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Automated Advanced Calibration and Optimisation of Thermochemical Models Applied to Biomass Gasification and Pyrolysis

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Table of Contents graphic. Schematic of statistical analysis workflow used for (1) model calibration and (2) process optimisation.

KEYWORDS Physico-chemical modelling, statistical analysis, biomass pyrolysis and gasification, parameter estimation, uncertainty propagation, and optimisation.

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ABSTRACT This article presents a methodology that combines physico-chemical modelling with advanced statistical analysis algorithms as an efficient workflow which is then applied to the optimisation and design of biomass pyrolysis and gasification processes. The goal was to develop an automated flexible approach for the analyses and optimisation of such processes. The approach presented here can also be directly applied to other biomass conversion processes, and in general to all those processes for which a parameterised model is available. A flexible physico-chemical model of the process is initially formulated. Within this model, a hierarchy of sensitive model parameters and input variables (process conditions) is identified, which are then automatically adjusted to calibrate the model and to optimise the process. Through the numerical solution of the underlying mathematical model of the process we can understand how species concentrations and the thermodynamic conditions within the

reactor evolve for the two processes studied. The flexibility offered by the ability to control any model parameter is critical in enabling optimization of both efficiency of the process as well as its emissions. It allows users to design and operate feedstock-flexible pyrolysis and gasification processes, accurately control product characteristics, and minimise the formation of unwanted by-products (e.g. tar in biomass gasification processes) by exploiting various productivity-enhancing simulation techniques such as parameter estimation, computational surrogate (reduced order model) generation, uncertainty propagation and multi-response optimisation.

INTRODUCTION An alternative and sustainable way of producing energy, fuels and chemicals with low, zero or negative carbon emissions and meeting the total global demand is crucial for providing the security of future supply long after the conventional fossil fuels run out. Biomass gasification and pyrolysis can ensure this due to feedstock sustainability, inherent carbon neutrality and ability to potentially achieve negative emissions when coupled with carbon capture and sequestration (CCS) technologies [1] [2].

A large number of biomass feedstocks, including energy crops, wastes and wood pellets, can be transformed into energy, biofuels and other chemicals via two main conversion routes, thermochemical and biological. The thermochemical route is more flexible in terms of the feedstocks that can be used and, when compared to the biological route, its products are also more compatible with those of existing petroleum refining operations (transport fuels and feedstock chemicals) [3]. Thermochemical conversion processes include direct combustion, pyrolysis and gasification. As mentioned earlier, this article will focus on two of these processes, namely pyrolysis and gasification.

During pyrolysis, the biomass is thermally degraded by heat in the absence of oxygen at lower temperatures compared to those used for direct combustion and gasification. From the degradation of the biomass, charcoal, bio-oil (or pyrolysis oil) and fuel gas are produced. Bio-oil can be used as fuel in boilers, internal combustion engines or gas turbines [4].

Gasification occurs when partial oxidation of biomass at elevated temperatures is carried out. Oxidation reactions takes place in the biomass gasifier at temperatures between 700-1400°C. The primary product in this case is a mixture of gases, also known as syngas or producer gas, primarily composed of H_2 , CO, CO_2 and CH_4 . Syngas can be converted into fuels, including H_2 , Fischer-Tropsch diesels and synthetic gasoline, as well as widely used chemicals such as methanol and urea [3] [5].

To promote these processes, cost-effective, low-emission and more optimally efficient technologies are required. One of the main challenges in biomass conversion processes like gasification and pyrolysis is to understand how operating conditions and feedstock composition affect the reactions within the process and, therefore, the product specifications [3]. Some of the main difficulties encountered when trying to model these correlations include the fact that biomass feedstock is often neither completely known nor homogeneous [6], the intrinsic reaction pathway of the pyrolysis reactions, central to the overall biomass thermal treatment process, are complex and not fully understood, and multiscale phenomena take place within the reactor [7]. Thus, it is important to gain a better understanding of the role of the feedstock components (composition) and the chemical reaction pathways as a function of the process operating conditions in order to evaluate operating efficiencies and emissions as a predictive output.

In optimally exploiting the flexibility and supply security offered by various biomass feedstocks and the intrinsic advantages in terms of the low CO₂ footprint of biomass gasification and pyrolysis technologies, digital engineering has a vital role to play as a key enabler in accelerated cost-effective technology development and TRL progression [8] [9] [10] [11] [12]. The use of high-fidelity physico-chemical model, the ability to rapidly calibrate such a model, and to apply it in a user-friendly workflow to gain insight into a process and the associated optimisation trade-offs, which is the purpose of the work presented here, provide an effective and robust strategy to tackle and address some of the gaps in the current understanding, listed above. Furthermore, optimal design and advanced process control will allow us to achieve the feedstock flexibility, and product yield and quality, that are necessary in order to make biomass pyrolysis and gasification processes to be exploited widely. Note that the current system level TRLs for both biomass pyrolysis as well as for biomass gasification processes with standard biomass feedstocks can be considered to be at moderately high level of 7. Further optimisation and process design to effectively account for the variability in biomass feedstocks, will contribute to advancing the TRLs to fully commercial (including competitive manufacturing) levels of 8 to 9 [2].

Considerable effort has been spent in formulating suitable models for the intrinsically complex biomass pyrolysis and gasification processes and in identifying kinetic model parameters, optimal reactor design, and operating conditions. Kinetic and process parameters have been identified either through experimental [13] [14] [15] or numerical modelling [16] [17] approaches. Much less work has been done in the field of advanced statistical analysis, automated model calibration, uncertainty propagation and model-based process optimisation [18] [19].

The present work attempts at addressing these gaps by combining physico-chemical models with statistical analysis in the form of “integrated workflows” to enable simulation engineers to effectively analyse high-dimensional parameter space that is typically encountered in design and optimisation of thermochemical processes such as biomass pyrolysis and gasification. The workflows developed in this work have been designed to be applicable even when the measurements data is not plentiful, which is typically the case for commercially sensitive industrial processes or where TRLs are low. The paper considers simulation and analysis of the following two processes:

- a) The biomass pyrolysis process using a reactor model with detailed chemical kinetic description in order to account for the varying biomass feedstock composition. The detailed chemical kinetic model is reduced to a skeletal scheme in order to lower the computational expense, whilst capturing the behaviour and pathways of the key chemical species. Both the chemical schemes are employed within a reactor model which is coupled with a statistical analysis toolkit, the combination termed as an integrated workflow, and is applied to calibrate the skeletal chemistry model on the basis of the comparison of the species evolution between the model and the data from a variety of experiments reported in the literature.
- b) A dedicated biomass gasification process that involves a multi-zonal reactor model with a reduced chemical kinetic description embedded within the statistical workflow, which is then applied to improve the model via parameter estimation, perform global sensitivity analysis, uncertainty propagation and finally, process optimisation. Again, in the second example, a variety of biomass feedstocks are considered.

The paper is organised as follows: The introduction section is followed by the description of the two physico-chemical models developed for biomass pyrolysis and biomass gasification applications respectively. The integrated workflow comprising these models together with the statistical algorithms is then presented. The results and discussion section describes the results of the integrated workflow applied to the two applications, and conclusions are drawn at the end.

MODELS AND WORKFLOW DESCRIPTION

For the biomass pyrolysis application, two commercial software toolkits developed by CMCL Innovations were used. The *kinetics & SRM Engine Suite* (hereafter referred as *kinetics*) software [20] that offers a suite of reactor models derived from first principles together with a statistical model development toolkit [21] has been used. The *kinetics* software has been widely applied elsewhere for the development of chemical kinetic schemes (fuel reformation, oxidation and emissions pathways [22] [23] [24] [25], as well as the modelling of organic [26] [27] and inorganic [28] nanoparticles synthesis. The library of the reactor models within the *kinetics* software contains sub-models to simulate heat transfer, chemical kinetics, turbulent mixing and injection of chemical species. In particular, the detailed chemical kinetic description entails significantly large number of chemical species that are required to describe the chemical pathways and interactions as a function of operating conditions such as temperature, pressure, as well as the composition of the feedstock and the oxidiser. At the same time, the number of species needs to be reasonable in order to avoid excessively high computational expense (stiff ordinary differential equation systems). In such cases, chemical mechanism reduction techniques are applied to reduce the detailed scheme to a skeletal one which is computationally efficient (tractable) and which still accounts for the evolution of the

key chemical species for the given operating conditions. To mimic the role of feedstock variability and flexibility and the associated emissions (including intermediates such as unburned hydrocarbons and carbon monoxide) within a process simulation, using either detailed or skeletal chemical mechanisms becomes essential. A single global chemical reaction between a feedstock and an oxidizer fails to account for these effects. For the first application, the biomass pyrolysis kinetic scheme developed by Ranzi et al. [29] was used. It defines the biomass as a mixture of three key components: cellulose, hemicellulose and lignin. These components can be mixed in different proportions depending on the type of biomass (e.g. softwood, hardwood, etc.). The model provides a lumped kinetic scheme describing the devolatilisation of these components, and the decomposition of the solid into permanent gases, condensable vapours (tars) and solid residues (char). The detailed kinetic scheme is completed by the mechanism for the secondary reactions of the released gas-phase species. A constant pressure homogeneous batch reactor model within the *kinetics* software was used to simulate the biomass pyrolysis process. Furthermore, the physico-chemical model was coupled with a commercial software, Model Development Suite (MoDS), also developed by CMCL Innovations, to form a model-based engineering workflow.

The reactor model setup and process conditions were defined in *kinetics*, which were then considered by MoDS to perform parameter estimation (model calibration). The post-processing part of the integrated workflow was also used to represent the dynamic evolution of both model inputs and calibrated parameters, as well as results from the model calibration (as well as other workflow functions such as sensitivity analysis, uncertainty propagation, etc.). A schematic of the workflow used for model calibration is presented in **Scheme 1**. Any model parameter available to *kinetics* can be estimated using MoDS via the workflow. MoDS

provides recommended calibration settings and can validate settings that the user customises. Experimental data can be read directly from DSV (delimiter separated values), for example CSV files, or XML files. MoDS automatically interpolates profile data to compare model and experimental data sampled at different times or reactor lengths [30].

In case of the second application involving biomass gasification, a four-zone (namely drying, pyrolysis, oxidation and reduction zones) integrated 1D kinetic model (written in Matlab) of a biomass downdraft gasifier, was used. The model enabled the investigation of the effect of inputs such as the moisture content, and air-to-fuel ratio as a function of the gasifier operating conditions and design specifications for each zone. The model output included the composition and tar content of the producer gas. Individual chemical kinetic schemes were used for each zone of the gasifier to describe the key stages of biomass drying, pyrolysis, oxidation and reduction [31] [32]. Similar to the first application, the physico-chemical Matlab-based model was combined with MoDS and the integrated workflow was applied to perform parameter estimation, sensitivity analysis, uncertainty propagation as well as process optimization to minimize the tar content and increase the heating value and yield of the syngas.

Scheme 1. MoDS-kinetics workflow for model calibration.

MoDS is a statistical analysis software that finds use in a number of applications, including parameter estimation [2] [33] [34] [35], optimal design of experiment, global sensitivity and uncertainty propagation analysis [36] [37], and process optimisation. MoDS uses a suite of numerical and statistical analysis algorithms to gain insight from external models, simulators or CAE (Computer Aided Engineering) toolkits, treating them as black boxes. Results from these analyses can be used to identify trends and improve predictions based on the original model [38]. In this work, MoDS was used to calibrate both the biomass gasification and pyrolysis models against existing experimental data. With the biomass gasification model, it was also used to perform sensitivity and uncertainty propagation analyses as well as the optimization of a biomass downdraft gasification system.

The calibration stages involved minimizing the sum of square residuals between the outputs of the model and the corresponding experimental values. The optimisation of the biomass gasification process was carried out in a similar way with the amount of tar being produced, as calculated from the model, being minimised by varying the process conditions of the model. Both of these processes were performed using Hooke and Jeeves' "direct search" method [39]. This algorithm was chosen out of the selection available in the MoDS software because it has previously been shown to work well when used to calibrate chemical-kinetic models [40].

The sensitivity analysis of the biomass gasification model was performed by calculating the global variation in the output variables due to each of the model parameters [41]. This was done by fitting HDMR (High Dimensional Model Representation) [42] [43] response surfaces to the model. To improve the accuracy of the response surface models the design of experiment used to fit them was generated from a Sobol' sequence [44]. The global

sensitivity (overall contribution to variance) of each model parameter, and the interactions between pairs of parameters, are proportional to, and can be directly inferred from, the coefficients of the response surface.

MoDS interface with models in *kinetics* and in Matlab: MoDS is designed to be a highly flexible software that simplifies model development using an advanced suite of numerical and statistical tools. The models can take different forms, including virtually any executable that can be run from the command line and reads its inputs and outputs from a file. Thus, MoDS treats client software toolkits or processes such as *kinetics*, Matlab, etc. as a “black-box”, and utilizes the built-in algorithms, for example, parameter estimation, surrogate generation, process optimisation, etc. to better inform the simulation engineers (**Scheme 2**).

Scheme 2: MoDS interface with models in *kinetics* and Matlab.

RESULTS AND DISCUSSION

This section contains the results of the integrated workflow applied to the biomass pyrolysis and biomass gasification applications.

Biomass pyrolysis application: The first step for the biomass pyrolysis system was to assess the accuracy of simulations that used the detailed chemical kinetic scheme developed by Ranzi et al. [29]. To do this thermogravimetric (TG) data were taken from the heated wire mesh reactor studies of Milosavljevic and Suuberg [45], who assessed cellulose pyrolysis as a function of different heating rates. The simulations were conducted in *kinetics* using a constant pressure homogeneous batch reactor model with an imposed temperature profile. It was assumed that at the beginning of the process only cellulose was present ($Y_{\text{cell}} = 1.0$). Figure 1 shows the simulation results when a heating rate of 5 K/min is used. It can be seen that a good agreement with the experimental data was obtained, when combining the detailed mechanism from Ranzi et al. [46] [47] and the model developed in *kinetics*.

Figure 1. Non-isothermal thermogravimetric curves for the pyrolysis of cellulose in inert gas - model predictions (line) and experimental data (points) [45].

We then sought to improve the match with the experimental data via parameter estimation but could not calibrate for all of the coefficients of the more than 20,000 reactions found in the detailed mechanism. To make this task tractable, the key chemical reactions for our system were identified by performing a mechanism reduction. The Directed Relation Graph with Error Propagation (DRGEP) [48] reduction technique, available in *kinetics*, was used to produce a hierarchy of reduced models from which the one that contained the fewest number of species and reactions whilst staying sufficiently faithful to the detailed (baseline) mechanism was selected. Each node in a DRGEP represents a species in the detailed mechanism, while the edges and their thickness represent the importance of these species relative to the initially selected target species. The target species are the ones that are retained

in the reduced mechanism. By using the DRGEP technique, and setting an adequate error threshold, a variety of possible scenarios were evaluated and the original detailed chemical mechanism containing 20,000 reactions [46] [47], was reduced to a skeletal mechanism containing 19 key reactions. Furthermore, the MoDS-kinetics workflow was used to perform the calibration of the frequency factor of just these 19 reactions. The evolution of the reactant (in this case, cellulose) as a function of the temperature using the detailed chemical mechanism and the calibrated reduced skeletal is depicted in Figure 2. Improved agreement between the skeletal model and the measurements data was obtained. The original and the modified values (as a result of the parameter estimation) of these 19 frequency factors are reported in Table 1.

Levoglucosan (LVG) and hydroxyacetaldehyde (HAA) are two of the major products of cellulose pyrolysis. Piskorz et al. [49] measured yields of these species produced during pyrolysis of a microcrystalline cellulose (Avicel pH-102) at different temperatures and at an average residence time in the reactor of 0.5 seconds. The moisture content was set to $Y_{H_2O} = 2.9\%$ [49]. The simulation duration was set equal to the average experimental residence time. The comparison of the LVG yields from measurements and the simulation data using the original detailed chemical model and the calibrated skeletal model with the frequency factors from Table 1, are presented in Figure 3. It can be seen that an improved agreement with the experimental data was achieved when using the calibrated reduced chemical model.

Figure 2. Non-isothermal thermogravimetric curves for the pyrolysis of cellulose in inert gas – original model (sim – kinetics) versus calibrated model (sim – workflow) predictions (points represent experimental data [45]).

Figure 3. Yield of Levoglucosan from the pyrolysis of microcrystalline cellulose (Avicel pH-102) – original model (sim – kinetics) versus calibrated reduced model (sim – workflow) predictions (points represent experimental data [49]).

Similar agreement was also observed when implementing the workflow to more complex systems. García-Pérez et al. [50] produced TG curves for softwood bark residue and hardwood rich in fibres at different heating rates under nitrogen. Softwood and hardwood can be described as a combination of cellulose, hemicellulose and lignins of specified composition [51]. Following this strategy and using the van Krevelen diagram to compute the feedstock composition from its elemental analysis [46], the thermal decomposition of softwood and hardwood was simulated. Some of these results with softwood as the feedstock are shown in Figure 4. In this specific case, a heating rate of 60 K/min was imposed. The original detailed model reproduced the experimental results well, however, the calibrated reduced skeletal scheme was capable of improving the agreement with the measurements.

Table 1. Key reactions from the mechanism of Ranzi et al. [46] [47] with original and calibrated frequency factors.

Reaction	Original Frequency Factor	Calibrated Frequency Factor	Unit of measure
CELLA $\rightarrow$ 5E-2*H ₂ + 0.93*H ₂ O + 0.61*CO + 0.36*CO ₂ + 0.3*CH ₂ O + 2E-2*HCOOH + 0.15*CH ₃ OH + 5E-2*C ₂ H ₂ O ₂ + 0.15*CH ₃ CHO + 0.4*C ₂ H ₄ O ₂ + 0.35*C ₂ H ₅ CHO + 5E-2*C ₃ H ₆ O ₂ + 0.25*C ₆ H ₆ O ₃ + 0.61*CSOLID + 0.2*H ₂ (S) + 5E-2CH ₄ (S)	2.50E+06	7.91E+02	1/s
CELLA $\rightarrow$ C ₆ H ₁₀ O ₅	3.30E+00	1.04E+03	1/K/s
CELL $\rightarrow$ 5*H ₂ O + 6*CSOLID	6.00E+07	6.00E+08	1/s
HCE1 $\rightarrow$ 0.4*H ₂ O + 0.16*CO + 0.12*C ₂ H ₂ O ₂ + 0.2*C ₃ H ₆ O ₂ + 0.2*C ₅ H ₄ O ₂ + 0.6*C ₅ H ₈ O ₄ + 8E-2*H ₂ (S)	3.00E+00	3.00E+02	1/K/s
HCE1 $\rightarrow$ 0.4*H ₂ O + 0.69*CO + 0.79*CO ₂ + 0.3*CH ₂ O + 5E-2*HCOOH + 0.875*CSOLID + 1E-2*CO ₂ (S) + 1E-2*CO(S) + 0.9*COH ₂ (S) + 0.35*H ₂ (S) + 0.625*CH ₄ (S) + 0.375*C ₂ H ₄ (S)	1.80E-03	1.80E-06	1/K/s
HCE2 $\rightarrow$ CSOLID + 0.2*H ₂ O + 0.275*CO + 0.275*CO ₂ + 0.4*CH ₂ O + 2.5E-2*HCOOH + 5E-2*C ₂ H ₄ O ₂ + 0.35*CH ₃ COOH + 0.1*C ₂ H ₅ OH + 0.3*CO ₂ (S) + 0.725*COH ₂ (S) + 0.25*CH ₄ (S) + 0.3*CH ₃ OH(S) + 0.225*C ₂ H ₄ (S)	5.00E+09	1.58E+10	1/s
LIGC $\rightarrow$ H ₂ O + 0.32*CO + 0.3*CH ₂ O + 0.41*C ₂ H ₄ + 8E-2*C ₆ H ₅ OH + 0.1*C ₉ H ₁₀ O ₂ + 5.735*CSOLID + 0.35*LIGCC + 0.7*COH ₂ (S) + 0.495*CH ₄ (S)	1.00E+11	1.00E+14	1/s
LIGCC $\rightarrow$ H ₂ + 0.7*H ₂ O + 1.4*CO + 0.65*CH ₄ + 0.6*C ₂ H ₄ + 0.35*C ₂ H ₄ O ₂ + 0.2*C ₆ H ₅ OH + 0.3*C ₉ H ₁₀ O ₂ + 6.75*CSOLID + 0.4*CO(S)	1.00E+04	1.00E+06	1/s
LIGOH $\rightarrow$ H ₂ O + 0.65*CO + 5E-2*CO ₂ + 5E-2*HCOOH + 0.1*CH ₄ + 0.6*CH ₃ OH + 0.1*C ₂ H ₃ CHO + 2.5E-2*C ₂ H ₂ O ₂ + 4.25*CSOLID + 0.9*LIG + 0.6*CO(S) + 0.85*COH ₂ (S) + 5E-2*H ₂ (S) + 0.35*CH ₄ (S) + 0.3*CH ₃ OH(S) + 0.2*C ₂ H ₄ (S)	1.00E+08	1.00E+07	1/s
LIG $\rightarrow$ 0.3*CO + 0.3*CH ₃ CHO + 0.3*C ₆ H ₅ OCH ₃ + 0.7*C ₁₁ H ₁₂ O ₄ + 0.3*CO(S)	4.00E+00	4.00E+01	1/K/s
LIG $\rightarrow$ 6*CSOLID + 2*COH ₂ (S) + 0.6*H ₂ O + 0.4*CO + 0.4*CH ₂ O + 0.2*CH ₄ + 0.2*CO(S) + 0.4*CH ₄ (S) + 0.4*CH ₃ OH(S) + 0.5*C ₂ H ₄ (S)	8.30E-02	8.30E-06	1/K/s
LIG $\rightarrow$ C ₂ H ₄ + 0.6*H ₂ O + 2.6*CO + 0.4*CH ₂ O + 1.1*CH ₄ + 0.4*CH ₃ OH + 4.5*CSOLID	1.00E+07	1.00E+03	1/s
CO ₂ (S) $\rightarrow$ CO ₂	1.00E+06	3.16E+06	1/s
CO(S) $\rightarrow$ CO	5.00E+12	5.00E+14	1/s
COH ₂ (S) $\rightarrow$ H ₂ + CO	1.50E+12	1.50E+14	1/s
H ₂ (S) $\rightarrow$ H ₂	5.00E+11	5.00E+13	1/s
CH ₄ (S) $\rightarrow$ CH ₄	5.00E+12	5.00E+15	1/s
CH ₃ OH(S) $\rightarrow$ CH ₃ OH	2.00E+12	6.32E+14	1/s
C ₂ H ₄ (S) $\rightarrow$ C ₂ H ₄	5.00E+12	5.00E+15	1/s

Figure 4. Non-isothermal thermogravimetric curves for the pyrolysis of softwood in nitrogen – original model (sim – kinetics) versus calibrated model (sim – workflow) predictions (points represent experimental data [50]).

Biomass gasification application: For this study, a 1D model originally developed by Salem and Paul [31] for a biomass downdraft gasifier was used. This is computationally non-intensive, robust and flexible thermochemical model that has been validated against a number of experimental results for different feedstocks. Initially, global sensitivity analysis and uncertainty propagation studies were performed on the model by applying the MoDS software. Some of the results from this study are presented in Figure 5 and Figure 6. Acronyms used in these figures are listed and explained in Table 2.

Only a selected limited number of results are presented here. The results presented in Figure 5 and Figure 6 were produced using Neem, with a 20% moisture content, as the feedstock [52]. A representative number of other samples were also studied, including bamboo, rubber wood, wood pellets, wheat straw and wood chips. The results from the studies carried out on all these samples were combined to identify the more sensitive inputs and uncertain outputs in the 1D model.

Figure 5 demonstrates the strong influence of the temperature of the drying zone on the fraction of hydrogen in the syngas and the tar content. The application of MoDS also shows how the diameter of the pyrolysis zone predominantly influences the power output of the gasification unit. These and other conclusions often cannot be directly inferred from a model without the aid of such advanced statistical analysis algorithms, which is the approach followed and promoted by the present work.

Figure 5. Global sensitivities of key outputs to input variables and model parameters for the biomass downdraft gasifier [31].

Figure 6 also shows that, for example, any uncertainty in the characterisation of the biomass feedstock substantially affects some important outputs and design parameters of the gasifier. In particular, we can see how the carbon content of the feedstock has a strong influence on the throat diameter of the downdraft gasifier. The relatively large number of interconnected terms contributing to the overall uncertainty of the outputs shows that many of the decision variables used by the model are strongly correlated. For example, the contributions of the combination of carbon and sulfur in the feedstock and that of carbon and oxygen in the

feedstock to the overall fraction of CO₂ in syngas are estimated at 7%, whereas the combination of carbon content of the feedstock and equivalence ratio is quantified to contribute at 5%.

Figure 6. Contribution of selected decision variables to key outputs uncertainties for the biomass downdraft gasifier [31].

Sensitivity analysis and uncertainty propagation studies were performed on the model to identify those model parameters, including reactions rate parameters, and decision variables that have the strongest effect on the model outputs. Similar to the previous biomass pyrolysis application, the model was initially calibrated against existing experimental data and the

calibrated model was benchmarked with the original model performance. A comparison between the simulation results from the original and the calibrated model is presented in Figure 7. Table 3 presents the full set of calibrated parameters that were used to generate the results shown in Figure 7. The experimental results deal with a wide variety of biomass with elemental composition ranging between, $38\% \leq C \leq 52\%$, $5.5\% \leq H \leq 7\%$, and $36\% \leq O \leq 45\%$. Other inputs such as moisture content, equivalence ratio and particle diameter were also varied in the experiments. The reasonably good agreement as shown in Figure 7 proves the ability of the 1D model to simulate wide range of biomass feedstocks.

Table 2. 1D model parameter acronyms [31].

Acronym	Parameter
C	Carbon in feedstock
H	Hydrogen in feedstock
O	Oxygen in feedstock
S	Sulphur in feedstock
ER	Equivalence ratio
h	Moisture content
T01	Initial temperature of feedstock
HR1	Heating rate in drying zone

Td	Drying temperature
Ed, Ad	Kinetic parameter for drying process
A1,2, 3, 4	Pre-exponential multipliers for reduction reactions
E1, 2, 3, 4	Activation energy for reduction reactions
T	Reduction zone temperature
Tar1, 2, 3	Multipliers for tar concentration in pyrolysis and oxidation models
char	Multipliers for char concentration in pyrolysis models
PO	Power Output

Finally, the calibrated model was used to optimise the process via MoDS. Major targets considered in this study were the minimization of undesired by-products (e.g. tar), the maximization of the syngas yield and heating value, and the production of specified composition for the syngas (e.g. specific CO/H₂ ratio for implementation of the syngas as chemical feedstock, or maximization of the H₂ ratio in the syngas for hydrogen separation and purification). Optimisation routines used in MoDS include the Hooke and Jeeves direct search solution method, the Metropolis-Hastings algorithm, the truncated Newton method and the COBYLA (Constrained Optimisation by Linear Approximation) algorithm.

Results from a multi-response optimisation aimed at minimizing the tar content, as well as the fraction of CO₂ and CH₄ (undesired, for example, in H₂ refinery or Fischer-Tropsch

processes), are presented in Figure 8. Initial and optimised process conditions and design specifications for the 20 kW downdraft gasifier are reported in Table 4. The optimisation routine (Hook and Jeeves method, for the particular example shown here) was able to effectively identify a set of optimal conditions and design details leading to a considerable improvement of the syngas quality.

Figure 7. Comparison of syngas composition as simulated by the original model of Salem and Paul [38] and its calibrated version (MoDS workflow) versus experimental results for different feedstocks [48] [49] [47].

Acronym	Model parameter	Unit	Initial value	Calibrated value
Ed	Activation energy - drying	kJ/mol	88	90.75
Ad	Frequency factor - drying	s-1	5.13E+05	5.24E+10
A1	Frequency factor - reduction (R1)	s-1	36.16	35.715
A2	Frequency factor - reduction (R2)	s-1	1.52E+04	1.51E+04
A3	Frequency factor - reduction (R3)	s-1	4.19E-03	4.24E-03
A4	Frequency factor - reduction (R4)	s-1	7.30E-02	7.42E-02
E1	Activation energy - reduction (R1)	kJ/mol	77.39	77.87
E2	Activation energy - reduction (R2)	kJ/mol	121.62	121.62
E3	Activation energy - reduction (R3)	kJ/mol	19.21	19.12
E4	Activation energy - reduction (R4)	kJ/mol	36.15	35.303

Table 3. Calibrated model parameters (Arrhenius coefficients for the chemical kinetic mechanism) [38].

Figure 8. Optimised process outputs (minimisation of tar content and undesired by-product (CO₂ and CH₄) fractions in the syngas) for a 20 kW biomass downdraft gasifier.

Table 4. Initial and optimal values of operating conditions and design specifications for a 20 kW biomass downdraft gasifier.

Parameter	Unit	Initial	Optimal
Equivalence ratio	-	0.3	0.44
Power output	kW	20	22.4
Temperature of the drying zone	K	400	470
Heating rate in drying zone	K/s	20	16.5
Temperature of the pyrolysis zone	K	873	873
Temperature of the reduction zone	K	1350	1139
Height of the drying and pyrolysis zone	cm	57.14	57.14
Height of the oxidation zone	cm	10.09	12.36
Diameter of the pyrolysis zone	cm	20.17	24.71
Throat diameter	cm	5.76	7.06
Area of air injection	cm ²	2.35	3.52
Air injection diameter	cm	16.14	19.77

CONCLUSIONS

Multiple aims entailing, rapid and cost-effective technology development, the design of flexible processes that efficiently transform different types of biomass, including wastes, into a number of products (e.g. electricity, fuels and chemicals), while simultaneously reducing pollutant emissions and unwanted by-products, can all be effectively achieved through the implementation of integrated digital engineering workflows. These requirements, coupled with the complexity and uncertainty of the chemistry for biomass pyrolysis and gasification, the variability and unpredictability of biomass feedstock characteristics, and the strong sensitivity of the product yields and quality to changes in the operating conditions, have proven challenging in the past and have led to a limited exploitation of biomass pyrolysis and gasification technologies. These biomass-based technologies are considered to play a vital role in achieving the sustainability of energy supply and industrial decarbonisation. An integrated digital engineering workflow comprising detailed physico-chemical models and advanced statistical algorithms was applied to these biomass-based processes in an attempt to simultaneously solve the multiple challenges listed above. Process insight was obtained through global sensitivity analysis and uncertainty propagation studies. By using flexible and non-computationally expensive mathematical models, we were able to achieve detailed system understanding, perform robust model calibration, and identify optimal design specifications and operating conditions for the technologies studied here in time frames compatible with those required by practical industrial applications. The digital framework demonstrated in this study is generic and easily applicable to a wider range of process engineering problems.

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