A TAR CONVERSION MODEL FOR FLUIDIZED BED BIOMASS GASIFIERS

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ABSTRACT: A comprehensive tar conversion model for biomass gasification has not been developed up to date due to the great deal of processes involved, whose stoichiometry and kinetics are not well known. Therefore, simplified schemes of reactions are assumed in existing models, reducing their capability to predict the tar composition in the gas. In this work a model to predict tar composition from wood gasification was developed. The model takes into account both tar generation from the fuel and secondary transformations of the gas in the gasifier, mainly focused on conditions applicable to fluidized beds. The model comprises a limited number of tar compounds and reactions representing the main tar species and conversion mechanisms, which stoichiometry and kinetics are based on literature data. Comparison with measurements from literature data is presented to discuss the applicability of the model.
Keywords: tar, model, fluidized bed, gasification, pyrolysis

1 INTRODUCTION

The presence of heavy organic compounds (tars) in the product gas of a biomass fluidized bed gasifier (FBG) reduces the efficiency of the process and limits the use of the gas to applications where it is not necessary to cool the gas, such as burning in kilns and boilers. In applications where the gas needs to be cooled, such as the power production in an engine, the key parameter characterizing the condensing behavior is not the total concentration of tar but the tar dew point. The tar dew point of a gas, defined as the temperature at which the tar mixture contained in a gas stream begins to condense, depends on the concentration and the nature of tar compounds [1], being especially sensitive to the amount of heavy tars (polyaromatic hydrocarbons).

In order to increase the efficiency and utilization of the gas, it is necessary to find alternative gasifier designs to favor the tar conversion. For such purposes, the understanding of tar conversion processes is necessary as well as simulation models to predict the evolution of tar composition under different conditions. Due to the huge number of reactions involved in the process, the models have been greatly simplified. A common approach is to lump the tar compounds in a limited number of classes (generally represented by model compounds) and to presume certain scheme of reaction and stoichiometry.

This paper presents a model to predict the tar composition in biomass gasifier, with special focus on FBG processing woody biomasses. The model uses seven tar models to represent the different tar classes and nine reactions to characterize the tar evolution. The stoichiometry and the kinetics of the reactions were obtained from experimental data from literature. The model is compared with measurements conducted both in pyrolysis and gasification conditions.

2 MODEL DEVELOPMENT

2.1 Application

In FBG units fuel devolatilization is usually controlled by the particle heating due to the large particle size used. The temperature of devolatilization at which tar compounds are released from the particle is lower than that in the bed, influencing the nature and yields of the tars.

The interaction between the oxidant and volatiles released from the fuel influences the evolution of tar in a gasifier [2,3,4]. In a conventional directly-heated FBG, the oxygen reacts mainly with light gas and, to less extent, with tar and char. On the other hand, in indirectly-heated FBG the conversion of tars takes place in the absence of oxygen, provided no oxygen carriers are used.

In conclusion, under the conversion conditions of FBG, the tar generation is occurring at lower temperature than that in the bed, the secondary conversion of tars along the gasifier is mainly driven by the temperature profile in it, and the reactions between tars and oxygen are limited. In the present model, the reactions with oxygen are not taken into account and the primary tars are consistent with FBG conditions. The fluid-dynamics in a FBG may also affect the contact efficiency between the reactants. In the present model this aspect is not considered but the work is focused on the global kinetics aspects.

2.2 Scheme of reaction

Fig. 1 presents the general scheme assumed. It comprises two sub-models representing the fuel devolatilization and the secondary conversion. The first sub-model accounts for fuel devolatilization where the primary tars are released from the fuel particle. This primary tars are further converted by secondary reactions, which modify the composition of the tar mixture. Secondary reactions increase the proportion of aromatic compounds and reduce the presence of oxygenated molecules. The extent of secondary conversion depends on the temperature profile in the gasifier.

2.3 Devolatilization sub-model

The model assumes that the fuel particles devolatilize at around 500ºC (nearly the temperature of maximum tar production), whose yield is calculated using the correlation by Neves et al. [5].

Assuming a typical wood composition with 49wt% carbon, 44wt% oxygen and 5.9wt% hydrogen (dry ash free fuel) the devolatilization yields 0.51 $kg_{tar}/kg_{daf\text{-}fuel}$ (at 500ºC) [5].

Two compounds are selected to represent the primary tar mixture, acetol ($C_3H_6O_2$) and catechol ($C_6H_6O_2$). These compounds are representative and abundant compounds of the devolatilization of lignocellulosic biomass. Additionally catechol is a predominant structural entity of lignin [6], which is the main source of lignocellulosic pyrolysis tars. Their relative yields was calculated by minimizing the mass difference between C, H, and O of the model tar mixture and that reported in [5] at 500 ºC (56.1wt% carbon, 35.6wt% oxygen and 6.6wt% hydrogen [5]), giving 0.24 and 0.27 $kg_{tar}/kg_{daf\text{-}fuel}$ for acetol and catechol respectively. In the present model, these primary yields of acetol and catechol are fixed , being the initial condition for the secondary conversion sub-model.

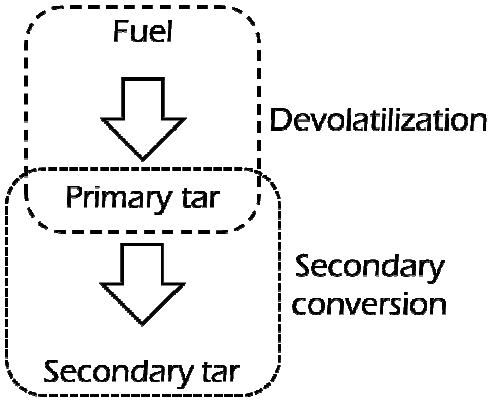

Figure 1: Scheme of conversion adopted for the tar model

2.4 Secondary conversion sub-model

Fig. 2 presents the scheme proposed for secondary tar conversion and Table 1 contains the stoichiometry and kinetics assumed for each reaction. The kinetics of all reactions are first order with respect to the tar concentration and the kinetic parameters have been taken from literature or calculated from measurements reported in literature (assuming plug flow and first order kinetics). Besides the primary tars (acetol and catechol), the tar compounds considered in the model are: phenol (representing tar class 2), toluene (representing tar class 3), naphthalene (representing tar class 4), pyrene (representing tar class 5) and benzene (here considered a tar). The model tars representing the different tar classes were selected because they are the most abundant compounds of the considered tar classes, and because their conversion has been widely studied.

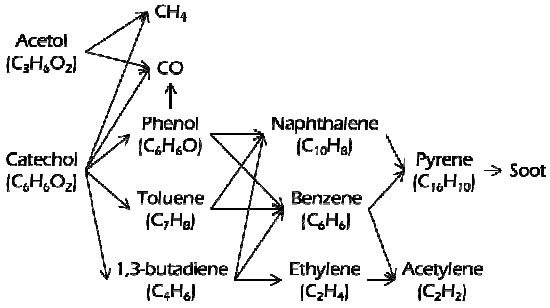

Figure 2: Scheme of reaction for secondary tar conversion (hydrogen was not included for a better visualization)

The stoichiometry of the thermal decomposition of acetol (R-1) was assigned from the non-catalytic steam reforming experiments [7], with kinetic parameters taken from [8]. It was assumed that the conversion of acetol only produces light gases, so catechol is the only source of secondary tar.

The decomposition kinetics of catechol was calculated analyzing the experimental results obtained by Ledesma et al. [6]. The stoichiometry of R-2 was set by assuming that the main products of the thermal decomposition of catechol (and other "primary" tars such as guaiacol and anisole [9,10]) are carbon monoxide and hydrocarbons such as cyclopentadiene and phenol [6]. The presence of toluene is justified by Diels-Alder reactions.

The conversion of small and unsaturated hydrocarbon chains, here represented by the butadiene, proceeds mainly by two different routes: C-C bond scission to produce lighter hydrocarbons and Diels-Alder reactions producing aromatic compounds. The stoichiometry of reaction R-3 was obtained considering measurements from Fairburn et al. [11] and Xu et al. [12] and the kinetic used correspond with that of C_3H_8 reported by [12].

Table I: Stoichiometry and kinetic parameters of the reactions included in the secondary conversion model

Reaction	**Stoichiometry**	**Kinetic ecuation** $-r_{tar}=k_0\exp(-E_a/RT)C_{tar}$	
		E_a (kJ/mol)	**k_0 (s^{-1})**
R-1	$C_3H_6O_2 \rightarrow CO + CH_4 + H_2$	100	$5\cdot10^5$
R-2	$C_6H_6O_2 \rightarrow 0.08\ C_7H_8 + 0.15\ C_6H_5OH + 1.85\ CO + 0.17\ CH_4 + 0.63\ C_4H_6$	198	$2.25\cdot10^{10}$
R-3	$C_4H_6 \rightarrow 0.07\ C_{10}H_8 + 0.2\ C_6H_6 + 1.05\ C_2H_4 + 0.02\ H_2$	260	$5.01\cdot10^{12}$
R-4	$C_6H_5OH \rightarrow 0.25\ C_{10}H_8 + CO + 0.42\ C_6H_6 + 0.75\ H_2$	263	$4.34\cdot10^{11}$
R-5	$C_7H_8 \rightarrow 0.17\ C_{10}H_8 + 0.89\ C_6H_6 + 0.67\ H_2$	315	$2.23\cdot10^{13}$
R-6	$C_{10}H_8 \rightarrow 0.625\ C_{16}H_{10} + 0.875\ H_2$	326	$1.94\cdot10^{13}$
R-7	$C_6H_6 \rightarrow C_2H_2 + 0.25\ C_{16}H_{10} + 0.75\ H_2$	264	$2.14\cdot10^{10}$
R-8	$C_2H_4 \rightarrow C_2H_2 + H_2$	155	$5.01\cdot10^5$
R-9	$C_{16}H_{10} \rightarrow 16C + 5\ H_2$	536	$7.94\cdot10^{23}$

The conversion of phenol was assumed to be due to decarboxylation to produce CO and cyclopentadiene [13,14]. The cyclopentadiene is further decomposed to light hydrocarbons [6] or reacts through Diels-Alder reactions to produce PAH [8,15,16]. The kinetic parameters were taken from [14].

The toluene evolution is influenced by the concentration of hydrogen in the bulk gas. In a hydrogen-rich atmosphere only light compounds are produced [17], whereas heavier PAHs are also produced in an inert atmosphere (Ar) [18]. In the present model, the kinetics for toluene conversion was obtained considering the conversion data obtained under inert atmosphere [14], so the applicability seems to be limited to stand-alone air-blown FBG, where the concentration of hydrogen in the gas is limited.

The naphthalene conversion reaction assumed was its dehydrogenation to produce pyrene and hydrogen. The kinetic parameters were determined by fitting measurements from [19]. The stoichiometry of benzene conversion was taken from [20] and [14], and the kinetic parameters from [20]. The kinetic of dehydrogenation of ethylene to produce acetylene comes from [12]. The only reaction that was considered to produce soot is the dehydrogenation of pyrene. The rate of pyrene conversion was assumed the same as that from "6 ring" formation reported in [21].

3 COMPARISON WITH EXPERIMENTAL RESULTS

Two different sets of experiments were simulated. The first one is a set of experiences under pyrolysis conditions between 800 and 1000ºC in an entrained drop-tube furnace [22]. This work analyzes the pyrolysis products of cypress sawdust paying special attention to the thermal cracking of tars. Table 2 compares the experimental conditions tested in [22] and the values used as inputs in the present model.

Table II: Experimental parameters tested in [22] and parameters used as model inputs for simulation

Parameter	Zhang et al. [22]	Model input
Fuel ult. analysis		
C (wt%)	49.2	49
H (wt%)	6.49	5.9
O (wt%)	44.2	44
Feeding flowrate (g/h)	60-70	65
Gas residence time (s)	2-4	3

Figure 3 presents the yields of the different tar classes (lumped according to the classification presented in [2]) reported in [22] and the tars calculated using the present model. The results show that the model predicts well the trends of the different tar classes. Quantitatively, the yield of tar class 2, 3 and benzene are seen to be well predicted, whereas the yield of tar class 4 is slightly sub-estimated, and the predicted yield of tar class 5 is clearly lower than that measured.

The second set of experiments simulated was conducted in an FBG, where both the stoichiometric ratio (SR) and the feeding flowrate were kept constant, while the reactor temperature was varied approximately in the range of 700-900ºC [1]. Table 3 summarizes the main conditions tested and the values used in the model to simulate the experiments. The main results of the simulation and comparison with the measurements are presented in Figure 4. It can be concluded that the model predicts well the effects of different operational parameters on the composition of the tar mixture. The ability of the model to qualitatively predict the trends is good both for pyrolysis and gasification tests. However, overestimation of the yields of tar class 2 and 4 were found. This could be due to the reactions that were not considered in the present model, probably related with the radicals produced during partial oxidation.

Table III: Experimental parameters tested [1] and parameters used as model inputs for simulation

Parameter	Van Paasen et al [1]	Model input
Fuel ult. analysis		
C (wt%)	49.4	49
H (wt%)	6	5.9
O (wt%)	39	44
Feeding rate (g/h)	900 (daf)	900
Gas residence time (s)	– (5 s aprox)	4.4 – 5.7
SR	0.22–0.23	–

4 CONCLUSIONS

A kinetic model to predict tar composition in biomass gasifiers mainly focused on conditions applicable to fluidized beds was presented. Both formation and secondary conversion processes were taken into account. Comparison with measurements reveals that the model predicts qualitatively well the main trends of the different tar classes under different operation conditions, for both pyrolysis and gasification. Good quantitative estimation of the tar yields was achieved for pyrolysis experiments, while considerable deviations for some yields were found in gasification conditions. The model is under further development. Consideration of reactions in oxidizing environment is expected to improve the model.

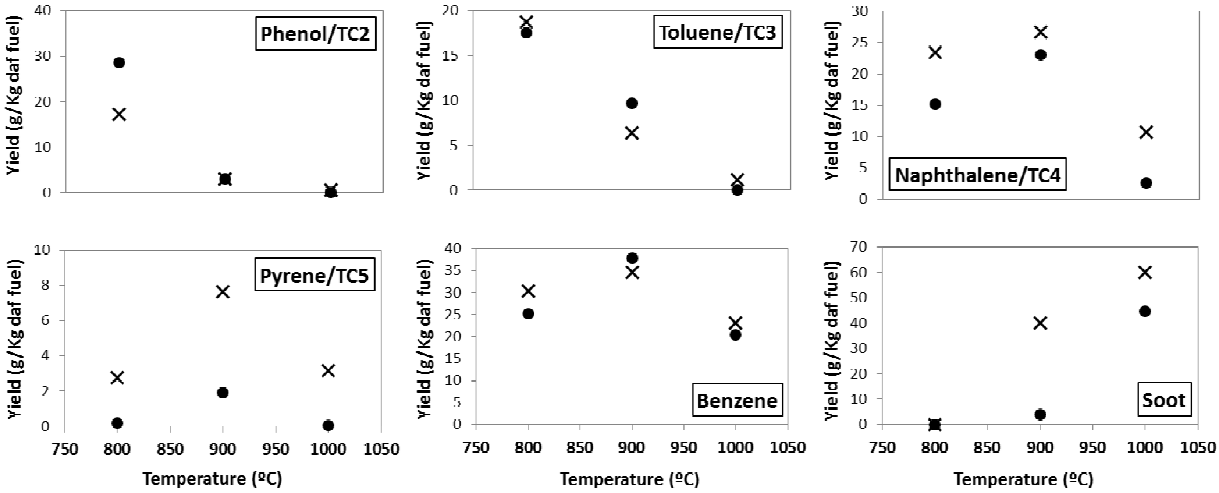

Figure 3: Composition of tar content predictions (dot markers) and experimental data [22] (cross markers).

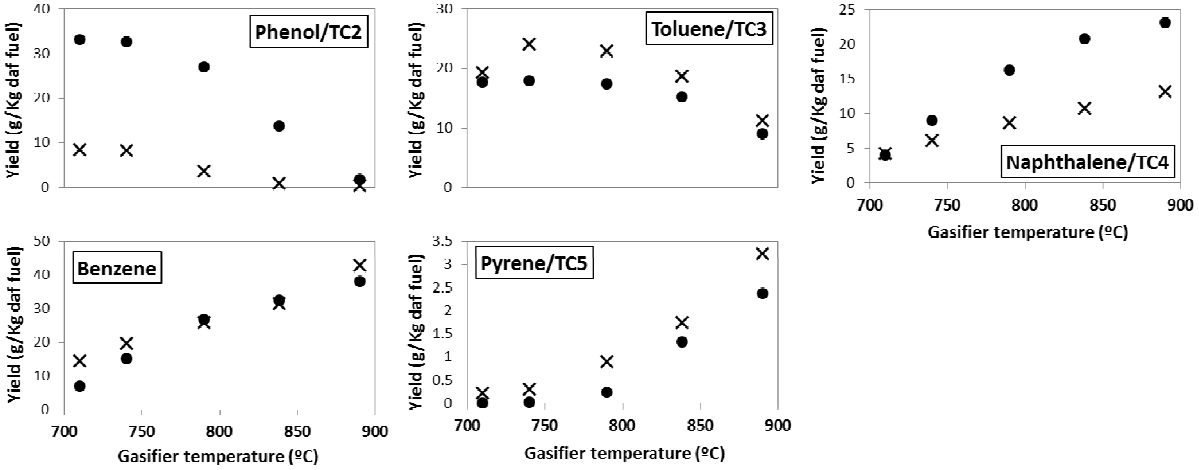

Figure 4: Composition of tar content predictions (dot markers) and experimental data [1] (cross markers).

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