FROM EQUILIBRIUM TO KINETIC MODELLING: THE GASIFICATION OF APPLE PRUNING RESIDUES IN A SPOUTED BED REACTOR

Filippo Marchelli[1]*, Cristina Moliner[2], Marco Baratieri[1], Barbara Bosio[2], Elisabetta Arato[2]
[1] Free University of Bozen-Bolzano, Faculty of Science and Technology, 39100 Bolzano, Italy
[2] University of Genova, Department of Civil, Chemical end Environmental Engineering, 16145 Genova, Italy
*corresponding author: fmarchelli@unibz.it

ABSTRACT: Biomass gasification is especially interesting when it is applied to low-value agricultural residues. This approach is still not widely established, and modelling activities may offer some useful insights for its optimisation. However, due to the complexity of the process, most of the activity has focused on equilibrium models, which have limited reliability. In this work, we focused on the gasification of apple pruning residues in a spouted bed reactor. Spouted beds feature good mixing properties and high heat and mass transfer rates. Hence, they are suitable to process irregular biomass residues. Moreover, the low diffusional limitations result in a good applicability of the TGA data. We simulated gasification experiments with the commercial program Aspen Plus, including a simplified kinetic mechanism. The results confirm the validity of applying the TGA data to spouted beds, and shows that this simple kinetic scheme allows overcoming the limitations of more classic approaches.
Keywords: agricultural residues, Aspen Plus, gasification, model.

1 INTRODUCTION

Gasification is one of the processes through which carbonaceous materials can be converted into energy or chemicals. It takes place at high temperatures, and operates the conversion through a gaseous agent: usually air, but in some cases CO_2 or steam. In the case of air, its mass flow rate must be a fraction of one required for stoichiometric combustion of the material. When gasification is applied to biomass, the process is carbon neutral and can generate renewable energy [1]. This has fostered the exploitation of gasification, which is now a very popular technology, abundantly studied by researchers and already applied on a commercial scale [2]. However, most commercial applications operate with wood chips or pellets. To enhance the environmental and economic merit of the process, it should be applied to agricultural residues. These are very abundant and constitute a cost and an environmental impact that farmers have to deal with [3]. Several studies have proved that they can be successfully gasified, thus generating energy [4,5]. Most of these studies deal with lab-scale devices, and further studies are necessary to optimise the technology and apply it on an industrial level, completely fulfilling the potentials of the circular economy principles.

In the framework of the optimisation of a technology, modelling is a critical activity that should always be undertaken. Accurately modelling a process permits to gain a more in-depth understanding of the underlying phenomena, allowing their optimisation without the need of performing costly and time-consuming experiments. Regarding gasification, modelling is a debated aspect among researchers, because the intricate structure of biomass and the extensive number of chemical reactions complicate the development of phenomenological models. A very common approach is to perform equilibrium calculations [6–8]: as the name suggests, the inclusion of the complex reactions' kinetics is thus avoided. However, since gasifiers practically never reach the chemical equilibrium, this approach fails to provide a realistic description of the process output, and can only give information on the theoretical maximum yield of the process [9]. Most notably, equilibrium models always predict the complete conversion of the initial biomass and of the char, with no solid material leaving the reactor (apart from ash). In reality, the carbon conversion is never total and the output char constitutes about 2 to 5 % of the initial biomass. Sometimes, in these cases, researchers employ methods to stop the reactions from reaching the theoretical equilibrium, such as by creating a by-pass or by performing the equilibrium calculations at a different temperature [10]. Given the empirical nature of these methods, the research should move towards the inclusion of the reaction kinetics in gasification models.

The whole scheme involves a high number of complex reactions, and few researchers have developed complete approaches [11–14]. Every scheme starts with the decomposition of biomass, which is the first reaction that the biomass undergoes. The decomposition behaviour varies from feedstock to feedstock, and its study allows understanding the reactivity of the biomass. From an experimental point of view, this is usually performed through thermo-gravimetric (TGA) analyses [15,16]. With this technique, the conversion rate of the biomass components (cellulose, hemicellulose and lignin) can be obtained as a function of the temperature. Then, through adequate calculation approaches, the kinetic parameters of the conversion reactions are also obtained. The parameter obtained from TGA are however not often applied to full-scale models. This is due to the fact that the conditions of the TGA and of the gasifier are very different in terms of size, fluid dynamics and temperature gradients, and hence the validity of these data at a higher scale is controversial [17]. Clearly, more research efforts are needed to close this knowledge gap.

Figure 1: The residues of apple pruning that were fed to the spouted bed gasifier

In this work, we have considered the gasification of apple pruning residues (APR, depicted in Fig. 1). Apples are cultivated abundantly throughout the world, with a global production of 89.3 Mton in 2016 [18], about 2.23 of which are harvested in Italy. Clearly, this generates a huge quantity of residues that must be properly handled. In our previous works, we performed a kinetic characterisation of APR, which allowed us to understand their thermal behaviour and obtain the kinetic parameters [19]. Then, we successfully gasified these residues in a pilot spouted bed gasifier [5]. Spouted bed reactors are similar to fluidised bed reactors, but better at handling coarse and irregular solid particles, and hence they are particularly suitable for agricultural residues [20,21]. Moreover, they feature very high mass and heat transfer rates. For this reason, it was previously proven that the data obtained from TGA can be applied in spouted bed models, since the diffusional limitations are overcome [22]. In this work, we have employed the commercial plant modeller Aspen Plus 10 to reproduce the experiments regarding APR gasification in the spouted bed, including the kinetic data. This is a valuable contribution for both the gasification technology and the spouted bed technology. Spouted beds are indeed very promising and provably suitable for different applications, but their industrial scale-up is still hindered by the lack of established criteria, and validated models represent a valid way to overcome this knowledge gap [17]. To the knowledge of the authors, this is the first work dealing with a kinetic model for the gasification of APR.

2 MATERIAL AND METHODS

2.1 Biomass properties

Regarding the composition of the biomass, the amount of carbon, hydrogen, nitrogen, sulphur, humidity and ash is based on our previous experimental analyses [5]. Conversely, the relative abundance of cellulose, hemicellulose and lignin (CHL) is based on literature data calculated for apple wood [23]. Table I summarises the biomass properties.

Table I: Properties of the biomass (% w/w on dry basis, besides for the humidity)

Proximate analysis	
Humidity	8.13
Ash	2.87
Fixed carbon	19.95
Volatile matter	77.18
Ultimate analysis	
C	48.88
H	5.71
N	0.26
S	0.13
O	42.15
Ash	2.87
CHL	
Cellulose	49.45
Hemicellulose	34.34
Lignin	16.21

2.2 Reactions and kinetics

Biomass gasification involves a complex network of chemical reactions, which leads to the formation of countless carbon-containing compounds. Given the preliminary nature of this work, we decided to consider the major compounds only, simplifying the procedure. Most notably, tar modelling was not included in this work, due to the lack of experimental data. The included components are thus:

- Solid components: biomass, ash, cellulose, hemicellulose, lignin, carbon, sulphur;
- Gaseous components: H_2, H_2O, CO, CO_2, CH_4, N_2, H_2S.

CHL were modelled as non-conventional solid components. Cellulose and hemicellulose have a regular polymeric structure, and thus we chose their monomers to represent them [14]. The structure of lignin is more irregular, and hence we adapted its formula so as to match the overall elemental balance for the biomass. Thus, the three molecular structures for CHL are respectively $C_6H_{10}O_5$, $C_5H_8O_4$ and $C_{20}H_{14}O_3$.

The first step is the decomposition of biomass into its constituents: cellulose, hemicellulose, lignin, sulphur, nitrogen, ash and water in the amounts that Table I reports. Then, CHL undergo pyrolysis reactions. Experimental data on the compounds formed from the pyrolysis of APR were not available, so we hypothesised the simplest possible reactions that allowed closing the elemental balance. The reactions and related kinetic laws (obtained from our previous work [19]) are schematised in Table II.

Table II: Pyrolysis reactions and related kinetic laws

Reaction	Kinetic law (kmol/(m^3 s))
$C_6H_{10}O_5 \rightarrow 5CO + 3H_2 + CH_4$	$r = 2.14 \cdot 10^{12} \exp\left(-\frac{145 \cdot 10^3}{RT}\right) \omega_{C6H10O5}^{0.27}$
$C_5H_8O_4 \rightarrow 4CO + 2H_2 + CH_4$	$r = 2.9 \cdot 10^{10} \exp\left(-\frac{120 \cdot 10^3}{RT}\right) \omega_{C5H8O4}^{2.31}$
$C_{20}H_{14}O_3 \rightarrow 3CO + H_2 + 3CH_4 + 14C$	$r = 1.06 \cdot 10^{8} \exp\left(-\frac{115 \cdot 10^3}{RT}\right) \omega_{C20H14O3}^{5.27}$

The remaining conventional compounds undergo the typical reactions involved in gasification (combustion, reforming, Bouduard, water-gas shift…). The reactions and associated kinetics, derived from literature works [24–26], are summed up in Table III. With regard to sulphur, Peters and colleagues [14] have pointed out that there is no agreement in the literature on how to predict the amount of it that is retained in the char. Besides, its quantity is marginal. Hence, we hypothesised half of the sulphur to stay in the char, and the other half to react with hydrogen and leave the reactor as H_2S.

Table III: Conventional compounds' reactions and related kinetic laws

Reaction	Kinetic law (kmol/(m^3 s))
$C + 0.5O_2 \rightarrow CO$	$r = 0.046 \exp\left(-\frac{112 \cdot 10^3}{RT}\right) \omega_C P_{O2} \rho_{char} / M_C$
$C + H_2O \rightarrow CO + H_2$	$r = 1.71 \cdot 10^7 \exp\left(-\frac{211 \cdot 10^3}{RT}\right) \omega_C {P_{H2O}}^{0.51} \rho_{char} / M_C$
$C + CO_2 \rightarrow 2CO$	$r = 9.1 \cdot 10^6 \exp\left(-\frac{166 \cdot 10^3}{RT}\right) \omega_C {P_{CO2}}^{0.8} \rho_{char} / (M_C T^{0.8})$
$C + 2H_2 \rightarrow CH_4$	$r = \exp\left(-\frac{66 \cdot 10^3}{RT} - 7.087\right) C_C \left(P_{H2} - \left(\frac{P_{CH4}}{\exp\left(-13.43 + \frac{10100}{T}\right)}\right)^{0.5}\right)$
$CO + H_2O \rightarrow CO_2 + H_2$	$r = 2.891 \cdot 10^8 \exp\left(-\frac{163 \cdot 10^3}{RT}\right) C_{CO} C_{H2O}$
$CO_2 + H_2 \rightarrow CO + H_2O$	$r = 1.246 \cdot 10^7 \exp\left(-\frac{196 \cdot 10^3}{RT}\right) C_{CO2} C_{H2}$
$H_2 + 0.5O_2 \rightarrow H_2O$	$r = 2.2 \cdot 10^9 \exp\left(-\frac{109 \cdot 10^3}{RT}\right) C_{H2} C_{O2}$
$CO + 0.5O_2 \rightarrow CO_2$	$r = 10^{10} \exp\left(-\frac{126 \cdot 10^3}{RT}\right) C_{CO} C_{O2}^{0.5} C_{H2O}^{0.5}$
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	$r = 2.119 \cdot 10^{11} \exp\left(-\frac{203 \cdot 10^3}{RT}\right) C_{CH4}^{0.2} C_{O2}^{1.3}$
$CH_4 + H_2O \rightarrow CO + 3H_2$	$r = 312 \exp\left(-\frac{125 \cdot 10^3}{RT}\right) C_{CH4}$

In these equations, T is the temperature of the reactor (K), R is the gas constant (8.314 J/(mol K)), ω_i is the mass fraction of the component i in the solid phase, P_i is the partial pressure (atm) of component i, ρ_{char} is the density of char (500 kg/m^3, as estimated in a previous work), M_C is the molar mass of carbon (12 kg/kmol), C_i is the molar concentration of component i (kmol/m^3).

2.3 Plant configuration

The configuration of the spouted bed pilot plant is described in detail in previous publications [5,27] and is schematised in Fig. 2. The spouted bed reactor, which has a total volume of 47.38 L, is the main unit. Ambient air is fed to it through a single nozzle located in the centre of the base, while the biomass is fed from the top of the reactor. The producer gas and the entrained char particles leave the device from the top of it and enter a cyclone, which separates the solid particles from the gaseous flow. Then, the gas enters a water scrubber, which removes the finest solid particles, tar and water. The obtained gaseous stream is analysed by the gas chromatograph (GC), and is then appropriately disposed of.

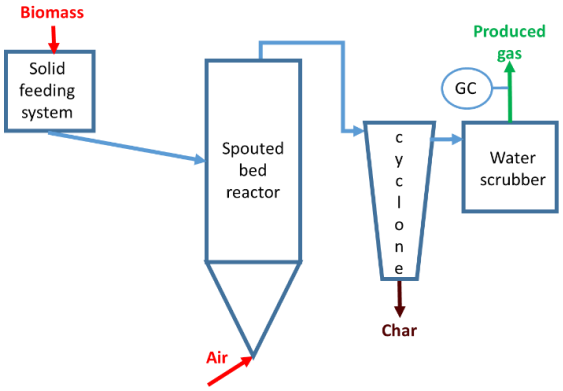

Figure 2: Scheme of the spouted bed gasification plant

2.4 Simulation set-up

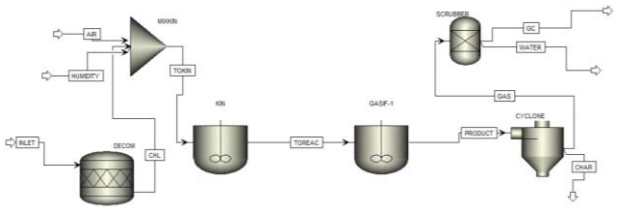

Figure 3: Aspen Plus flowsheet of the gasification plant

The Aspen Plus flowsheet is depicted in Fig. 3. It is based on the original plant scheme, with some additions:

- The reactor DECOM (RYIELD) performs the decomposition of biomass in cellulose, hemicellulose, lignin, N, S and ash. It operates with complete conversion.
- To avoid unwanted vapour-liquid calculations, the biomass humidity is directly added to the reactor as water (stream HUMIDITY).
- The gasifier is simulated through two RCSTR units. This is because because CHL are inserted in Aspen Plus as solid non-conventional components, and some reaction schemes do not work with them. In the first reactor (KIN), the pyrolysis of CHL takes place. In the second reactor (GASIF-1), the other reactions take place.
- The separator CYCLONE (CYCLONE) reproduces the cyclone, and separates all solid components with complete efficiency.
- The separator SCRUBBER (SEP) reproduces the scrubber, and separates water with complete efficiency.

The results for the producer gas composition are obtained from the GC stream, as it happens in the experiments. The results for the char are obtained from the CHAR stream. The latter contains unreacted

cellulose, hemicellulose, lignin and sulphur, as well as the inert ash. For a better comparison with the experimental data, the simulated char composition is then converted into its constituent elements (C, H, O, S and the ash).

Table IV summarises the parameters for the two studied experimental conditions.

Table IV: Operating conditions for the two equivalent ratios (ER)

Parameter	ER = 0.42	ER = 0.65
Air inlet flow rate (Nm^3/h)	17	
Biomass inlet flow rate (g/min)	150	99
Reactor temperature (°C)	880	911
Reactor volume (l)	47.38	
Reactor pressure (atm)	1	

3 RESULTS AND DISCUSSION

3.1 Pyrolysis step

The first kinetically modelled step is the pyrolysis of CHL. Since, as explained in the previous Section, this step is performed in a separate reactor, it is possible to analyse these results separately. For the potential benefit of readers, we wish to emphasise that the very high pre-exponential factors and activation energies of the reactions cause problems to Aspen Plus. We had to modify the standard numerical scheme settings in order to make the program converge. Fig. 4 reports a graph in which the conversion of the three components is calculated as a function of the reactor temperature, in a range that is reasonable for a gasifier.

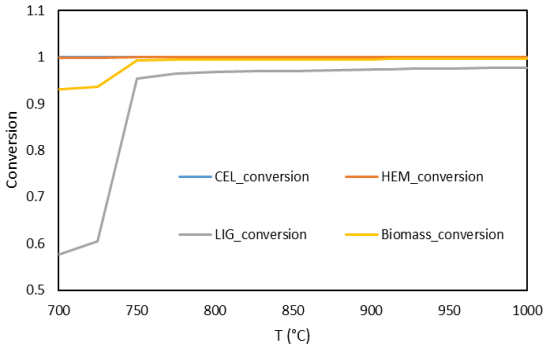

Figure 4: Conversion of CHL and of the whole biomass as a function of temperature

Clearly, cellulose and hemicellulose are completely converted in the whole range of temperature. Conversely, lignin is more resistant to the effect of temperature: at 700 °C, less than 60 % of it gets pyrolysed, and even at higher temperature a small residue remains, as the literature reports [19]. Overall, according to the input kinetic data, the pyrolysis does not seem to represent a limiting step in the gasification of APR, which is again coherent with the literature [22]. This may be consistent with the fact the char obtained by their gasification is very poor in carbon [28].

3.2 Gasification results

After the pyrolysis step, all the components undergo the typical gasification reactions that have been introduced in Section 2.1. Then, the gaseous components are separated from the solid, and water and other heavy components are removed by the scrubber, similarly to what happens in the experimental procedure. The thus-obtained gaseous stream is then analysed to assess the accuracy of the results. Figures 5 and 6 schematise the composition of the producer gas for the two studied ERs. The comparison includes the experimental data and the results obtained with a pure equilibrium model.

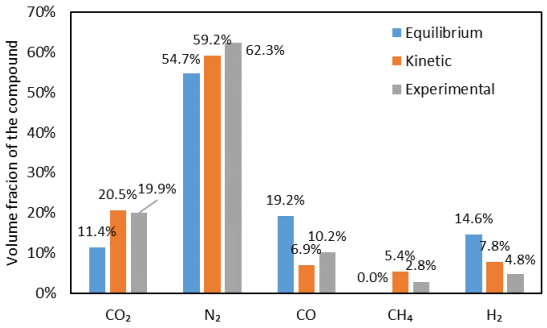

Figure 5: Comparison of the results obtained through an equilibrium model, the kinetic model and experiments for an ER of 0.42

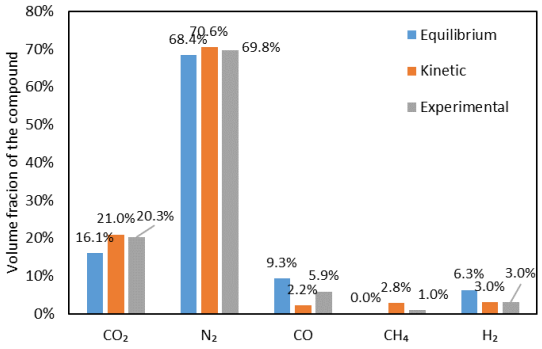

Figure 6: Comparison of the results obtained through an equilibrium model, the kinetic model and experiments for an ER of 0.65

The results clearly show the superiority of the kinetic model to the equilibrium model. This is mostly evident for the lower ER, which is the furthest away from equilibrium conditions. Most notably, the equilibrium model overestimates the concentration of carbon monoxide and hydrogen, while it underestimates the concentration of carbon dioxide and predicts nearly no formation of methane. These limits are overcome by the kinetic model, which gives reasonable predictions of all of the considered compounds. The kinetic model also provides a good prediction of the change in the producer gas composition that is caused by the ER increase. Due to it, the concentration of nitrogen increases, while those of carbon monoxide, methane and hydrogen decrease.

The better prediction of the composition of the producer gas is also reflected in the calculated LHV (obtained with the equation of Gai and Dong [29]). Fig. 7 shows the results. For the lower ER the prediction of the kinetic model is still better than the equilibrium model,

but not so close to the experimental number. This is caused by the higher predicted concentrations of hydrogen and methane. As expected, both models give better prediction for the higher ER, where the conditions are more similar to those of equilibrium.

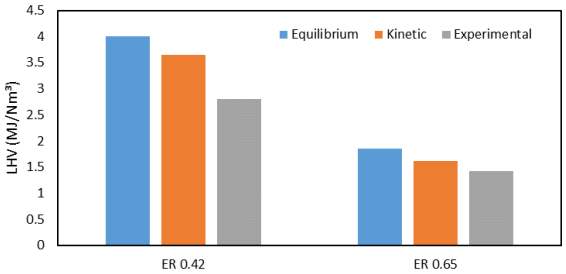

Figure 7: LHV of the producer gas for the two ERs

Finally, it is possible to compare the results in terms of the obtained cold gas efficiency (CGE). This is calculated with the following formula:

$$CGE = \frac{\dot{m}_{gas} HHV_{gas}}{\dot{m}_{biom} HHV_{biom}}$$

In this, $\dot{m}$ are the mass flow rates (kg/h) of the producer gas and of biomass respectively, and HHV are the high heating values (MJ/kg) of the producer gas and of the biomass. The flow rate of the producer gas was obtained from the experimental results through the hypothesis that the inlet and outlet flows of nitrogen are equal. The HHV of the producer gas was calculated on the basis of the HHVs of its components. The HHV of biomass was calculated experimentally and is reported in a previous work [5]. Fig. 8 provides a visualisation of the results. Similarly to the LHV, the accuracy of the kinetic model is better, and the accuracy of both models is better when the ER is higher.

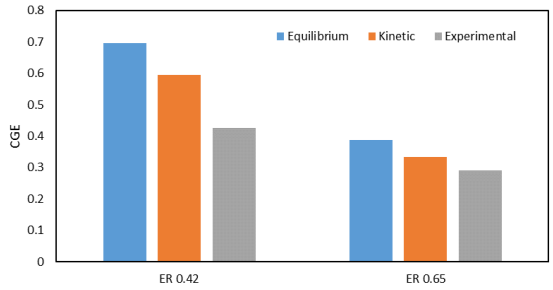

Figure 8: Cold gas efficiency (CGE) calculated from simulations and experiments

With regards to the H_2S, the predicted concentrations in the producer gas are 165 and 130 ppmv for ER of 0.42 and 0.65, respectively. Even if the modelling of this compound's formation is very simplified, these values' order is coherent with what the literature reports [30].

3.3 Char results

In gasifiers, the conversion of carbon is usually not complete, and a solid by-product called char is generated. Char is usually rich in carbon, and hence a high amount of it is a symptom of a low carbon conversion in the reactor, which is not good for the economy of the process. Moreover, char represents a cost for plant owners, who have to dispose of it at a significant cost. In recent years, researchers have tried to establish ways to valorise the gasification char, in order to turn it into a valuable product [31–33]. Nonetheless, minimising the char production is still the most desirable option, and modelling may help finding the most appropriate conditions to do so. Equilibrium models cannot predict any formation of char, which is another reason to choose a kinetic model. The composition of the obtained char is summarised in Table V. The table also includes some experimental data obtained from the characterisation of the char obtained from the gasification of APR in the same spouted bed reactor. In this case, the gasification experiments were performed with slightly different ERs (0.32 and 0.42).

Table V: Char production and composition (% w/w, beside for the mass flow)

	Aspen, ER 0.42	Aspen, ER 0.65	Experimental, ERs 0.32 and 0.42
Mass flow (kg/h)	0.281	0.182	n/a
C	10.89	9.64	13.61
H	0.64	0.57	0.11
O	2.20	1.94	0.00
S	4.93	3.68	0.40
N	0.00	0.00	0.13
Ash	84.36	85.91	85.75

As the table shows, the simulations provide a good prediction of the char composition, especially since the relative abundance of ash is almost the same. The predicted carbon amount is of an appropriate order, even if the experimental value is higher. The sulphur amount is largely overestimated, suggesting that the hypothesis that 50 % of the sulphur remains in the char is inadequate.

To sum up, the developed kinetic model correctly showed that the gasification of APR for these ERs features a very high carbon conversion, so that the produced char is mostly composed of ash. It may be interesting to apply the model to a case in which the produced char contains more carbon, and it will be the focus of a future work.

3.4 Future developments

The results of the previous paragraphs have shown that the use of a kinetic model allows obtaining more accurate results than an equilibrium model. Despite its simplistic nature, the studied kinetic model can overcome some of the issues of equilibrium models, such as the lack of methane and char formation. In the future, the accuracy of the simulations may be further enhanced removing by including some phenomena. This will be the focus of future works. Most notably, the present model does not consider the tar fraction, which is a relevant factor in the design and operation of a gasifier. Moreover, we plan to include the reaction enthalpies, so as to study the thermal stability of the gasifier in other conditions.

Another possible path to enhance the results may be considering the various fluid dynamic and thermic conditions that particles encounter in spouted bed reactors. The temperature of the gas increases along the height of the spouted bed, and this affects the reaction

rates. This effect is not considered here, since the reactor is modelled as an ideal CSTR. Similarly, further effort may provide a better reproduction of the residence times of the gaseous and solid phases. At present, they are most likely overestimated, due to the fact that the gasifier is reproduced through two units. In the reactor, char is actually entrained upwards and out of the reactor as soon as its size becomes fine enough. The literature indeed provides examples in which researchers tried different methodologies to model reacting spouted beds more realistically [17]. One of the most popular approaches is the stream-tube model by Lim and Mathur [34]. Recently, Niksiar and Nasernajad applied it to develop a model of a spouted bed gasifier that is able to predict the Brunauer-Emmet-Teller (BET) surface area of the produced activated carbons [35]. In the modelling of coal gasification, Lucas et al. set different reactions rate for the spout and annulus [36]. Du and colleagues assessed the fluid dynamic behaviour of a spouted bed through CFD-TFM (computational fluid dynamics – two fluid method) simulations, and on these basis developed an equivalent reactor network that they implemented in Aspen Plus [37]. We think this multiscale approach can combine the advantages of two different modelling methodologies, which can provide data for different time scales, and hence we will apply it in future works, taking advantage of our validated CFD-DEM (discrete element method) simulation methodology [38]. This methodology is not only more reliable than the TFM [39], but it would also be indeed more appropriate for the purpose. This is because the trajectories of each particle are tracked, giving detailed information about the residence time distribution.

4 CONCLUSIONS

In this work, we have considered gasification experiments performed in an innovative pilot-scale spouted bed reactor. The aim of the work was to reproduce these experiments with the aid of the commercial program Aspen Plus, considering the kinetics of the reaction scheme. Most notably, we have included the data from TGA for the pyrolysis of the biomass. The suitability of these at higher scales is in some cases disputed, but reportedly appropriate for spouted bed reactors due to their low diffusional limitations.

The simulations confirmed the accuracy of this approach. Due to the high temperature of the reactor, cellulose and hemicellulose pyrolyse almost completely, while a small residue of lignin (about 3 %) remains unconverted. The inclusion of the reaction kinetics yields in a good prediction of the producer gas composition. Most notably, some typical issues of equilibrium models are overcome, such as the overestimation of the carbon monoxide and hydrogen abundance, or the neglection of the formation of methane. The accuracy of the prediction is also confirmed by the better similarity of the producer gas' LHV and the cold gas efficiency, even if some discrepancies remain. With regard to char, the proposed model gives an almost perfect prediction of the amount of ash, while it slightly underestimates the amount of carbon.

These results confirm that including a preliminary kinetic scheme can notably enhance the prediction of the producer gas and char composition. As explained in the paper, there are still some limitations, including the lack of tar modelling. Moreover, not considering the fluid dynamics of the reactor may possibly lead to an incorrect estimation of the residence time of the biomass, which is a key parameter for its decomposition behaviour. These issues will be addressed in future works.

5 REFERENCES

[1] A. Molino, S. Chianese, D. Musmarra, Biomass gasification technology: The state of the art overview, J. Energy Chem. 25 (2016) 10–25. doi:10.1016/j.jechem.2015.11.005.

[2] F. Patuzzi, D. Prando, S. Vakalis, A.M. Rizzo, D. Chiaramonti, W. Tirler, T. Mimmo, A. Gasparella, M. Baratieri, Small-scale biomass gasification CHP systems: Comparative performance assessment and monitoring experiences in South Tyrol (Italy), Energy. 112 (2016) 285–293. doi:10.1016/J.ENERGY.2016.06.077.

[3] C. Moliner, R. Teruel-Juanes, C. Primaz, J. Badia, B. Bosio, P. Campíns-Falcó, C. Molíns-Legua, F. Hernandez, L. Sanjuan-Navarro, P. Madramany, J. Morán, J. Castro, F. Sanchis, J. Martínez, F. Hiddink, A. Ribes-Greus, E. Arato, C. Moliner, R. Teruel-Juanes, C.T. Primaz, J.D. Badia, B. Bosio, P. Campíns-Falcó, C. Molíns-Legua, F. Hernandez, L. Sanjuan-Navarro, P. Madramany, J. Morán, J. Castro, F.J. Sanchis, J.D. Martínez, F. Hiddink, A. Ribes-Greus, E. Arato, Reduction of Nitrates in Waste Water through the Valorization of Rice Straw: LIFE LIBERNITRATE Project, Sustainability. 10 (2018) 3007. doi:10.3390/su10093007.

[4] C. Moliner, B. Bosio, E. Arato, A. Ribes, Thermal and thermo-oxidative characterisation of rice straw for its use in energy valorisation processes, Fuel. 180 (2016) 71–79. doi:10.1016/j.fuel.2016.04.021.

[5] D. Bove, C. Moliner, M. Curti, M. Baratieri, B. Bosio, G. Rovero, E. Arato, Preliminary Tests for the Thermo-Chemical Conversion of Biomass in a Spouted Bed Pilot Plant, Can. J. Chem. Eng. (2018). doi:10.1002/cjce.23223.

[6] C. Moliner, D. Bove, B. Bosio, A. Ribes, E. Arato, Simulation Activities for the Pseudo-Equilibrium Modelling of the Gasification of Agricultural Residues, Eur. Biomass Conf. Exhib. Proc. (2016) 934–940. doi:10.5071/24theubce2016-2cv.3.54.

[7] X. Li, J.. Grace, A.. Watkinson, C.. Lim, A. Ergüdenler, Equilibrium modeling of gasification: a free energy minimization approach and its application to a circulating fluidized bed coal gasifier, Fuel. 80 (2001) 195–207. doi:10.1016/S0016-2361(00)00074-0.

[8] A.M.. Ahmed, A. Salmiaton, T.S.. Choong, W.A.K.G. Wan Azlina, Review of kinetic and equilibrium concepts for biomass tar modeling by using Aspen Plus, Renew. Sustain. Energy Rev. 52 (2015) 1623–1644. doi:10.1016/j.rser.2015.07.125.

[9] D. Bernocco, B. Bosio, E. Arato, Feasibility study of a spouted bed gasification plant, Chem. Eng. Res. Des. 91 (2013) 843–855. doi:10.1016/j.cherd.2012.09.012.

[10] C. Moliner, D. Bove, B. Bosio, A. Ribes Greus, E. Arato, Simulation activities for the pseudo-equilibrium modelling of the gasification of agricultural residues, in: Eur. Biomass Conf. Exhib.

Proceedings, 6-9 June 2016, Amsterdam, Netherlands, 2016: pp. 934–940.
[11] A. Sanz, J. Corella, Modeling circulating fluidized bed biomass gasifiers. Results from a pseudo-rigorous 1-dimensional model for stationary state, Fuel Process. Technol. 87 (2006) 247–258. doi:10.1016/j.fuproc.2005.08.003.
[12] C. Font Palma, Model for Biomass Gasification Including Tar Formation and Evolution, Energy & Fuels. 27 (2013) 2693–2702. doi:10.1021/ef4004297.
[13] E. Ranzi, A. Cuoci, T. Faravelli, A. Frassoldati, G. Migliavacca, S. Pierucci, S. Sommariva, Chemical Kinetics of Biomass Pyrolysis, Energy & Fuels. 22 (2008) 4292–4300. doi:10.1021/ef800551t.
[14] J.F. Peters, S.W. Banks, A. V. Bridgwater, J. Dufour, A kinetic reaction model for biomass pyrolysis processes in Aspen Plus, Appl. Energy. 188 (2017) 595–603. doi:10.1016/J.APENERGY.2016.12.030.
[15] C. Moliner, B. Bosio, E. Arato, A. Ribes-Greus, Comparative study for the energy valorisation of rice straw, Chem. Eng. Trans. 37 (2014) 241–246. doi:10.3303/CET1437041.
[16] C. Moliner, K. Aguilar, B. Bosio, E. Arato, A. Ribes, Thermo-oxidative characterisation of the residues from persimmon harvest for its use in energy recovery processes, Fuel Process. Technol. 152 (2016) 421–429. doi:10.1016/j.fuproc.2016.07.008.
[17] C. Moliner, F. Marchelli, B. Bosio, E. Arato, Modelling of Spouted and Spout-Fluid Beds: key for their successful scale up, Energies. 10 (2017) 38. doi:10.3390/en10111729.
[18] FAOSTAT, Food and agriculture data, (2019). http://www.fao.org/faostat/en/#home (accessed March 21, 2019).
[19] D. Bove, C. Moliner, M. Baratieri, B. Bosio, E. Arato, Kinetic Characterization of the Residues from the Pruning of Apple Trees for their Use as Energy Vectors, Chem. Eng. Trans. 50 (2016). doi:10.3303/CET1650001.
[20] C. Moliner, M. Curti, B. Bosio, E. Arato, G. Rovero, Experimental Tests with Rice Straw on a Conical Square-Based Spouted Bed Reactor, Int. J. Chem. React. Eng. 13 (2015) 351–358. doi:10.1515/ijcre-2014-0172.
[21] C. Moliner, F. Marchelli, M. Curti, B. Bosio, G. Rovero, E. Arato, Spouting behaviour of binary mixtures in square-based spouted beds, Particuology. 43 (2019) 193–201. doi:10.1016/j.partic.2018.01.003.
[22] M.O. Maider Amutio, Gartzen Lopez, Roberto Aguado, Maite Artetxe, Javier Bilbao, M. Amutio, G. Lopez, R. Aguado, M. Artetxe, J. Bilbao, M. Olazar, Kinetic study of lignocellulosic biomass oxidative pyrolysis, Fuel. 95 (2012) 305–311. doi:10.1016/j.fuel.2011.10.008.
[23] M.R. Al-Masri, M. Zarkawi, Effects of gamma irradiation on cell-wall constituents of some agricultural residues, Radiat. Phys. Chem. 44 (1994) 661–663. doi:10.1016/0969-806X(94)90227-5.
[24] C.Y. Wen, T.Z. Chaung, Entrainment Coal Gasification Modeling, Ind. Eng. Chem. Process Des. Dev. 18 (1979) 684–695. doi:10.1021/i260072a020.
[25] J. Xie, W. Zhong, B. Jin, LES-Lagrangian modelling on gasification of combustible solid waste in a spouted bed, Can. J. Chem. Eng. 92 (2014) 1325–1333. doi:10.1002/cjce.21941.
[26] L. Yan, Y. Cao, H. Zhou, B. He, Investigation on biomass steam gasification in a dual fluidized bed reactor with the granular kinetic theory, Bioresour. Technol. 269 (2018) 384–392. doi:10.1016/J.BIORTECH.2018.08.099.
[27] D. Bove, C. Moliner, M. Curti, G. Rovero, M. Baratieri, B. Bosio, E. Arato, G. Garbarino, F. Marchelli, Experimental studies on the gasification of the residues from prune of apple trees with a spouted bed reactor, in: Eur. Biomass Conf. Exhib. Proc., 2016.
[28] F. Marchelli, C. Moliner, M. Curti, G. Rovero, M. Baratieri, B. Bosio, E. Arato, Characterisation of the Char Obtained from Biomass Gasification in a Spouted Bed Reactor, in: Eur. Biomass Conf. Exhib. Proc., 2017: pp. 847–852. doi:10.5071/25thEUBCE2017-2CV.3.47.
[29] C. Gai, Y. Dong, Experimental study on non-woody biomass gasification in a downdraft gasifier, Int. J. Hydrogen Energy. 37 (2012) 4935–4944. doi:10.1016/j.ijhydene.2011.12.031.
[30] P.J. Woolcock, R.C. Brown, A review of cleaning technologies for biomass-derived syngas, Biomass and Bioenergy. 52 (2013) 54–84. doi:10.1016/j.biombioe.2013.02.036.
[31] F. Marchelli, E. Cordioli, F. Patuzzi, E. Sisani, L. Barelli, M. Baratieri, E. Arato, B. Bosio, Experimental study on H2S adsorption on gasification char under different operative conditions, Biomass and Bioenergy. 126 (2019) 106–116. doi:10.1016/J.BIOMBIOE.2019.05.003.
[32] G. Ravenni, Z. Sárossy, J. Ahrenfeldt, U.B. Henriksen, Residual Char from Gasification Integrated in a Tar Removal System, Eur. Biomass Conf. Exhib. Proc. (2018) 546–549. doi:10.5071/26theubce2018-2bo.14.5.
[33] V. Benedetti, F. Patuzzi, M. Baratieri, Characterization of char from biomass gasification and its similarities with activated carbon in adsorption applications, Appl. Energy. (2017) 1–8. doi:10.1016/j.apenergy.2017.08.076.
[34] C.J. Lim, K.B. Mathur, A flow model for gas movement in spouted beds, AIChE J. 22 (1976) 674–680. doi:10.1002/aic.690220407.
[35] A. Niksiar, B. Nasernejad, Modeling of gasification reaction to produce activated carbon from pistachio shells in a spouted bed, Biomass and Bioenergy. 119 (2018) 97–108. doi:10.1016/J.BIOMBIOE.2018.09.008.
[36] J.P. Lucas, C.J. Lim, A.P. Watkinson, A nonisothermal model of a spouted bed gasifier, Fuel. 77 (1998) 683–694. doi:10.1016/S0016-2361(97)00237-8.
[37] Y. Du, Q. Yang, A.S. Berrouk, C. Yang, A.S. Al Shoaibi, Equivalent reactor network model for simulating the air gasification of polyethylene in a conical spouted bed gasifier, Energy and Fuels. 28 (2014) 6830–6840. doi:10.1021/ef501667n.
[38] F. Marchelli, C. Moliner, B. Bosio, E. Arato, A CFD-DEM sensitivity analysis: The case of a pseudo-2D spouted bed, Powder Technol. 353 (2019) 409–425. doi:10.1016/j.powtec.2019.05.035.

[39] C. Moliner, F. Marchelli, N. Spanachi, A. Martinez-Felipe, B. Bosio, E. Arato, CFD simulation of a spouted bed: Comparison between the Discrete Element Method (DEM) and the Two Fluid Model (TFM), Chem. Eng. J. (2018). doi:10.1016/j.cej.2018.11.164.

6 ACKNOWLEDGEMENTS

This work was funded through the LIFE LIBERNITRATE project (LIFE16 ENV/ES/000419).

7 LOGO SPACE