product formation profiles in the subsequent vapor-phase reactions.
9 Unfortunately, however, some of the products included in the NV could not be identified
10 and were missing.

11 To understand the significance of the missing products on the product distribution in the
12 subsequent vapor-phase reactions, further analytical pyrolysis experiments were performed
13 that varied the vapor-phase residence time of the NV. The pyrolysis experiments were
14 numerically simulated by the DCKM with the batch-reactor model. The solid lines in Fig. 2
15 shows the computation results with neglecting the reactions of the missing products ($K = 0$).
16 When the missing products were neglected by substitution with an inert gas such as
17 nitrogen in the composition of the NV, the computational results for hydrogen, carbon
18 monoxide, and methane were under-predicted compared with the UTSR experiment,
19 whereas carbon dioxide was accurately predicted. The composition of the carbon dioxide is
20 more or less constant at entire range of the residence time as observed from the pyrolysis
21 experiments with the USTR. Due to this reason, carbon dioxide is not considered in the
22 global reaction, in fact, this composition is well predicted alone with the DCKM.

The under-predictions found for the yields of hydrogen, carbon monoxide, and methane likely originate from the lack of information about the reactions of the missing products included in the NV. The under-predictions of the computational yields versus the experimental ones could potentially be minimized by assuming in the simulation that the missing products undergo chemical reactions.

To account for the formation of hydrogen, carbon monoxide, and methane, the global reaction for the missing products at 700°C was formulated as;

The solid lines in Fig. 2 ($K = 0.3$) are computation results obtained by the DCKM combined with the global reaction. The kinetic constant k_{G700} of the global reaction was optimized to be 0.3 s^{-1} , which minimized the gap between the computational and experimental results.

Without a global reaction at 800°C, the yields of hydrogen, carbon monoxide, and methane were under-predicted. Similarly, the global reaction for the missing products at 800°C was formulated as

where the kinetic constant was optimized as $k_{G800} = 0.8 \text{ s}^{-1}$ (Fig. 3). The global reaction along with the DCKM at 800°C affected the predictions of major products composition slightly. This may be due to the small amount of missing products (11%) in the NV at this temperature.

3.3. Numerical simulation of the POx of the NV in the second stage of the TSR

A plug-flow reactor model coupled with both the DCKM and the global reaction was used to simulate the POx of the NV derived from cedar sawdust at 700 and 800°C. The distribution of the species concentrations along the axial length of the second stage of the TSR from the plug-flow simulation is shown in Fig. 4 (O/C ratio 0.5 and 700°C). Oxygen is completely consumed in the initial part of the reactor (~0.015 m), and major changes are observed between the reactor inlet and the next 0.1 m length of the reactor. The product distributions along the reactor reveal increasing yields of carbon monoxide, carbon dioxide, and water. Decreases in hydrogen, methane, and C₂–C₄ hydrocarbon yields along the TSR length are observed. Also, the yields of mono-aromatic compounds decrease in the presence of oxygen, whereas the yields for di-aromatic compounds increase slowly along the length of the reactor.

3.4. Critical evaluation of the kinetic model

The numerical results of the species concentrations at the reactor exit as a function of O/C ratio were compared with the experimentally obtained results from the gas-phase POx of NV in the TSR. Figure 5 shows these comparisons for partial oxidation at 700°C. The DCKM well predicts the vapor-phase POx of the NV at 700°C under varying O/C conditions. When the O/C ratio increases, hydrogen (Fig. 5 a) and methane (Fig. 5 d) decrease; these predictions are well correlated with the experimental data at different O/C ratios. The decreasing trend in hydrogen yield may be explained primarily by the abundant oxygen that is available for hydrogen oxidation. An increasing O/C ratio also affects the methane partial oxidation. The methane steam reforming reaction is enhanced by the formation of steam from hydrogen oxidation, which results in a decreased methane yield

1 with increasing O/C ratio. The model also well predicts the experimental results for carbon
2 monoxide (Fig. 5 b) and carbon dioxide (Fig. 5 c), which increase with increasing O/C ratio.
3 The increasing trend in carbon dioxide yield is due to carbon monoxide oxidation and
4 perhaps also from the water gas shift reaction. The carbon monoxide yield increases due to
5 partial oxidation and the steam reforming reactions of methane and light hydrocarbons.

6 In addition to the major products, the DCKM results also capture the experimentally
7 observed trends for the minor gas-phase hydrocarbons and aromatics. Although the partial
8 oxidation products contain very low yields of C₂–C₄ hydrocarbons and aromatic
9 compounds (< 3 mol-C/100-mol-C-fuel), these can nevertheless be used to validate the
10 DCKM in this work. The amounts of minor products such as ethylene, ethane,
11 acetaldehyde, propylene, propane, C₄ hydrocarbons, benzene, and naphthalene could be
12 predicted and validated by the experimental data. Discrepancies were observed between the
13 simulations and experiments for ethylene (Fig 6 a), which is somewhat overestimated at
14 low O/C ratios, and ethane (Fig 6 b), which is slightly underestimated at high O/C ratios.
15 The decreasing trends of ethylene and ethane yields with increasing O/C ratio are mainly
16 due to partial oxidation. The acetaldehyde yields are given in Fig. 6 c. Acetaldehyde is
17 consumed with increasing O/C ratio, and good agreement is observed with the experimental
18 measurements. Fair agreement is observed for propylene (Fig. 6 d) and propane (Fig. 7 a);
19 although there are small gaps between the predictions and experimental measurements, the
20 results show that propane and propylene are mainly consumed by oxygen atom addition
21 reactions. The amounts of C₄ are also validated by the experimental measurements (Fig 7 b),
22 and the predictions show fair reproduction of the experimental trends.

1 The yields of aromatic products, which are constituents of tar, are presented in Fig. 7.
2 Calculated benzene (Fig. 7 c) yields at different O/C ratios reproduce the experimental
3 results, although they were slightly over-predicted at lower O/C ratios and under-predicted
4 at higher O/C ratios. These contradictory results might be related to the complexity of
5 benzene formation, which involves many reactions [32]. The model predictions for
6 naphthalene perfectly capture the experimental profiles (Fig. 7 d), suggesting that the major
7 reactions leading to naphthalene are incorporated into the current kinetic model and that
8 their rate parameters are reasonable. Overall, the numerical simulations with DCKM
9 indicate decreasing yields of aromatic compounds with increasing O/C ratios, and reveal
10 that these tar compounds can be effectively reduced in the partial oxidation process.

11 The predictions of major and minor product yields suggested that the DCKM is fairly
12 capable to predict the experimental trends. The major and minor product yields were under-
13 predicted when only the DCKM was used. The model predictions are satisfactory when
14 adding the global reaction along with the DCKM. This may be due to the missing products
15 (high molecular mass compounds) were decomposed into the major products during the NV
16 reforming.

17 Comparisons between the model predictions and experimental results from the gas-phase
18 POx of NV in the TSR at 800°C are presented in Fig. 8. The model can also reproduce the
19 experimentally observed trends well showing that the DCKM can capture the
20 experimentally observed trends for the effect of not only oxygen to fuel ratio but also the
21 temperature on the product distributions in the POx of the NV from cedar sawdust. In this
22 study, the DCKM predictive capabilities are exhaustively studied in regard with the both

major and minor products. Fair agreements were obtained between the predictions and the experimental concentration profiles of the major products, as well as minor products such as benzene and naphthalene, which are important precursors/constituents of tar. This level of capabilities cannot be expected from the traditional lumping approach and strongly enhances the significance of this approach in modeling complex biomass thermo-chemistries.

4. Conclusions

The non-catalytic partial oxidation of gas mixtures from the fast pyrolysis of cedar sawdust was simulated with a DCKM. A global reaction was combined with the DCKM to represent the cracking of experimentally ill-defined constituents in the NV. The NV were approximated by 52 chemical species. The resultant kinetic model, with 8159 reactions and 548 species, was further coupled with a plug-flow reactor model to reproduce the two-stage pyrolysis experiments. The predictions agreed well with the experimental concentration profiles of the major products, as well as minor products such as benzene and naphthalene, which are important constituents of tar. With almost no adjustable parameters in the kinetic model, such agreement are derived at molecular level.

Acknowledgements

This work was supported in part by the Network Joint Research Center for Materials and Devices and was funded by the MOST-JST, Strategic International Collaborative Research Program SICORP. N.T. is grateful for support in the form of a Japanese Government Scholarship (Monbukagakusho scholarship).

1 **References**

- 2 [1] M.D. Brown, E.G. Baker, L.K. Mudge, Environmental design considerations for
3 thermochemical biomass energy, *Biomass*. 11 (1986) 255–270.
- 4 [2] D.C. Dayton, B.M. Jenkins, S.Q. Turn, R.R. Bakker, R.B. Williams, D. Belle-Oudry,
5 et al., Release of Inorganic Constituents from Leached Biomass during Thermal
6 Conversion, *Energy & Fuels*. 13 (1999) 860–870.
- 7 [3] I. De Bari, D. Barisano, M. Cardinale, D. Matera, F. Nanna, D. Viggiano, Air
8 Gasification of Biomass in a Downdraft Fixed Bed: □ A Comparative Study of the
9 Inorganic and Organic Products Distribution, *Energy & Fuels*. 14 (2000) 889–898.
- 10 [4] S. Hosokai, K. Kishimoto, K. Norinaga, C.-Z. Li, J. Hayashi, Characteristics of Gas-
11 Phase Partial Oxidation of Nascent Tar from the Rapid Pyrolysis of Cedar Sawdust
12 at 700–800 °C, *Energy & Fuels*. 24 (2010) 2900–2909.
- 13 [5] A.A. Khan, W. de Jong, P.J. Jansens, H. Spliethoff, Biomass combustion in fluidized
14 bed boilers: Potential problems and remedies, *Fuel Process. Technol.* 90 (2009) 21–
15 50.
- 16 [6] X.T. Li, J.R. Grace, C.J. Lim, a. P. Watkinson, H.P. Chen, J.R. Kim, Biomass
17 gasification in a circulating fluidized bed, *Biomass and Bioenergy*. 26 (2004) 171–
18 193.
- 19 [7] T. Okuno, N. Sonoyama, J. Hayashi, C.-Z. Li, C. Sathe, T. Chiba, Primary Release
20 of Alkali and Alkaline Earth Metallic Species during the Pyrolysis of Pulverized
21 Biomass, *Energy & Fuels*. 19 (2005) 2164–2171.
- 22 [8] K. Salo, W. Mojtahedi, Fate of alkali and trace metals in biomass gasification,
23 *Biomass and Bioenergy*. 15 (1998) 263–267.
- 24 [9] X. Wei, U. Schnell, K.R.G. Hein, Behaviour of gaseous chlorine and alkali metals
25 during biomass thermal utilisation, *Fuel*. 84 (2005) 841–848.
- 26 [10] H. Knoef, ed., *Handbook Biomass Gasification*. 2005.
- 27 [11] M. Asadullah, Biomass gasification gas cleaning for downstream applications: A
28 comparative critical review, *Renew. Sustain. Energy Rev.* 40 (2014) 118–132.
- 29 [12] C. Li, K. Suzuki, Tar property, analysis, reforming mechanism and model for
30 biomass gasification-An overview, *Renew. Sustain. Energy Rev.* 13 (2009) 594–604.

- 1 [13] P. McKendry, Energy production from biomass (part 3): gasification technologies,
2 Bioresour. Technol. 83 (2002) 55–63.
- 3 [14] J. Han, H. Kim, The reduction and control technology of tar during biomass
4 gasification/pyrolysis: An overview, Renew. Sustain. Energy Rev. 12 (2008) 397–
5 416.
- 6 [15] A. Paethanom, S. Nakahara, M. Kobayashi, P. Prawisudha, K. Yoshikawa,
7 Performance of tar removal by absorption and adsorption for biomass gasification,
8 Fuel Process. Technol. 104 (2012) 144–154.
- 9 [16] Y. Wang, T. Namioka, K. Yoshikawa, Effects of the reforming reagents and fuel
10 species on tar reforming reaction., Bioresour. Technol. 100 (2009) 6610–4.
- 11 [17] S. Schmidt, S. Giesa, A. Drochner, H. Vogel, Catalytic tar removal from bio
12 syngas—Catalyst development and kinetic studies, Catal. Today. 175 (2011) 442–
13 449.
- 14 [18] M.P. Aznar, M.A. Caballero, J. Gil, J.A. Martín, J. Corella, Commercial steam
15 reforming catalysts to improve biomass gasification with steam-oxygen mixtures. 2.
16 Catalytic tar removal, Ind. Eng. Chem. Res. 37 (1998) 2668–2680.
17 [http://www.scopus.com/inward/record.url?eid=2-s2.0-](http://www.scopus.com/inward/record.url?eid=2-s2.0-0032105553&partnerID=tZOtx3y1)
18 [0032105553&partnerID=tZOtx3y1](http://www.scopus.com/inward/record.url?eid=2-s2.0-0032105553&partnerID=tZOtx3y1).
- 19 [19] J. Corella, A. Orío, J.-M. Toledo, Biomass Gasification with Air in a Fluidized
20 Bed: Exhaustive Tar Elimination with Commercial Steam Reforming Catalysts,
21 Energy & Fuels. 13 (1999) 702–709.
- 22 [20] L. Ma, J.F.M. Denayer, G. V. Baron, Improving catalytic hot gas cleaning in
23 biomass gasification by oxygen addition, in: AIChE 100 - 2008 AIChE Annu. Meet.
24 Conf. Proc., 2008. [http://www.scopus.com/inward/record.url?eid=2-s2.0-](http://www.scopus.com/inward/record.url?eid=2-s2.0-79953828165&partnerID=tZOtx3y1)
25 [79953828165&partnerID=tZOtx3y1](http://www.scopus.com/inward/record.url?eid=2-s2.0-79953828165&partnerID=tZOtx3y1).
- 26 [21] Y. Su, Y. Luo, Y. Chen, W. Wu, Y. Zhang, Experimental and numerical
27 investigation of tar destruction under partial oxidation environment, Fuel Process.
28 Technol. 92 (2011) 1513–1524.
- 29 [22] P.A. Jenssen, E. Larsen, K.H. Jørgensen, Tar reduction by partial oxidation, in:
30 Proceedings of the 9th European bioenergy conference (1996), pp. 1371–1375, 1996:
31 p. 1996.
- 32 [23] J. Ahrenfeldt, H. Egsgaard, W. Stelte, T. Thomsen, U.B. Henriksen, The influence of
33 partial oxidation mechanisms on tar destruction in TwoStage biomass gasification,
34 Fuel. 112 (2013) 662–680.

- 1 [24] M. Houben, H. Delange, A. Vansteenhoven, Tar reduction through partial
2 combustion of fuel gas, *Fuel*. 84 (2005) 817–824.
- 3 [25] J. Corella, M.A. Caballero, M.-P. Aznar, C. Brage, Two Advanced Models for the
4 Kinetics of the Variation of the Tar Composition in Its Catalytic Elimination in
5 Biomass Gasification, *Ind. Eng. Chem. Res.* 42 (2003) 3001–3011.
- 6 [26] E. Ranzi, A. Cuoci, T. Faravelli, A. Frassoldati, G. Migliavacca, S. Pierucci, et al.,
7 Chemical Kinetics of Biomass Pyrolysis, *Energy & Fuels*. 22 (2008) 4292–4300.
- 8 [27] C. Dupont, L. Chen, J. Cances, J.-M. Commandre, A. Cuoci, S. Pierucci, et al.,
9 Biomass pyrolysis: Kinetic modelling and experimental validation under high
10 temperature and flash heating rate conditions, *J. Anal. Appl. Pyrolysis*. 85 (2009)
11 260–267.
- 12 [28] E.-J. Shin, M.R. Nimlos, R.J. Evans, Kinetic analysis of the gas-phase pyrolysis of
13 carbohydrates, *Fuel*. 80 (2001) 1697–1709.
- 14 [29] P. Morf, P. Hasler, T. Nussbaumer, Mechanisms and kinetics of homogeneous
15 secondary reactions of tar from continuous pyrolysis of wood chips, *Fuel*. 81 (2002)
16 843–853.
- 17 [30] M. Nowakowska, O. Herbinet, A. Dufour, P.-A. Glaude, Detailed kinetic study of
18 anisole pyrolysis and oxidation to understand tar formation during biomass
19 combustion and gasification, *Combust. Flame*. 161 (2014) 1474–1488.
- 20 [31] T. Shoji, K. Norinaga, O. Masek, J. Hayashi, Numerical Simulation of Secondary
21 Gas Phase Reactions of Coffee Grounds with a Detailed Chemical Kinetic Model, *J.*
22 *Japan Inst. Energy*. Vol. 89 (2010) 955–961.
- 23 [32] K. Norinaga, T. Shoji, S. Kudo, J. Hayashi, Detailed chemical kinetic modelling of
24 vapour-phase cracking of multi-component molecular mixtures derived from the fast
25 pyrolysis of cellulose, *Fuel*. 103 (2013) 141–150.
- 26 [33] K. Norinaga, H. Yang, R. Tanaka, S. Appari, K. Iwanaga, Y. Takashima, et al., A
27 mechanistic study on the reaction pathways leading to benzene and naphthalene in
28 cellulose vapor phase cracking, *Biomass and Bioenergy*. 69 (2014) 144–154.
- 29 [34] Deutschmann O., S. Tischer, S. Kleditzsch, C.C. V.M. Janardhanan, M.H. D.
30 Chatterjee, N. Mladenov, H. D. Minh and H. Karadeniz, DETCHEM Software
31 package, 2.5 ed., (2014).

- 1 [35] K. Norinaga, V.M. Janardhanan, O. Deutschmann, Detailed chemical kinetic
2 modeling of pyrolysis of ethylene, acetylene, and propylene at 1073–1373 K with a
3 plug-flow reactor model, *Int. J. Chem. Kinet.* 40 (2008) 199–208.

4

5

1
2
3
4

Table 1. Boundary conditions for numerical simulations

Experiment	Reactor model	Mechanism	Conditions	
			Temperature	Linear velocity
POx at 2 nd stage in TSR	PLUG	DCKM		
		- 548 species		
		- 8159 elementary step like reactions	700°C	0.237 m/s
		Global reaction		
		- $C_8H_{12}O_4 \rightarrow 2 H_2 + 1.5 CH_4 + 4 CO +$ $0.5 C_2H_4 + Soot (C_2), k_{G700} = 0.3 s^{-1}.$		
		- $C_6H_5O \rightarrow CO + CH_4 + Soot (C_4H_1),$ $k_{G800} = 0.8 s^{-1}.$	800°C	0.237 m/s
Thermal cracking of NV in UTSR	BATCH	DCKM	700°C,	
		- 548 species	800°C	-
		- 8159 elementary step like reactions		

1 **Table 2:** Primary pyrolysis product distribution

	Mass fraction	700° C			Mass fraction	800° C		
		C	H	O		C	H	O
Feed biomass	100	50.20	6.30	43.50	100	50.20	6.30	43.50
Products (Volatiles)								
Hydrogen	0.39	0.00	0.39	0.00	1.25	0.00	1.25	0.00
Carbon monoxide	24.96	10.70	0.00	14.26	36.000	15.44	0.00	20.56
Carbon dioxide	8.23	2.25	0.00	5.98	8.040	2.19	0.00	5.85
Water	10.00	0.00	1.12	8.88	15.900	0.00	1.78	14.12
Methane	2.78	2.08	0.70	0.00	4.810	3.60	1.21	0.00
Acetylene	0.16	0.15	0.01	0.00	0.263	0.24	0.02	0.00
Ethylene	2.21	1.89	0.32	0.00	4.351	3.73	0.63	0.00
Ethane	1.29	1.03	0.26	0.00	0.432	0.35	0.09	0.00
Propadiene	0.02	0.02	0.00	0.00	0.035	0.03	0.00	0.00
Methyl-acetylene	0.11	0.10	0.01	0.00	0.105	0.09	0.01	0.00
Propylene	2.00	1.71	0.29	0.00	0.499	0.43	0.07	0.00
Propane	0.44	0.36	0.08	0.00	0.022	0.02	0.00	0.00
Methanol	1.30	0.49	0.16	0.65	0.461	0.17	0.06	0.23
Acetaldehyde	1.95	1.06	0.18	0.71	0.081	0.04	0.01	0.03
1-Butene	2.38	2.04	0.34	0.00	0.332	0.28	0.05	0.00
n-Butane	0.12	0.10	0.02	0.00	0.006	0.01	0.00	0.00
Ethanol	0.08	0.04	0.01	0.03	0.009	0.00	0.00	0.00
2-Butyne	0.36	0.20	0.03	0.13	0.006	0.00	0.00	0.00
Cyclopropene	0.36	0.23	0.03	0.10	0.020	0.01	0.00	0.01
Furan	0.44	0.31	0.03	0.10	0.051	0.04	0.00	0.01

Acetone	0.27	0.17	0.02	0.08	0.088	0.06	0.01	0.03
2-Propanol	0.00	0.00	0.00	0.00	0.000	0.00	0.00	0.00
2-methyl-1,3-Butadiene	0.02	0.02	0.00	0.00	0.005	0.00	0.00	0.00
1,4-Pentadiene	0.12	0.11	0.01	0.00	0.074	0.06	0.01	0.00
1-Pentene	0.03	0.02	0.00	0.00	0.002	0.00	0.00	0.00
Acetic-acid	0.59	0.24	0.04	0.32	0.198	0.08	0.01	0.11
Cyclopentadiene	0.19	0.17	0.02	0.00	0.338	0.31	0.03	0.00
Methyl-furan	0.16	0.12	0.01	0.03	0.016	0.01	0.00	0.00
2,5-Dimethylfuran	0.12	0.09	0.01	0.03	0.005	0.00	0.00	0.00
Hydroxy-acetone	0.29	0.14	0.02	0.12	0.039	0.02	0.00	0.02
Benzene	0.11	0.10	0.01	0.00	1.421	1.31	0.11	0.00
Dimethyl-furan	0.00	0.00	0.00	0.00	0.000	0.00	0.00	0.00
Toluene	0.28	0.26	0.02	0.00	0.670	0.61	0.06	0.00
Fural	0.23	0.14	0.01	0.08	0.081	0.05	0.00	0.03
Ethylbenzene	0.08	0.07	0.01	0.00	0.072	0.07	0.01	0.00
Phenylacetylene	0.00	0.00	0.00	0.00	0.020	0.02	0.00	0.00
Styrene	0.10	0.10	0.01	0.00	0.216	0.20	0.02	0.00
Phenol	0.85	0.65	0.05	0.14	0.285	0.22	0.02	0.05
Benzofuran	0.09	0.08	0.00	0.01	0.124	0.10	0.01	0.02
Indene	0.18	0.17	0.01	0.00	0.188	0.17	0.01	0.00
Cresol	0.29	0.23	0.02	0.04	0.069	0.05	0.01	0.01
3-Methyl-1, 2-Benzenediol	0.12	0.08	0.01	0.03	0.063	0.04	0.00	0.02
Naphthalene	0.18	0.17	0.01	0.00	0.192	0.18	0.01	0.00
Naphthalene,1-methyl-	0.00	0.00	0.00	0.00	0.047	0.04	0.00	0.00
Naphthalene,2-methyl-	0.00	0.00	0.00	0.00	0.059	0.05	0.00	0.00
1-Butene-3-yne	0.02	0.02	0.00	0.00	0.027	0.02	0.00	0.00
1,2-Butadiene	0.01	0.01	0.00	0.00	0.003	0.00	0.00	0.00

1,3-Butadiene	0.54	0.48	0.06	0.00	0.537	0.48	0.06	0.00
1-Butyne	0.01	0.01	0.00	0.00	0.001	0.00	0.00	0.00
1-Hexen-3-yne	0.00	0.00	0.00	0.00	0.025	0.02	0.00	0.00
Cyclohexane	0.02	0.02	0.00	0.00	0.000	0.00	0.00	0.00
2,3-Butanedione	0.06	0.03	0.00	0.02	0.015	0.01	0.00	0.01
Total (volatiles)	63.45	28.42	4.35	31.75	77.55	30.89	5.58	41.09
Char (N₂)	13.26	11.46	0.17	0.91	11.55	10.01	0.08	0.44
Unknown (difference)	23.29	10.32	1.78	10.84	10.9	9.3	0.64	1.97
Total	100	50.20	6.3	43.5	100	50.2	6.3	43.5

1

2

3

4

Fig. 1. Schematic representation of the idealized plug-flow reactor for numerical simulations. A two-stage tubular reactor (TSR), consisting of two sections divided by a quartz filter, is externally heated by an electric furnace. Fast pyrolysis of cedar sawdust particles in the upstream section of the TSR generates nascent volatiles, which are partially oxidized downstream in the second stage of the reactor.

Fig. 2. A comparison between the model predictions at $K=0$ and $K=0.3 \text{ s}^{-1}$, and fast pyrolysis experiment of cedar sawdust at 700°C for major gas phase species. The solid and dashed lines show the model predictions with and without global reaction, respectively.

Fig. 3. A comparison between the model predictions at $K=0$ and $K=0.8 \text{ s}^{-1}$, and fast pyrolysis experiment of cedar sawdust at 800°C for major gas phase species. The solid and dashed lines show the model predictions with and without global reaction, respectively.

Fig. 4. Distributions of temperature and species concentrations along the axial length of the plug-flow reactor.

Fig. 5. Comparisons between model predictions and experimental observations under isothermal conditions (700 °C) for the major gas-phase species H₂, CO, CO₂, and CH₄. Error bars show the standard error in the experimental measurements and solid lines show the model predictions.

Fig. 6. Comparisons between model predictions and experimental observations under isothermal conditions (700 °C) for the minor gas-phase species C₂H₄, C₂H₆, CH₃CHO, and C₃H₆. Error bars show the standard error in the experimental measurements and solid lines show the model predictions.

Fig. 7. Comparisons between model predictions and experimental observations under isothermal conditions (700 °C) for the minor gas-phase species C₃H₈, C₄ (C₄H₁₀ and C₄H₈), C₆H₆, and C₁₀H₈. Error bars show the standard error in the experimental measurements and solid lines show the model predictions.

Fig. 8. Comparisons between model predictions and experimental observations under isothermal conditions (800 °C) for the major gas-phase species H₂, CO, CO₂, and CH₄. Error bars show the standard error in the experimental measurements and solid lines show the model predictions.