Kinetic mechanism reduction methodology for secondary gas phase reactions in biomass gasification

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October 2021

Abstract

Biomass gasification is an energy-generating process widely recognized as an efficient and sustainable technology, representing a viable alternative to the burning of fossil fuels. However, the formation of tars and impurities during biomass gasification raises the necessity of enhancing the gasification process in order to eliminate these unwanted products and improve the efficiency of the process. Numerical modelling is an attractive solution to perform detailed analysis to the gasification process in order to find possible solutions for this problem. A few studies available in the literature present highly detailed mechanisms that are able to accurately predict the gasification kinetic behavior. However, these models are extremely complex and comprise long computational times. The main objective of this work is to propose a reduced mechanism that is able to predict the secondary gas-phase reactions during biomass gasification. A scanning method and an error-based species and reactions elimination technique are applied to a detailed secondary gas-phase mechanism with 134 species and 4533 reactions, maintaining its essential characteristics. Finally, the selected reduced mechanism is validated by comparing the obtained results with the data from the original mechanism. The reduction method applied in this work is found to effectively obtain reduced mechanisms capable of accurately predicting the gas yield, final gas composition and H_2, CO and CO_2 release rate curves of the initial detailed mechanism together with significantly reduced computation time. A mechanism with 89 species and 476 reactions is one of the mechanisms obtained from the reduction process that has the characteristics mentioned in the previous statement, with a computational time reduction of 52.91%. The sensitivity analysis carried out on the biomass components proved that this reduced mechanism can be used for a wide range of biomass fuels.

1. Introduction

The increased awareness of the risks of burning fossil fuels and their potential devastating consequences has turned the world's attention to alternative, renewable and clean energy sources such as wind, solar, geothermal and bioenergy [1]. Bioenergy is the energy that is generated from organic matter, known as biomass. It is considered that both biomass and its respective biofuels do not contribute to enhance greenhouse effect, as the released carbon dioxide originated from the thermochemistry processing of the biomass is balanced with the absorption of that same carbon dioxide during the flora live span [2]. Therefore, the focus on bioenergy has been increasing over the last years, as it is a valuable means to face global warming.

Gasification is a thermochemical process that is able to convert solid biomass into gaseous products (producer gas) that can be further used in energy-generating processes or synthesized into other value-added chemicals [3]. Gasification, presented in Figure 1, is a multistage process that includes different stages, i.e., drying, pyrolysis, partial oxidation or combustion, cracking and char reduction. In particular, pyrolysis that has great importance in gasification is a thermal treatment that decomposes organic materials into liquid, solid (char) and gaseous (light permanent and combustible gases) forms in the absence of oxygen [4]. The liquids released from biomass pyrolysis include H2O, low weight molecular species and tars. Tars are heavy hydrocarbons that represent one of the utmost challenges in industrialization of biomass gasification infrastructures, since these components are often converted into impurities/particles [5] that lead do the necessity of producer gas (syngas) treatment after the gasification process. An efficient way to mitigate these occurrences is enhancing the gasification processes, where tars can be reformed under the presence of oxidizing atmospheres. It is still a challenge to operate gasifiers using biomass as feedstock and often suboptimal results are delivered. In this sense, numerical modelling is a very attractive solution to overcome these barriers [6].

A few studies have considered very detailed mechanisms that are able to predict release rate curves, product yields and product speciation under different gasification uses [7–10]. However, these models often comprise long computational times and chemical stiffness. Within this perspective, applying reduction methodologies is highly recommended to reduce detailed kinetic mechanisms while keeping their essential features [13].

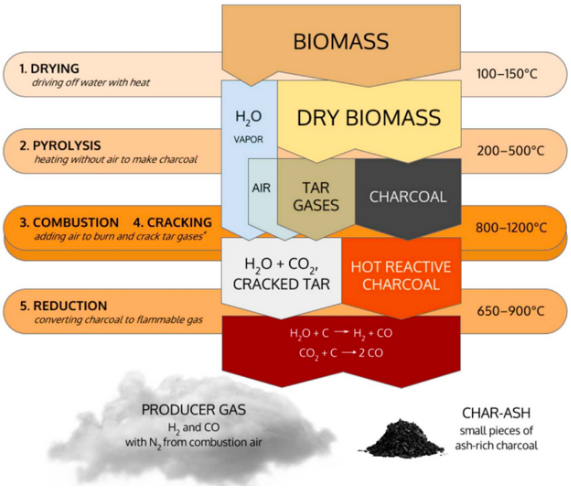

Figure 1 - Gasification process steps.

In the given context, the main objective of this work is to implement a numerical tool that is able of reducing the CRECK-S-BIO mechanism [8]. while keeping its characteristic features. The reduced mechanism should be able to accurately predict the behavior of the initial detailed mechanism, comprising less computational time. Within this aim, reduction techniques will be applied to both species and reactions to obtain a reduced mechanism. Focus will be given to the gasification of wheat straw (agricultural residue) in a drop tube furnace (DTF) considering the typical range of gasification operation conditions.

2. Numerical Modelling

2.1 Kinetic Mechanism

Debiagi et al. [8] proposed a very detailed mechanism that is able to describe biomass pyrolysis behavior and secondary gas-phase reactions under gasification conditions, taking into account 161 species and 4561 reactions (pyrolysis: 52 species and 28 reactions; secondary gas-phase mechanism: 134 species and 4533 reactions). This mechanism, named CRECK-S-

BIO, considers that biomass is constituted by seven reference components for modelling purposes: cellulose (CELL), hemicellulose (HCE), three structures of lignin identified as LIGH, LIGO, and LIGC rich in hydrogen, oxygen, and carbon, respectively, and hydrophobic (TGL) and hydrophilic (TANN) extractives [4,7]. In this mechanism, pyrolysis takes place first resulting in the decomposition of the seven solid biomass components [4]. After the pyrolysis phase, the secondary gas phase reactions take place, where the partial oxidation of the released volatiles occurs, with tars also undergoing thermal cracking. A scheme of this mechanism is presented in figure 2:

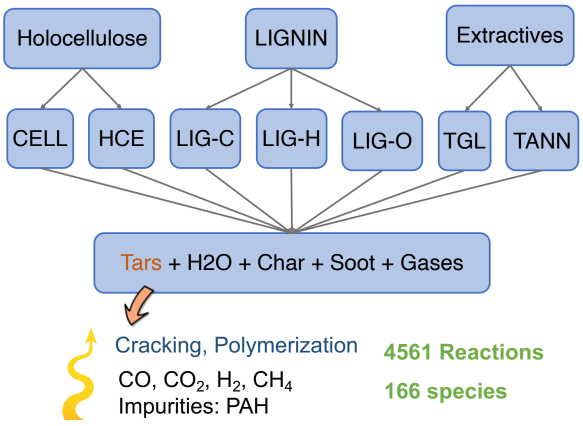

Figure 2 - Biomass gasification kinetic mechanism (CRECK-S-BIO).

2.2 Reactor Modelling

Ferreiro et al. [5] developed the kinetic-diffusion controlled model used in this work. This one-dimensional model considers a spherical biomass particle entering the DTF along with a carrier gas (in this case nitrogen) where both are heated through convection and radiation. The release rate of the volatiles and the heat transfer between the particle and its surroundings is calculated along the axial direction of the DTF. Figure 3 shows a concept visualization of the adopted model with the specifications of this work regarding temperature profile, gasifying agent and carrier gas composition:

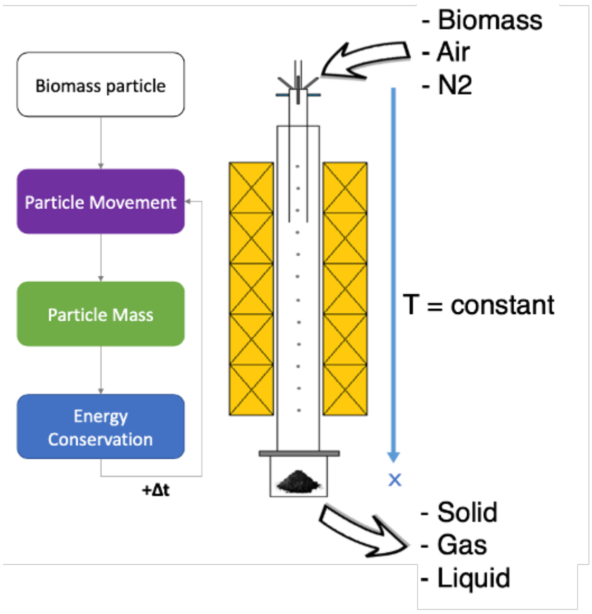

Figure 3 - Reactor model.

The model inputs are measured temperature profiles, biomass composition (obtained experimentally in a previous work [12]) and the reactor and mass flow characteristics. In this work in specific, the temperature is kept constant along the entire length of the reactor with values varying between (900-1200ºC), the steam to biomass ratio varies between 0-1.7, the reactor has 1320 mm and the air and nitrogen flow rates are 0.5L/min and 10L/min, respectively. This model comprises three main governing equations: mass balance, energy balance, and particle trajectory. In order to solve the previous equations, the species conservation and in order to determine the reaction rates and final product yields, a stiff ordinary differential equation solver (CVODE) is implemented in Python with assistance of the Cantera library [13]. A more detailed description of this model and the above equations can be found in a previous work [5].

2.3 Mechanism Reduction Modelling

The reduction process is developed in Python as a sub-routine of the numerical tool described above. Figure 4 shows the algorithm used in the reduction process. Firstly, the reference mechanism (CRECK-S-BIO) is initialized. The reduction process starts by scanning all species. This method consists in computing the error caused by deleting a single specie from the reference mechanism, repeating this process for each specie. The error represents the difference between the results obtained for the reference mechanism and the ones obtained for the reference mechanism without the specie. Afterwards, the species are ordered according to their associated errors. The goal of the scanning method is to evaluate the importance of each specie in the secondary gas-phase reactions behavior, with the ones with lower associated errors being the less important to the reference mechanism. The deletion of a specie is achieved by eliminating every reaction where this specie is a product and/or a reactant. In the second stage of the reduction process, a range of error margins is established. Species with lower error magnitude than the applied margin are deleted. Consequently, for each margin, a new mechanism is obtained and the error between the new and the reference mechanisms is estimated. Then, the same reduction techniques (scanning and elimination) are applied to the remaining reactions of the reduced mechanisms obtained previously. New further reduced mechanisms with the same number of eliminated species but with a higher number of eliminated reactions are obtained. A post-processing analysis is performed to the obtained results and a reduced mechanism is selected. The reduction methodology is then applied for a range of typical operating conditions, with a reduced mechanism being selected for each condition. Finally, all the selected mechanisms are merged, originating a final mechanism that contains all the reactions from the unified mechanisms.

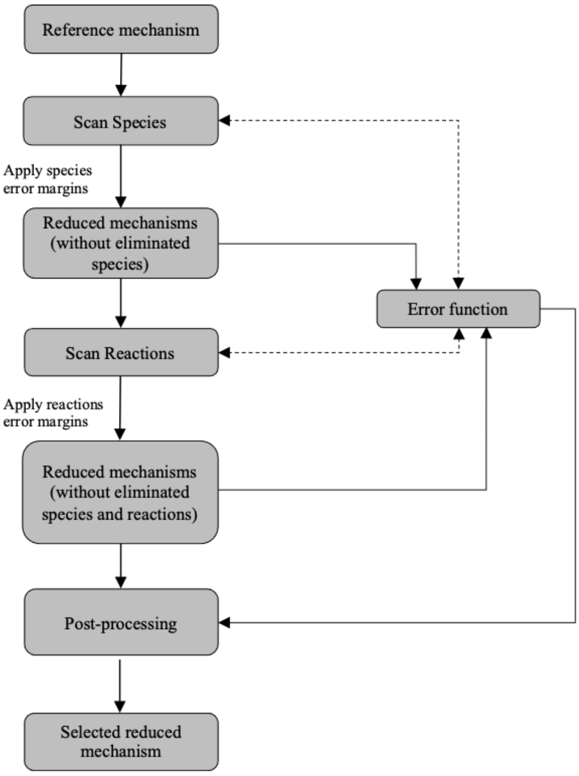

Figure 4 - Algorithm of the reaction model.

In the present work, the error between the reference and the reduced mechanisms is determined through an error function that is formulated to preserve the behavior and the characteristics of the reference mechanism. Seven different characteristics are considered: the total gas yield, the H_2, CO and CO_2 yields and release rate peaks. The error associated with the yield parameters represents the difference between the yield values from the reference and reduced mechanisms. The peak error parameters represent the error corresponding to the larger difference between the maximum values (peaks) of the gases release rates (H_2, CO_2 and CO) between the reference mechanism and the values of the release rates points of the reduced mechanism at the same time/position. For each above-mentioned characteristic points, a specific error function, based on the relative error, is defined as:

$$\boldsymbol{\delta_i} = \frac{|Y_{reference,i} - Y_{reference,i}|}{Y_{reference,i}} \quad (1)$$

$$\delta = \frac{1}{N}\sum_{i=0}^{N} \delta_i \quad (2)$$

where δ_i represents the error of the ith characteristic point, Y the output value of the evaluated characteristic point. The total error is a result of seven (N) different error contributions, which are important for the analysis of the mechanism's final products and its behavior along the secondary gas-phase reactions of the gasification process. The selected reduced mechanism, as the reference mechanism, will be able to predict the secondary gas-phase reactions that occur during biomass gasification, including mass loss profiles, product speciation, release rates, gas composition and product yields, as function of time/position in a DTF.

3. Results and Discussion

Figure 5 shows five different sets of operating conditions that undergo the reduction process. From each selected condition, a reduced mechanism is obtained and posteriorly merged with the remaining obtained reduced mechanisms, to generate a reduced mechanism that is able to predict the secondary gas-phase reactions of the gasification process in the typical range of biomass gasification operating conditions. The selected conditions represent the boundaries of the operating conditions regarding temperature and steam to biomass ratio (red points) and also a set corresponding to the condition equidistant (green central point) from the minimum and maximum boundaries. To assess the importance of the central operating condition in the reduction process, the final reduced mechanism will be obtained using two different methodologies: i) using only the conditions set as the boundaries and ii) adding the central point to the aforementioned conditions.

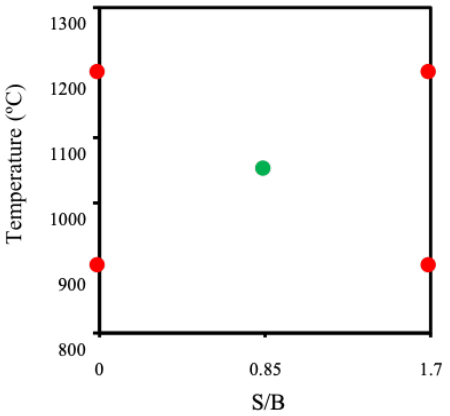

Figure 5 - Selected operating conditions used in the reduction process.

Figure 6 shows the data of the reduced mechanisms obtained through the species and reactions reduction steps for a temperature of 1200 ºC and a steam to biomass ratio of 0 (top left condition shown in Figure 5). These results and their consequent analysis are similar to the ones obtained for the remaining sets of operating conditions, hence, only the results for this specific condition are shown here.

Figures 6a and 6b, show the results obtained for the species reduction step. It was selected a range of 21 different species error margins. For each margin, species with lower mean error values than that margin are eliminated, and a new reduced mechanism is obtained. From the inspection of Figure 6a, it is possible to see that the magnitude of the mean error presents a clear growing tendency with respect to the raise of the value of the species error margin. This result is expected since the higher the value of the species error margin, the higher is the number of eliminated species.

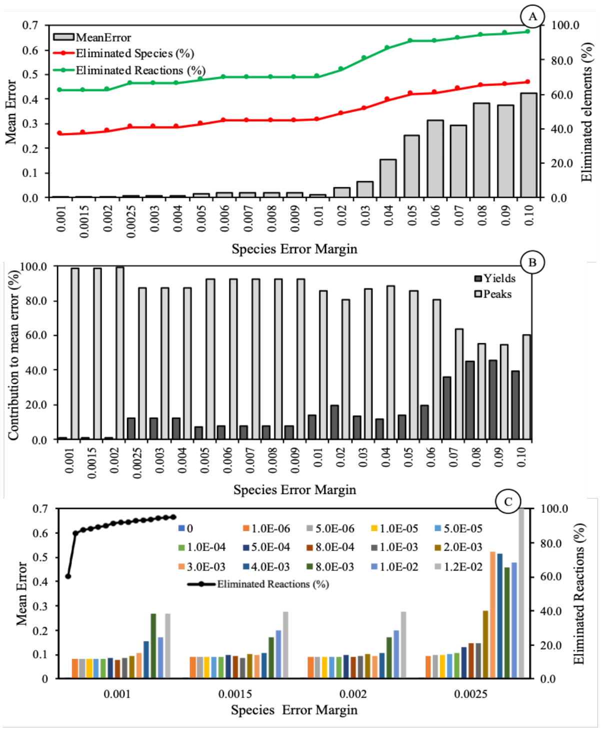

Figure 6 - a) Mean error for the mechanisms obtained from species reduction, b) Contribution of the peaks and yields errors to the mean error (%) and c) Mean error for mechanisms originated from species and reactions reduction for a temperature of 12

Figure 6b shows the contribution of the release rate peaks and the yields for the mean error. The results show that generally, with the increase of the error margin, the contribution of the errors associated with the peaks decreases, whereas the contribution of the errors associated with the yields increase. In the area of interest, where the mechanisms that present mean error values lower than 15% (mechanisms that are found to retain the characteristic features of the reference mechanism) are situated, the contribution of the errors associated with the yields of the final products are very low in magnitude and much smaller when compared to the contributions from the peak errors. For the mechanisms with mean error values approximately higher than 30**%**, the contributions of the yields and peaks errors are similar, with the yields error even surpassing the peaks error in some cases (as shown in the supplementary material in Figures S1 to S4). Figure 6c shows the mean error and the percentage of eliminated reactions for the reactions reduction step and for the same operating conditions as the ones considered in the species reduction step. It is worth to emphasize that the reactions reduction step is implemented for mechanisms already reduced in the species reduction step. Each group of columns is associated with a single species error margin. The four groups of bars presented in Figure 6c are associated with the first four (lower values) species error margins selected from the species reduction step. This specific selection is due to the fact that the higher the value of the species error margin (higher number of eliminated species), the more sensitive the mechanisms get to the elimination of reactions. This high sensitivity is demonstrated through the mean error values shown in Figure 6c, which are higher for species error margins with higher magnitude, reinforcing the idea that species error margins higher than 0.0025 do not present meaningful results for the purpose of this work. For the four mechanisms associated with the four species error margins considered in Figure 6c, a range of 14 reactions error margins was selected and analyzed. With the raise of the value of the reactions error margin, a growing tendency of the mean error value is again identified. This is an expected result, as the higher the reactions error margin, the higher the number of eliminated reactions. A black line corresponding to the percentage of eliminated reactions is also shown for the species error margin 0.001 and, through its inspection, an initial significant jump can be identified between the mechanism obtained only through species reduction and the mechanism obtained through species and reactions reduction, followed by small increments of eliminated reactions with the increase of the reaction error margin. The percentage of eliminated reactions trends corresponding to the remaining species error margins are similar to the one shown for the species error margin of 0.001, hence, these are not shown.

Table 1 - Selection criteria for mechanisms to undergo the merging step

Criteria Name / Limit variables	Yields error (%)	Mean error (%)
Regular	< 2	< 15
Conservative	< 1	< 5
Super Conservative	< 1	< 1

The main objective of the selection process is to select a mechanism from each considered set of operating conditions, so that they can be posteriorly merged in order to obtain a new reduced mechanism. This mechanism will present itself as a viable solution to predict the secondary gas-phase reactions that occur during biomass gasification in a DTF within the selected range of operating conditions presented in Figure 5. The selection process is based on the post-processing analysis of the results obtained in the reduction step. The selection criteria used in this work was chosen through a preliminary analysis of the results of the reduction process and the characteristics of the mechanisms obtained in that process. The criteria, which is based on the mean error and the yields error obtained for each mechanism, is shown in Table 1. The super conservative approach was not considered on the mechanisms obtained through the reduction of both species and reactions since none of the mechanisms presents mean error values lower than 1%.

The results obtained through the error calculation for the selected ten mechanisms are shown in Figure 7 and the number of reactions, species and computational time of each mechanism are shown in Table 2. The error scale upper limit is 12% to enable a clear vizualization of the differences between small error values. The computational time associated with the detailed mechanism is 86.9 seconds.

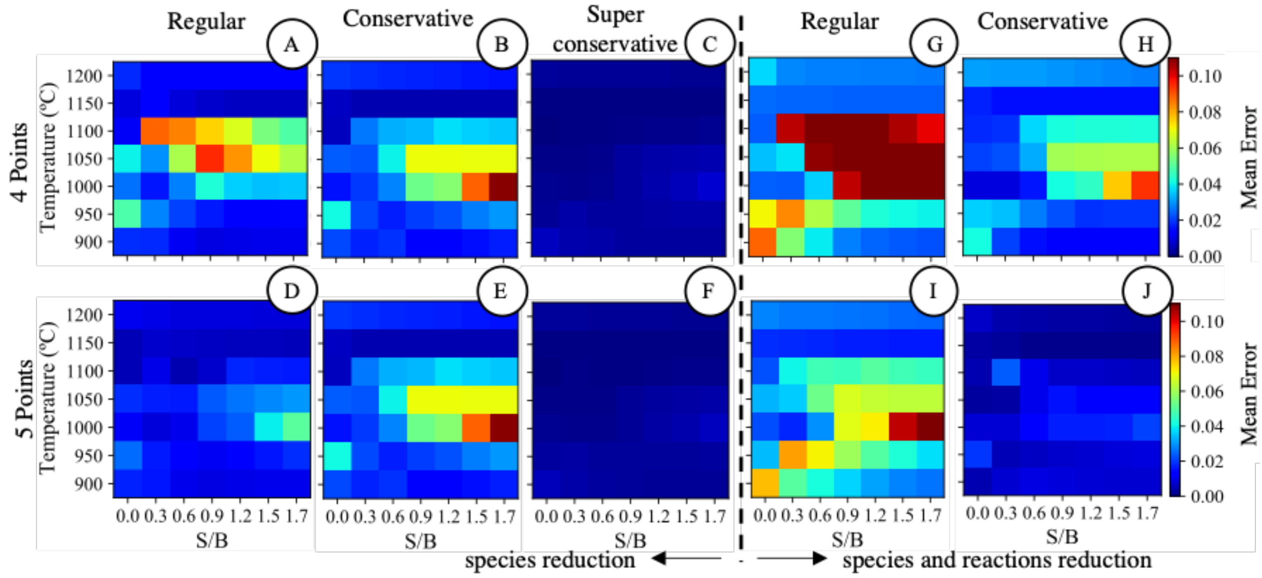

Figure 7 - Mechanisms originated from species reduction with 4 points A) regular, B) conservative, C) super conservative; and 5 points D) regular, E) conservative; F) super conservative. Mechanisms from species and reactions reduction with 4 points G.

Table 2 - Characteristics of the reduced mechanisms obtained in the merging step.

Mechanism /Properties	Reduction Type	N of used points	Criteria Name	N reactions	N Species	Average error (%)	Computational time reduction (%)
A	Species	4	Regular	1182	95	3.1	49.6
B			Conservative	1423	99	2.9	46.0
C			Super Cons.	1776	109	0.3	38.3
D		5	Regular	1202	96	1.5	49.0
E			Conservative	1423	99	2.9	46.3
F			Super Cons.	1778	109	0.2	38.1
G	Species + Reactions	4	Regular	298	111	6.7	55.7
H			Conservative	362	116	3.0	42.1
I		5	Regular	322	113	4.3	55.2
J			Conservative	476	116	0.8	52.9
Reference	-	-	-	4533	166	-	-

It is clear from the analysis of the Figure 7 that for the cases where the central operating condition is not considered, the higher values of the error are located for operating conditions close to the ones associated with that point, with the error generally decreasing when approaching minimum or maximum boundaries of both temperature and steam to biomass ratio. From the general analysis of all six mechanisms resulting from species reduction (Figures 7A-F), it can be concluded that when using more conservative approaches, which originates the merge of the mechanisms with higher number of reactions, the mechanisms obtained with or without the inclusion of the central operating point tend to be very similar or even equal. The previous conclusion is supported by the similarity of the remaining studied parameters (number of reactions, number of species and computational time) for the mechanisms obtained through the conservative and super conservative approaches, listed in Table 2. Therefore, the influence of the central point is only visible in Figure 7 for the mechanisms with lower number of reactions (Figure 7A,D, Figure 7G,I, Figure 7H,J).

Similar conclusions were found between the mechanisms originated from the species reduction (Figures 7A-F) and the ones originated from the reduction of both species and reactions (Figures 7G-J). However, it can be identified a higher influence of the central point in the behavior of the final reduced mechanisms obtained through species and reactions reduction. This sustains the conclusion previously stated that the higher the number of reactions of the merged mechanisms (and, therefore, of the final mechanism), the higher the similarities between mechanisms obtained using the same selection criteria with and without the consideration of the central point of operating conditions.

In Table 2 it is shown the reduction of the computational time obtained when using the

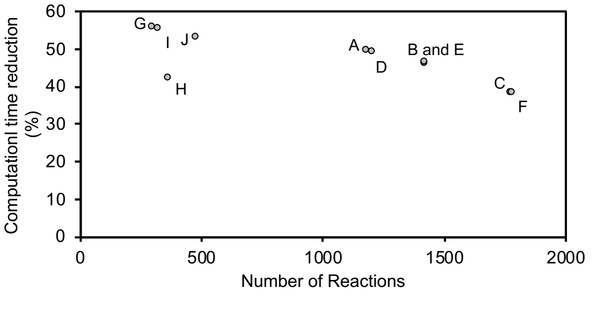

Figure 8 - Computation time (%) as a function of the number of reactions.

reduced mechanisms compared to the original mechanism. It can be identified reductions up to 55.71 % on the computational time. Due to the low mean error values associated with mechanisms D, C, F and J, shown in Figure 7, it is possible to consider these mechanisms the most viable alternatives to the initial detailed mechanism when predicting the secondary gas-phase reactions that occur during biomass gasification. Analyzing Figure 8, it can be concluded that the reduction of computational time increases as the number of reactions decrease, which is what it was expected, with the exception being mechanism H. This exception may be due to different reaction paths that occur during the gasification process in this mechanism, which leads to a higher time for the CVODE solver [13] implemented in the numerical tool used in this work to conclude its calculations. A very good result was found for mechanism J which presents not only a very low number of reactions and a very low error values for all sets of operating conditions, but also a very high percentage of computational time reduction (52.91%).

4. Conclusions

The main conclusions that can be withdrawn from this work are the following:

- The reduction methodology applied in this work is found to effectively reduce the reference mechanism, obtaining reduced mechanisms capable of accurately predicting the behavior of the reference mechanism together with significantly reducing the computational time, which are the cases of mechanisms C, D, F and J.
- The remaining mechanisms retain the essential characteristic features of the reference mechanism, but are not able to predict with a very high precision the release rate curves of the major non-condensable gases (H_2, CO and CO_2) for some operating conditions;
- The errors obtained for the mechanism in the interest region have an near-exclusive contribution of the magnitude of the release rate peaks, with the yield values and the location of those peaks presenting very identical values to the ones obtained with the reference detailed mechanism;
- The consideration of operating conditions located at the interior of the parametric domain in the merging step of the reduction process generally leads to the construction of mechanisms better suited to predict the mechanism behavior for the entire range of operating conditions when compared to the mechanism built from the merge of reduced mechanism obtained using only boundary operating conditions.
- A tendency of mechanisms with lower number of reactions presenting higher errors is verified. However, the presence of a small minority of mechanisms that do not respect this tendency reveals the absence of a full linearity regarding the aforementioned relation when using this reduction method;
- The computational time decreases with the decrease of the number of reactions, with the reduction being more significant the higher the number of reactions of the mechanisms compared;
- Different rection paths for different operating conditions and different mechanisms can cause of a higher difficulty in the prediction of the mechanism’s behavior for those same operating conditions and the raise in computational time, respectively;
- One can highlight that in order to obtain a suitable reduced mechanism able to predict the

reference mechanism's behavior, the mechanism reduction procedure strongly depends on the following main aspects: the selection criteria used to select the reduced mechanisms to be merged, the choice of the operating conditions to represent the parametric domain boundaries and the addition of operating conditions at the interior of the parametric domain.

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