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Estimation of lignocellulosic biomass pyrolysis product yields using artificial neural networks

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ABSTRACT

As the push towards more sustainable ways to produce energy and chemicals intensifies, efforts are needed to refine and optimize the systems that can give an answer to these needs. In the present work, the use of neural networks as modelling tools for lignocellulosic biomass pyrolysis main products yields estimation was evaluated. In order to achieve this, the most relevant compositional and reaction parameters for lignocellulosic biomass pyrolysis were reviewed and their effect over the main products yields was assessed. Based on relevant literature data, a database was set up, containing parameters and experimental results from 32 published studies for a total of 482 samples, including both fast and slow pyrolysis experiments performed on a heterogeneous collection of lignocellulosic biomasses. The parameters that in the database configured as best predictors for the solid, liquid and gaseous products were determined through preliminary tests and were then used to build reduced models, one for each of the main products, which use five parameters instead of the full set for the estimation of yields. The procedures included hyperparameter optimizations steps. The performances of these reduced models were compared to those of the ones obtained using the full set of parameters as inputs by using the root mean squared error (RMSE) as metric.

For both the char and gas products, the best results were consistently achieved by the reduced versions of the network (RMSE 5.1 wt% ar and 5.6 wt% ar respectively), while for the liquid product the best result was given by the full network (RMSE 6.9 wt% ar) indicating substantial value in proper selection of the input features. In general, the char models were the best performing ones. Additional models for the liquid and gas product featuring char as additional input to the system were also devised and obtained better performance (RMSE 5.5 wt % ar and 4.9 wt% ar respectively) compared to the original ones. Models based on single studies were also included in order to showcase both the capabilities of the tool and the challenges that arise when trying to build a generalizable model of this kind.

Overall, artificial neural networks were shown to be an interesting tool for the construction of setup-unspecific biomass pyrolysis product yield models. The obstacles standing currently in the way of a more accurate modelling of the system were highlighted, along with certain literature discrepancies, which hinder reliable quantitative comparison of experimental conditions and results among separate studies.

1. Introduction

The increasing concern regarding environmental change, the looming depletion of conventional fossil fuel reserves together with the also increasing need for energy self-reliance and the global concern surrounding their use, lead to the employment of alternative and sustainable resources for heat and power generation, fuels and chemicals production. Biomass constitutes a potentially clean and renewable fuel, which is also readily available worldwide, being the third most abundant fuel source after coal and oil. Biomass thermochemical conversion is a candidate for the production of heat, power, chemicals and fuels production, with pyrolysis, torrefaction, gasification, combustion and hydrothermal liquefaction constituting the majorly employed thermochemical conversion methods [1].

Pyrolysis can be defined as the thermochemical process of biomass decomposition, either in the absence of an oxidation medium, or with a

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Table 1
Implementation of ANNs for the description of biomass thermochemical conversion processes in literature.

#	Thermochemical process	Biomass Type	Architecture	Number of hidden layers	Transfer function	Training algorithm	Output type*	Data sets – Data sources**	Model inputs	Model outputs	Accuracy	Ref.
1	Pyrolysis	Cattle manure	FF	2	n.d.	n.d.	MISO	33	Pyrolysis temperature, heating rate, holding time, moisture content, sample mass	Biochar yield	$R^2 = 0.804$	[5]
2	Pyrolysis	Pine sawdust	FF	1	logsig, purelin	BP/LM	MIMO	14***	Space velocity, pyrolysis temperature, particle size	H_2, CO, CH_4 and CO_2 selectivity	$R^2 = 0.999$	[24]
3	Pyrolysis	Lignocellulosic biomass (from literature)	FF	1	tansig, purelin	BP/LM	MISO	150−28	Cellulose, hemicellulose and lignin content	Pre-exponential factor, activation energy and reaction order	n.a.	[21]
4	Pyrolysis	Durian rinds, Banana peels	FF	2,1	tansig, purelin	BP/LM	MISO	176	Pyrolysis temperature, time	Weight loss	$R^2 = 0.999$	[17, 18]
5	Pyrolysis	Olive oil residue, lignocellulosic forest residue	FF	1,2	tansig, logsig	BP/LM	MISO, MIMO	8000	Heating rate, temperature	Weight loss	n.a.	[19]
6	Pyrolysis	Algal mat	FF	1	tansig	BP/LM	MISO	n.d.	Instantaneous temperature, target temperature, heating rate	Weight loss	$R^2 > 0.97$	[20]
7	Pyrolysis	Various (from literature)	FF	1	tansig	n.d.	MIMO	163	Cellulose, hemicellulose and lignin content, heating rate	Pre-exponential factor, activation energy and reaction order	$R^2 > 0.81$	[6]
8	Pyrolysis	Various (from literature)	FF, CF	2	logsig	BP/LM	MIMO	72 – 44	Moisture, volatile, fixed carbon, ash, C, H, O, N contents, HHV, heating rate, temperature	Char, liquid and gas products	RMSE = 5.71–9.16	[22]
9	Pyrolysis	Cotton, tea, olive and hazelnut	FF	1	logsig, tansig	BP/ Gradient descent with adaptive learning	MIMO	18	Lignin, cellulose, hemicellulose, fixed carbon, volatile, moisture and ash contents, temperature	Char, liquid and gas products	$R^2 = 0.99$	[23]
10	Pyrolysis (carbonization)	Various (from literature)	FF	1	tansig, purelin	BP/LM	MISO	168−20	C, H, O content, fixed carbon, volatile matter and ash content, carbonization temperature and time, activation temperature, time and steam to biochar ratio	Activated carbon yield and BET surface area	$R^2 > 0.92$	[25]
11	Combustion	MSW – coal mixture	FF	1	tansig, purelin	BP/LM	MISO	2200	Feeding rate, temperature, change rate of temperature, outlet gas temperature, steam flow, temperature and pressure, primary and secondary air flow	Heating value	n.a.	[36]
12	Combustion	Various (from literature)	FF	1	tansig, purelin	BP/LM	MISO	100−34	Fixed carbon, volatile and ash contents, O_2 concentration and equivalence ratio	Pre-exponential factor, activation energy and reaction order	$R^2 > 0.94$	[29]
13	Gasification	Woody biomass (from literature)	FF	1	tansig, purelin	BP/LM	MISO	18, 36 – 2, 4	Moisture, ash, C, H and O content, gasification temperature and equivalence ratio	Product gas composition (CO, CO_2, CH_4 and H_2) and total gas yield	$R^2 > 0.98$	[30]
14	Gasification	n.d.	n.d.	n.d.	n.d.	Gaussian curve membership function	MISO, MIMO	600****	Fuel flow, air flow, time from last fuel supply and syngas temperature	Temperature and product gas	n.a.	[26]

(*continued on next page*)

Table 1 (*continued*)

#	Thermochemical process	Biomass Type	Architecture	Number of hidden layers	Transfer function	Training algorithm	Output type*	Data sets – Data sources**	Model inputs	Model outputs	Accuracy	Ref.
										composition (CO, CO_2, CH_4 and H_2)		
15	Gasification	Poplar sawdust, pine saw-dust, comminuted sugar cane bagasse and cotton stem	FF	1	logsig, n. d.	Chemotaxis algorithm	MISO	7 or 6 *****	Bed temperature and gasification time	Product gas composition (CO, CO_2, CH_4 and H_2) and total gas yield	n.a.	[37]
16	Gasification	n.d.	FF,CF	1,2	tansig, logsig, purelin	BP/LM	MISO	213	C, H, O, moisture and ash content, equivalence ratio, reaction temperature, steam/ biomass ratio and bed material	Product gas composition (CO, CO_2, CH_4 and H_2) and total gas yield	$R^2 = 0.9394 – 0.9734$	[33]
17	Gasification	Sawdust, coconut shell, coffee husk, sugarcane bagasse and ground nutshell	FF	1	tansig, purelin	BP/LM	MIMO	70	C, H, O, moisture and ash content, equivalence ratio and reaction temperature	Product gas composition (CO, CO_2, CH_4 and H_2)	$R^2 = 0.987$	[38]
18	Gasification	Wood sawdust	FF	1	tansig, tansig	BP/LM	MISO, MIMO	n.d.	Equivalence ratio, steam to biomass ratio and axial position in the reactor (only for the temperature model)	Gasification temperature and product gas composition (N_2, CO, CO_2, CH_4 and H_2)	$R^2 = 0.968$	[27]
19	Gasification	n.d.	FF	1	tansig, purelin	BP/LM	MISO	63 – 18	C, H, O, moisture and ash content and reduction zone temperature	Product gas composition (N_2, CO, CO_2, CH_4 and H_2)	$R^2 > 0.98$	[39]
20	Gasification	MSW	FF	2	tansig, logsig, purelin	BP/LM	MISO, MIMO	67	C, H, O, N, S, moisture and ash content, equivalence ratio and gasification temperature	LHV and LHV_p of product gas and product gas yield	$R^2 > 0.98$	[40]
21	Gasification	MSW	FF	1	tansig, logsig, purelin	n.d.	MIMO	91	Percentages of wood, paper, kitchen garbage, plastic and textile in the samples, equivalence ratio, temperature	LHV of gas, LHV of gasification products, gas yield	Relative error: 8.7–22.3 %******	[41]
22	Gasification	Various (from literature)	FF	1	tansig	n.d.	MISO, MIMO	181 – 21	Moisture, ash, volatile, C, H and O content, equivalence ratio, steam/biomass ratio, temperature and gasification agent	H_2, CO, CH_4, CO_2 and C_2H_n yields	Pearson R – correlation: 0.98 – 0.99	[31]
23	Gasification	Pinecone, wood	FF, CF, Time-delay, Elman, NARX	1	tansig	BP/LM	MIMO	3831	Temperature distribution, Equivalence ratio, air flow rate, C, H, O, N, Moisture, Volatile, Fixed Carbon, Ash contents	CO, CO_2, CH_4, H_2 yields and LHV_{gas}	$R^2 > 0.98$	[34]
24	Gasification	Various (from literature)	FF	1,2	tansig, logsig, purelin	BP/LM	MISO	120 – 16	C, H, O, moisture and ash contents, equivalence ratio, temperature	Total tar concentration (including benzene)	$R^2 > 0.96$	[28]

* The output type refers to multiple input – multiple output (MIMO) or multiple input – single output (MISO) models.
** In case the data were obtained from literature, the data sources number corresponds to the number of studies used. The data sets include the training, validation and testing sets.
*** The number of data sets was not explicitly mentioned in the study. It was calculated by the authors by adding the data points of each input variable (5, 6 and 3 respectively).
**** Experimental data from five gasification experiments were used for a total time of 60 min with a sampling interval of 30 s.
***** Separate models were built for each biomass specie and each gaseous compound studied.
****** The relative error was calculated as the predicted value minus the experimental value, all divided by the experimental value.

minor amount that does not enable gasification to an appreciable extent [2]. The main products of pyrolysis are char, bio-oil and gases and their quality and quantity are dependent on the reactor's operational conditions. Furthermore, pyrolysis is a sub-process of gasification and tar formation therein. Primary and secondary pyrolysis reactions occur during gasification among other reactions such as the water – gas shift and char oxidation [3]. Pyrolysis and gasification processes can be modelled or simulated using a variety of different models such as thermodynamic equilibrium models, kinetic models, computational fluid dynamics (CFD) models or machine learning techniques [4]. The important developments in the computer science and data analysis fields have led to an increase in the implementation of machine learning techniques for biomass thermochemical conversion processes and especially gasification. Artificial neural networks (ANNs) are widely used for this purpose (Table 1), as well as other machine learning models like the support vector machine (SVM) [5] or the random forest (RF) method [6]. However, the present work focuses exclusively on ANNs.

Artificial Neural Networks (ANNs) can be defined as structures comprised of densely interconnected adaptive simple processing elements (artificial neurons or nodes), capable of performing massively parallel computations for data processing and knowledge representation. Constituting drastic abstractions of their biological counterparts, ANNs employ the functionality of the biological networks in the effort to solve complex problems, rather than replicating their operation [7]. ANNs have several features that make them an attractive option for predictive tasks. To begin with, in contrast with traditional model-based methods, ANNs are data-driven self-adaptive methods, which do not include, at least to an appreciable extent, a priori assumptions regarding the problem under study. Additionally, the generalization capabilities of ANNs allow them to infer the unseen part of the sample data correctly, even if significant noise exists, given the obtained right training parameters and data. Furthermore, the ANNs are universal function approximators, a characteristic that allows them to approximate any continuous function to a desired accuracy, no matter how complex or non-linear [8]. However, the use of ANNs comes with some inherent disadvantages, such as the limitation to identify possible causal relationships between inputs and outputs explicitly. ANNs are actually a "black box". Furthermore, ANNs are often computationally expensive and sometimes prone to overfitting, while model development is somehow empirical and methodological issues remain to be resolved [9].

Several studies employing ANN models for the prediction of biomass thermochemical conversion processes product yields or behaviour in general can be found in the literature. As can be seen in Table 1, the majority of the cases concerns biomass gasification, however substantial work has been also performed regarding pyrolysis. Despite that fact, important lessons can be learned from the implementation of ANNs in biomass gasification processes modelling also concerning their use in pyrolysis models. Additionally, it is interesting to note that a substantial amount of work has been dedicated to the prediction of biomass higher heating value using ANN models [10–16]. Regarding pyrolysis ANN models, researchers appear to focus mostly on the use of thermogravimetric analysis (TGA) results aiming either to the prediction of the weight loss [17–20] or to the determination of the kinetic parameters (activation energy, pre-exponential factor, reaction order) [6,21]. Fewer studies deal with the pyrolysis products composition [22,23] or pyrolysis gas composition in particular [24], while char yield and its characteristics have also been investigated [5,25]. The overview of the gasification ANN models is much more one sided, since the vast majority of the studies focuses on the prediction of the product gases yield and composition (Table 1). Interestingly, in some of these studies the gasification temperature [26,27] is introduced as a prediction of the model, while Serrano et al. [28] aimed exclusively to the prediction of the total tar yield. In general, the inherent ability of ANN models to process large amounts of data has led to the development of quite a few models that employ data available from multiple literature sources for pyrolysis [6, 21,22,25], combustion [29] and gasification [28,30,31]. Nevertheless, the most common approach in ANN development remains the employment of one reactor setup for the generation of the data. In the studies where literature data were employed, biomass composition in terms of major constituents (cellulose, hemicellulose, lignin) [6,21] or proximate and ultimate analysis [22,25,28–31] were the main model inputs. Depending on the process and the desired outputs, operational parameters were also introduced as inputs but they were limited in the temperature [22] and heating rate [6] for pyrolysis and in temperature, equivalence ratio [28,30,31], gasification agent and steam/biomass ratio [31] for gasification. On a final note, it is interesting to mention that the increasing interest on ANNs within the biomass thermochemical conversion field is manifested by the fact that the majority of the relevant studies was published after 2015.

The artificial neuron is the base unit of ANNs, in which an array of inputs is fed along with a scalar weight and a bias resulting in a scalar. This scalar is subsequently passed on using an output function. The most common classes of output functions are step, linear (purelin) and sigmoidal (logistic – logsig or hyperbolic tangent – tansig). Multiple neurons can be arranged to generate complex and different architectures. Often, neurons are arranged in layers, where they are placed in parallel, receiving the same inputs but producing different outputs based on the individual weights, biases and transfer functions. The multilayer feedforward (FF) network (MFNN) is a series of neuron layers of which the outputs are used sequentially as inputs to the next layer. Depending on the definition, the inputs of the model can be considered as a layer, while the model outputs constitute the output layer. Any number of layers in the middle are the hidden layers and in general, a network with more than one layer is defined as an MFNN [32]. MFNNs are almost exclusively used in biomass thermochemical conversion ANNs as can be observed in Table 1. Alternative architectures are used in some cases [22,33,34] with the cascade forward (CF) operation being the most prominent one. In a CFNN, each neuron layer is connected to all the neurons of the previous layers [33]. In terms of network training, supervised training by the means of the Levenberg – Marquardt (LM) backpropagation (BP) method is mostly applied in the context of biomass thermochemical conversion ANNs. The BP algorithm firstly propagates the input forward through the network, secondly propagates also the sensitivities backward through the network (last up to the first layer) and finally updates the weights and the biases using the approximate steepest descent rule [35].

In this work, ANNs were employed for the prediction of the solid, liquid and gas yields from pyrolysis processes. A database was constructed using literature data from pyrolysis experiments, focused solely on batch type reactors. In this context, a wide range of input parameters was selected (lignocellulosic, ash and moisture content, pyrolysis temperature, heating rate, gas residence time, holding time, particle and sample size) and their effect on each product type prediction capabilities as well as the ability of the ANNs to successfully learn the expected trends were evaluated. As it can be also extracted from Table 1, ANN models for the prediction of pyrolysis products based on multiple studies from different researchers are scarce in the literature. According to the authors knowledge, the only attempt similar to the one presented in this study was by Merdun et al. [22], since other literature based pyrolysis ANN models focus either on the estimation of kinetic parameters through TGA data or on the char product specifically. However the study of Merdun et al., used a smaller amount of samples and the literature data were limited only on studies conducted in Turkey. Therefore, the applicability of ANNs for a condensed and simplified description of a pyrolysis process is going to be investigated, in terms of both accuracy and scientific meaningfulness using a large amount of input data and parameters.

Table 2
Biomass pyrolysis experimental parameters obtained from literature sources, which were included in the database, serving as inputs and outputs of the developed ANN model respectively.

Inputs	
Parameter	Range
Cellulose content (wt % a.r.)	0–90.5
Hemicellulose content (wt % a.r.)	0–95.3
Lignin content (wt % a.r.)	0–93
Ash content (wt % a.r.)	3–21
Moisture content (wt % a.r.)	0.1–23.5
Pyrolysis temperature (°C)	227–1129
Heating rate (Ks^{-1})	0.12–10000
Gas residence time (s)	0–4803
Holding time (s)	0–3600
Average particle size (mm)	0.035–17.5
Sample size (mg)	0.2–250000
Outputs	
Parameter	Range
Char yield (wt % a.r.)	0–98.9
Liquid yield (wt % a.r.)	0–81.5
Gas yield (wt % a.r.)	1–69.5

2. Methods

2.1. Database development

The experimental data required for the development of the ANN model within this work, were extracted from literature studies focused on biomass pyrolysis according to the following two criteria. Firstly, most of the selected parameters (Table 2) need to be reported in the study. Secondly, parameters necessary for the database, but not reported in the study can be reasonably estimated through data from the study itself or external sources. An example of the latter was the derivation of the cellulose, hemicellulose and lignin content from the Phyllis2 database [42] when they were not reported in the selected study. Gas residence time is another parameter, that although it plays a significant role in a pyrolysis process, it is seldom reported in the relevant studies. For this purpose, when necessary, its value was calculated based on the reported reactor volume and the gas flow rate of the purging gas. Of course, in this case the impact of the release of volatiles during pyrolysis was neglected.

The parameters reported and therefore extracted from the literature sources, are summarized in Table 2, along with their respective range. The complete database is provided in the supplementary information.

From Table 2, it is apparent that a wide range of biomass feedstocks as well as experimental conditions was studied. This choice was made in order to evaluate the (inherent) applicability of ANN models for a wide range of biomass feedstocks and operating conditions. With respect to the latter, as it is evident from the ranges of the heating rates, gas residence and holding times, both slow and fast pyrolysis processes were taken into consideration. When it comes to the reactor type, the only type that was explicitly excluded from the investigation were continuous feeding reactors, thus such reactor based studies were removed from the database. The significant differences in the definition of the aforementioned parameters (e.g. heating rate, holding time, etc.), would render the introduction of such setups problematic for the development of the ANN model. Some operational parameters are either not applicable in a continuous process or their estimation would require delving into uncertain assumptions regarding transport phenomena and devolatilization behaviour in a system. For example, the heating rate, in most cases is irrelevant for continuous processes operating in a steady state temperature and it concerns mostly the heating rate of each particle. The holding time, can also not be easily defined in a continuous pyrolysis process, since it required extensive knowledge of a feedstocks devolatilization behaviour. To correctly define or assume values of such operational parameters, the knowledge of additional parameters such as the particle size and the residence time distributions would also be required. Furthermore, the amount of data available for batch – type setups was significantly larger compared to continuous systems. The inclusion of continuous setups would be possible if certain operational parameters were removed. However, the choice was made to rather differentiate between the two reactor categories, although this way high throughput systems are excluded from the study (large scale reactors are typically continuous). Regarding the average particle size, this value was calculated (when not reported explicitly) according to the upper and lower values of the sieves used. The selected studies along with the respective biomass types are presented in Appendix A– Table A1. Each study was assigned an ID number with which they will be referred with in this work. The database includes in total 482 data points.

The char, liquid and gas yield of the pyrolysis process, were selected as the outputs of the ANN model. The char yield refers to the solid residue of the pyrolysis process, therefore including ash if present. The liquid yield, in the context of the present database and model, includes all the condensable pyrolysis products including water. For this purpose, when the water produced from the pyrolysis was mentioned separately in a study it was added to the total liquid product. Otherwise, it was considered part of it unless explicitly mentioned. Finally, the gas yield refers to the total amount of non-condensable gases produced from the pyrolysis process. All the respective yields were converted to a wt% ar basis, according to the data provided in each study.

At this point, it should be mentioned that significant discrepancies might arise from the incorrect employment of different bases (ar, db and daf) and conversion between them, in the expression of experimental pyrolysis product yields. This particular issue was encountered in the construction of the present database, but it can also have important implications for the comparability of different literature studies that focus on the determination of pyrolysis product yields both in terms of classes (gas, liquid, solid) and specific compounds (tars, gases, etc.). Such discrepancies reduce the scientific accuracy and therefore the value of a number of studies and hinder significantly the development of a comparative review or of a predictive model for biomass pyrolysis.

The use of different bases of analysis, is typically meant for the expression of the composition of a fuel in an as – received (ar), air – dry, total – dry (db) or dry and ash – free (daf) basis. This allows the easier comparison of different fuels with respect to their volatile matter and fixed carbon content. The problem arises when such bases are used for the expression of the product yields of in this case pyrolysis. When the gravimetrically or volumetrically measured products are expressed on a db or daf basis without the simultaneous subtraction of the moisture and regarding daf also ash content from the respective products, the mass balance closure values have to add up to more than 100 %. This issue does not often manifest for two particular reasons. Firstly, incomplete experimental mass balance closures, which are often the case, can compensate for the overestimation of these products. Secondly, another common practice in the literature, the calculation of a product class by difference when the other two classes' yields are measured also masks such discrepancies. In the context of the present work, only two studies in which the mass of ash and moisture of the initial sample were explicitly subtracted from the solid and the liquid product respectively, were found [43,44]. This particular method assumes that all of the ash of the initial sample ends up in the solid product, as does the moisture in the liquid and in general can be viewed as a fair assumption. However, one should keep in mind that depending on the temperature, volatile ash can also end up in the liquid product [45], while moisture could remain in the vapour phase and be collected along with the gases.

The ambiguities arising from the abovementioned different approaches regarding the expression of pyrolysis product yields can easily be bypassed by the authors stating firstly the calculation procedure followed for the conversion to db or daf basis as done for example by Park et al. [43] and Lee et al. [44]. Furthermore, it is essential for the authors to always provide the moisture and ash values necessary for the

conversion to the basis used. Surprisingly, these values are frequently not provided [45–50]. Finally, closing the mass balances by difference often masks intrinsic mass losses of the apparatus used, but this can also lead to incorrect conclusions and misplaced amounts of mass in certain product yields. This practice was noted in literature more widely, especially for the gas yield [48,51–55], and can have a negative influence on model development but also scientific accuracy.

2.2. ANN development

Keras, a high level Python based neural network application programming interface (API), was chosen as the main tool for the design of the ANN model. *Keras'* high degree of flexibility and ease of use were the main reasons behind this choice. *TensorFlow* was used as backend, handling low level operations such as tensor products, convolutions, etc. For the training of the models *Adam* was used, which is a back-propagation algorithm for first-order gradient-based optimization of stochastic objective functions [56]. *Adam* performed better than other algorithms tested (*RMSprop* and the stochastic gradient descent) and, in general, it is well suited for large data and parameter applications. Furthermore, hyperparameters (the model parameters controlling the learning process) have intuitive interpretations leading to fewer tuning requirements. With respect to the testing set, it consisted of studies that were excluded from the training of the network, representing a wide range of input space. In particular, the references with IDs 6, 17, 28, 30, 36, 37 and 38 were used, which in total contribute to 11 % of the entire dataset. In general, in the samples selected for the sensitivity analysis there is a lower contribution of fast pyrolysis samples. Sample 17 is indeed corresponding to fast pyrolysis, as well as 28 and 30, however the latter two are rather on the limit with slow pyrolysis. Unfortunately, this is representative of the amount of fast pyrolysis studies present in the total database itself, which is indeed somewhat lower compared to slow pyrolysis. It should also be mentioned that it is not possible to take specific samples out of a study and use them as part of the testing set as this would skew the analysis by making us obtain artificially good performance.

In total, three different ANN models were developed, each corresponding to each pyrolysis product class studied (char, liquid and gas yield), following a MISO approach. Each of the ANN models developed was a feedforward network consisting of three layers: the input layer, one hidden layer and the output layer. The number of neurons in the hidden layer of each model was determined through a trial and error optimization process. The transfer functions employed were hyperbolic tangent. In order to prevent overfitting, Gaussian noise was added to the connection weights of the inputs during training. As long as the amount of added noise is contained, it can lead to better generalization, since the network becomes less prone to memorization of the data points [57,58]. For the same purpose, dropout was also employed. The key idea of this technique is to randomly drop neurons (along with their connections) from the network during training. During testing, the full network is used, albeit with the connection weights scaled down by the retention probability for the related unit, in order to compensate for the higher number of neurons [59]. Both the noise standard deviation (σ) and the dropout probability (p) were determined during the optimization of the network's hyperparameters.

Features of the database, namely the inputs: heating rate, gas residence time, holding time, average particle size and sample size, have values that span over multiple orders of magnitude. In order to emphasize the order of magnitude of the features and avoid non-meaningful representation, the features were passed through a base 10 logarithmic function (Eq. (1)), modified to account for the possibility of 0 values. In Eq. (1), x is the original value of the feature and x_{low} is the lowest value in the dataset for this specific feature, excluding zero.

$$f(x) = \begin{cases} log_{10}(x), \ for \ x \geq x_{low} \\ log_{10}(x_{low}) - 1, \ for \ x = 0 \end{cases} \quad (1)$$

The first step was the scaling of the database input and output values to zero mean and unit variance using Eq. (2), where x stands for each value of the feature, μ is the average of the feature being scaled and σ is its standard deviation. This equation is also used for the inverse transformation of the outputs, by solving for x.

$$z = \frac{x - \mu}{\sigma} \quad (2)$$

The scaling operation, although not necessary, prevents the network from having to learn how to adjust the weights of the connections to cope with the different magnitudes of the features described [60]. The weights of the connections are randomly initialized by selecting them from a normal distribution with zero mean and 0.05 standard deviation. Scaling provides a tangible performance boost, by reducing the amount of epochs required by the model.

Concerning the input layer of the ANN model, the high degree of correlation between heating rate and sample size, led to the decision for the removal of the latter from the list. This choice was made using mostly qualitative criteria, since the meaningfulness of the correlations was not evaluated using hypothesis – testing methods. This particular correlation is presented and analysed in Section 3.1 more extensively. This choice limits the flexibility of the model in possible future iterations with additional data; however, it is appropriate in the context of the present database. In general, there is a trade-off when the inputs of an ANN model are selected. A high number of inputs and therefore a high number of free parameters, makes overfitting more likely to occur. On the other hand, reducing the amount of inputs may lead to loss of information and consequently impaired prediction capability. In this work, two different approaches regarding the input features of the model were followed. The first one was to include all the possible (10, excluding the sample size) pyrolysis parameters as inputs of the model. The second one was to build a "reduced" inputs model, including only the parameters that showed the highest influence on the network. This selection was carried out by performing two kinds of tests (hereby called *powerset* and *sequential*), as described in [60]. From this procedure, only temperature was excluded, since it was considered a fundamental predictor both in a conceptual way (related to the pyrolysis process) but also due to its high degree of correlation with the products as it was evident by the analysis of the database (Section 3.1).

A *powerset*, which is the set of all the possible subsets of the database features, was used to test every possible input combination for each the three networks (char, liquid and gas). To perform this test, five ANN models were trained for each combination of inputs and then tested on different portions of the database according to a five-fold cross validation procedure. The mean squared error of the validation set, which was selected as the performance metric, was averaged and recorded for each input combination. From this analysis, the heating rate emerged as a strong predictor for the models, scoring consistently low MSE values, followed by the particle size. This result was highly expected, given the heating rate's primary role in a pyrolysis process. In the sequential test, temperature and heating rate were considered as fundamental predictors, meaning that they were always included in the network's inputs. For this testing, the remaining candidate inputs were introduced one by one, cyclically to the list of inputs. Five ANN models were trained in the same way as it was described for the *powerset* test. For each cycle, the MSE for the inclusion of each input was recorded and the one that scored

Table 3
Results of the sequential test. The parameters are reported in descendent order of strength as predictors.

Char		Liquid		Gas	
Parameter	*Score*	*Parameter*	*Score*	*Parameter*	*Score*
Lignin	152	Lignin	170	Gas residence time	170
Ash	112	Particle size	124	Moisture	130
Particle size	100	Cellulose	79	Particle size	110

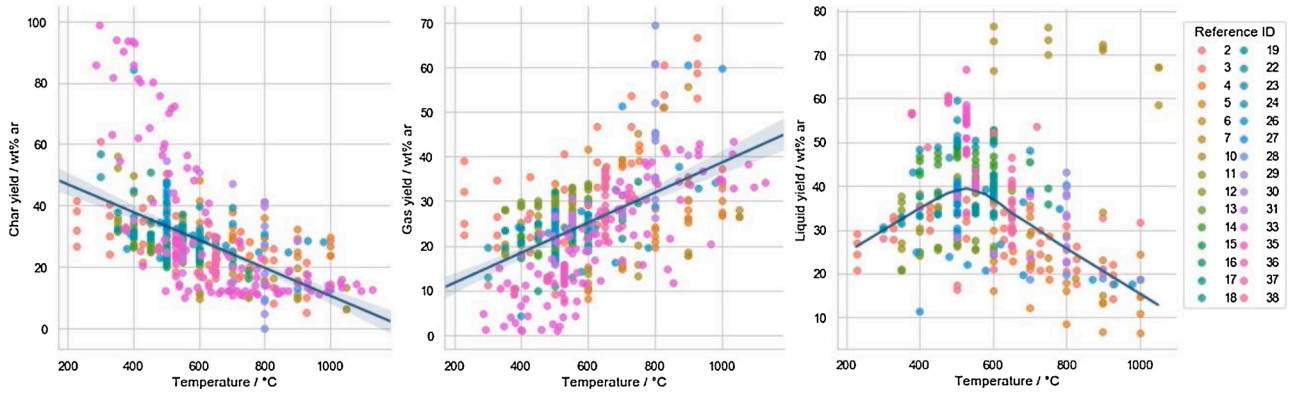

Fig. 1. Char yield (left), gas yield (middle) and liquid yield (right) over temperature for the pyrolysis experiments database, excluding reference with ID 34 for the liquid product. Linear regression along with 95 % confidence interval is shown for char and gas (R = 0.5226 and R = 0.5376 respectively) and a locally weighed linear regression for the liquid.

the lowest was added to the list of inputs. The cycle was repeated until the depletion of the input candidates. The results of the sequential test were evaluated using a simple order-to-score assignment. The three top scoring parameters for each one of the three networks were selected for the reduced versions of the ANNs along with the temperature and the heating rate and they are presented in Table 3. The values of the hyperparameters used in both the *powerset* and sequential tests are mentioned in Appendix B.

Lignin (content) was found to be the strongest predictor for both the char and the liquid ANN models. Lignin can be considered as the main source of char formation for biomass materials pyrolysis as it has also been reported in the literature [61,62]. However, the effect of lignin in the prediction of the liquid yield can be viewed as an indirect effect of its influence on the char yield. Ash content, which is the second stronger predictor for the char model, is also positively correlated with char formation due to its presence in the solid residue in general. Particle size was a strong predictor for all three models. A small value of particle sizes favouring volatile production, has the opposite effect on char production and is in general a crucial factor in a pyrolysis process due to its effects on heat and mass transport phenomena [63,64]. The cellulose content of biomass mainly contributes to volatiles formation [65], so its presence in the list of strong predictors for the liquid model can be explained. Gas residence time scored higher than all parameters for the gas model. Long gas residence times, favour secondary tar cracking thus yielding higher gas yields [2]. However, the qualification of moisture as a strong predictor for the gas model can be viewed as a surprise. Moisture, on the one hand, can contribute to the formation of smaller molecules via hydrolysis and reforming reactions, however other parameters such as the lignocellulosic content for example, were expected to have a bigger impact on the gas yield. A possible explanation could be that the model sees an indirect correlation between the liquid yield and moisture and this is passed on to the gas model. Nevertheless, as it was also mentioned in the previous chapter, the calculation of the gaseous yield by difference, adds a certain degree of unreliability to parts of the database that correspond to these particular measurements.

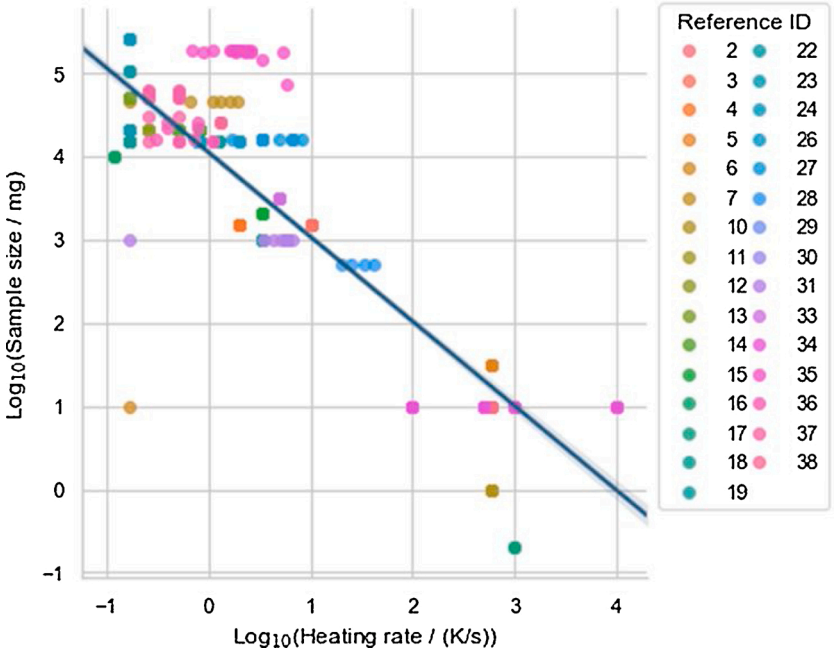

Fig. 2. Logarithmic plot of sample size over heating rate. Linear regression along with 95 % confidence interval is shown (R = 0.9293).

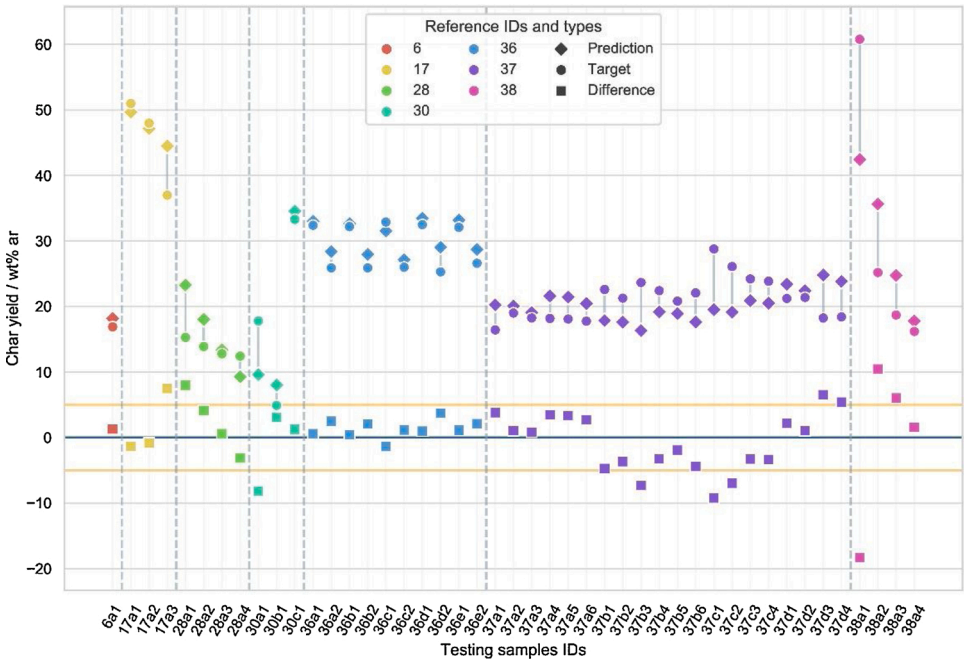

Fig. 3. Performance of the reduced char ANN over the test set. Predictions of the networks are shown alongside the targets for each single sample in the test set. Indicative boundary lines are shown ±5 wt% ar around the zero line.

3. Results and discussion

3.1. Analysis of literature data

In order to identify trends in the available data regarding both input and output parameters, 2D scatter plots of all the possible combinations were generated. Additionally, the Pearson's correlation coefficient (R) values of the distributions were calculated. The purpose of this process was to validate the database by identifying trends known from the literature, as well as provide some feedback for the development of the ANN model. It should be noted, that while high R values do identify correlations, low R values do not exclude them in the particular case studied. During biomass pyrolysis a wide variety of parameters have an effect on the process and its yields, therefore the correlation between just two of them may not always be direct. Finally, as it was also mentioned in Section 2, hypothesis – testing methods need to be employed in order to fully evaluate the quality of the correlations.

Regarding correlations between inputs and outputs, the one between char yield and gas yield with temperature was the most obvious. Fig. 1 shows that with increasing temperatures the char yields decrease, in contrast to the gas yield. Both trends have been well established in literature [66–68]. As for the relationship between temperature and the liquid yield, the correlation becomes more evident with the removal of part of the dataset and in particular of the values corresponding to ID 34 [69]. In this work, a wide set of conditions is studied, with temperatures ranging between 300 and 1100 °C and heating rates between 100 and 10,000 Ks^{-1}. Along with the large amount of data points from this study (97), this wide range of conditions on the one hand helps to expand the input domain of the database and the corresponding ANN model. On the other hand though, it does not allow this particular 2D visualization by skewing it significantly. By removing reference ID 34 from the data set and using a locally weighed linear regression fit, a trend showing the liquid yield increasing until a temperature of 550 °C before decreasing emerges. This behaviour is consistent with secondary tar cracking as it has been described in literature [66,70,71].

From this analysis of the database interesting correlations can also arise between inputs. An example is presented in Fig. 2, where the sample size is plotted against the heating rate with a high value of R (0.9293). The trend shown does not represent a causal relationship between the two parameters, but it rather shows that usually fast pyrolysis experiments are conducted with small samples sizes, while the contrary holds for slow pyrolysis experiments. This observation has a two-fold effect on the ANN model development. Firstly, it assists in defining the boundaries of the input space since by showing that the network has little or no information on how to behave in the case of slow pyrolysis with small sample sizes or fast pyrolysis with big sample sizes. Furthermore, the strong correlation between the two parameters indicates that they contain the same redundant information in the context of the database. Similar correlations were found between heating rate and particle size and gas residence time, although to a lesser extent (R values of 0.6615 and 0.4587, respectively).

3.2. ANN results

3.2.1. Full and reduced models performance

The optimal values of the hyperparameters obtained through the optimization process are presented in Appendix B, while the values of weights and biases for the hidden and output layers are included in the supplementary information. Furthermore, the analysis and presentation of the results was performed with root mean square error (RMSE) as a metric. However, in order to facilitate comparison with other models, the corresponding R^2 values are also presented in Appendix D.

The reduced char model (Fig. 3), using temperature, heating rate, lignin content, ash content and particle size as input parameters, performed better compared to the full model in the prediction of the char yield (root mean square value of 5.1 wt% ar versus 5.9 wt% ar). In general, char constituted the product for which the best estimations were achieved for both types of models used. The fact that the reduced model performed better, supports the argument that a reduced representation of data can lead to better results due to improved generalization capabilities. Among the data points used in this ANN's testing, 38a1 appears to be the main outlier. The high magnitude of the error for this point can be attributed to the combination of an especially large particle size (10 mm), a very low pyrolysis temperature (300 °C) along with a value of heating rate which lies in the margin between slow and fast pyrolysis (80 $Kmin^{-1}$). This combination makes this particular point

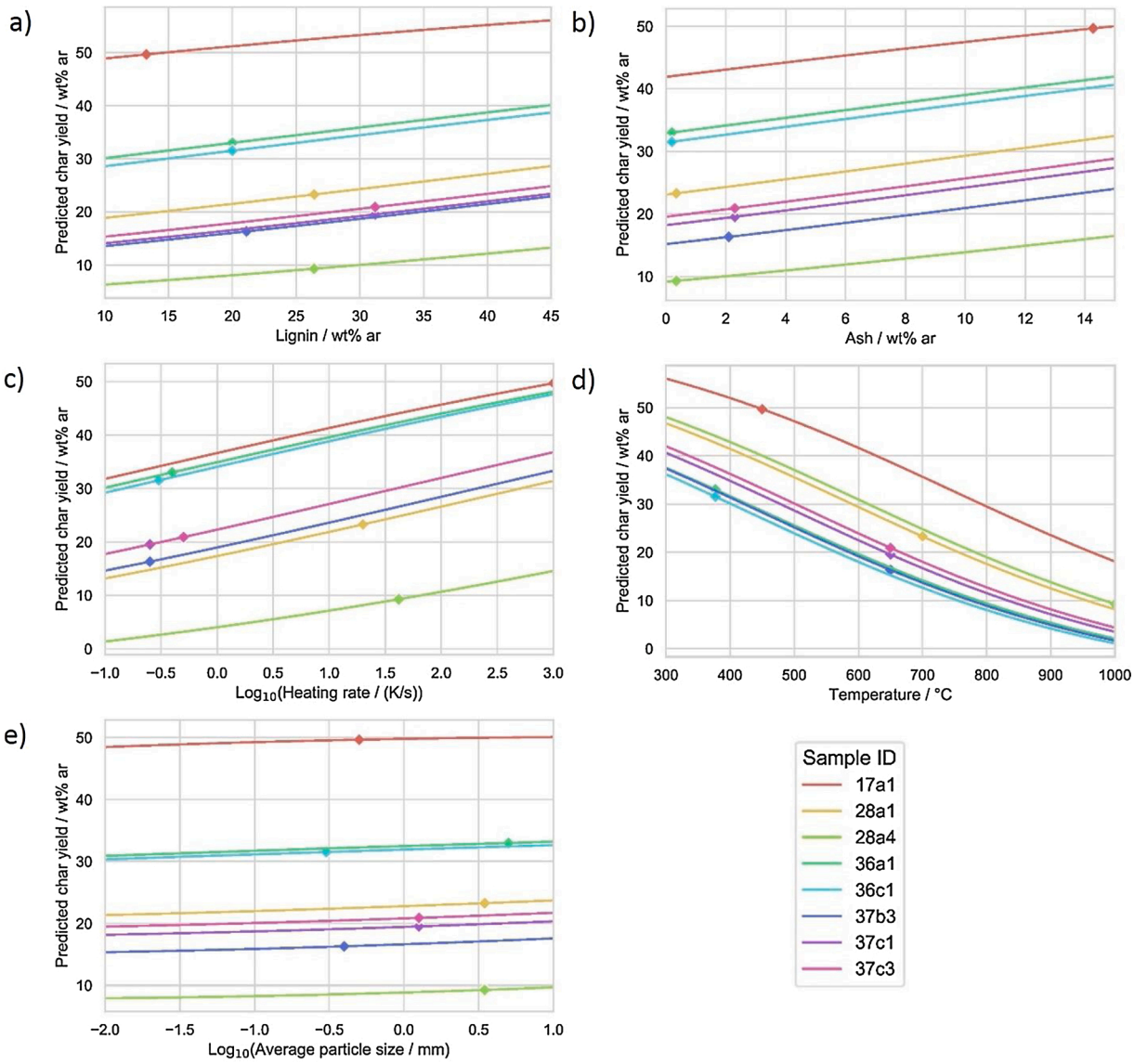

Fig. 4. Predictions of the reduced char ANN for varying values of lignin (a), ash (b), heating rate (c), temperature (d) and average particle size (e) for specific test samples.

stand out among the rest, making it difficult for the ANN to successfully predict the value. Similar high error values were obtained for this data point also in the full char ANN.

In order to evaluate the influence of each parameter on the best performing networks behaviour, a sensitivity analysis was performed by varying each one while keeping the rest unaltered. The purpose of this sensitivity analysis is mostly to signify the importance of analysing the performance of an ANN not only in terms of the RMSE values obtained but also on whether it is able to indeed "learn" the required scientific correlations from the inputs. For this analysis, eight specific samples from the testing set were used, each representing different conditions and combinations. In particular, 17a1 corresponds to a sample with a high ash content that underwent fast pyrolysis at a very high heating rate (1000 °C s^{-1}), while 28a1 and 28a4 differ in terms of pyrolysis temperature (700 °C and 1000 °C, respectively). Samples 36a1 and 36c1 correspond to low pyrolysis temperature (377 °C) with different particle sizes (0.3 mm versus 5 mm). Finally, 37b3 has a lower lignin and higher cellulose content than 37c1 and 37c3, while the latter two differ in terms of heating rate (0.25 Ks^{-1} versus 0.5 Ks^{-1}). The results of this analysis are presented in Fig. 4 and as can be observed, char yield values decrease with increasing temperature. An increase of the lignin and ash content also appears to lead to an increase of the char yield, as it is the case for increasing particle sizes, although to a lesser extent. The latter can be seen as a surprise, since a more intense correlation was expected between char yield and particle size. A positive correlation between the heating rate and the char yield was also established. Although it is difficult to examine the effect of heating rate irrespectively of the rest of the pyrolysis conditions, generally slower heating rates favour char production [72]. However, faster heating rates can also be linked to lower conversion levels, thus leading to an increase of the solid residue yield, which apart from char can also contain some unreacted volatiles, which rather contradicts the previous statement. Of course, it is difficult to say whether the ANN shows this behaviour due to the aforementioned reason. In general, it appears that the reduced char ANN reproduces the trends established by literature successfully. Similar trends were observed also in the corresponding analysis of the full char ANN, however some overfitting behaviour was presented for the cases of ash content and particle size.

In the case of the liquid model, the full version (Fig. 5) performed significantly better (RMSE of 6.9 wt% ar) compared to the reduced one (RMSE of 9.3 wt% ar) with temperature, heating rate, lignin and cellulose content and particle size as inputs. For the liquid models, being the

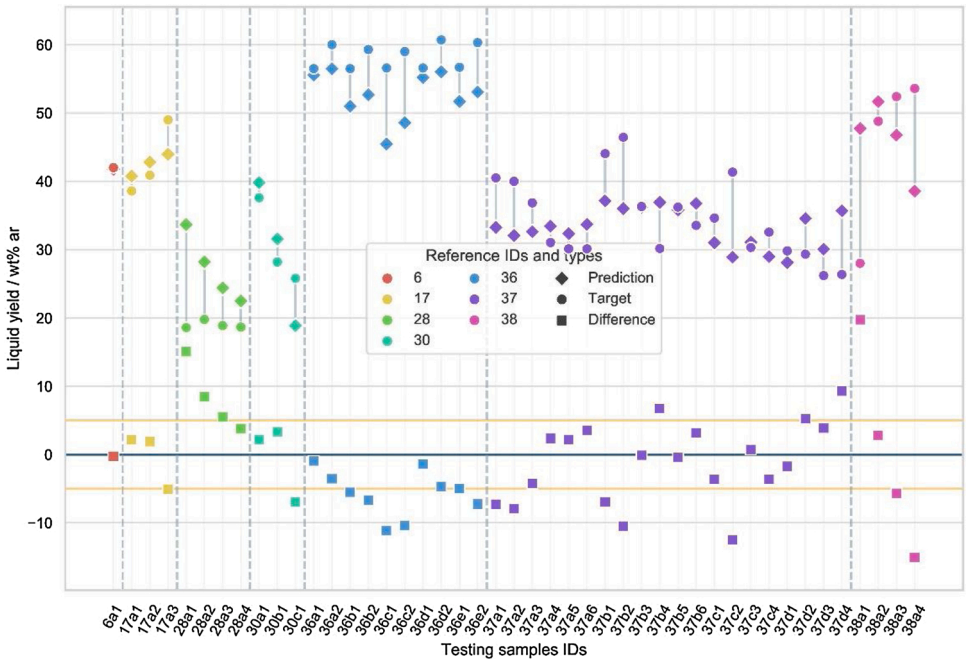

Fig. 5. Performance of the full liquid ANN over the test set. Predictions of the networks are shown alongside the targets for each single sample in the test set. Indicative boundary lines are shown ±5 wt% ar around the zero line.

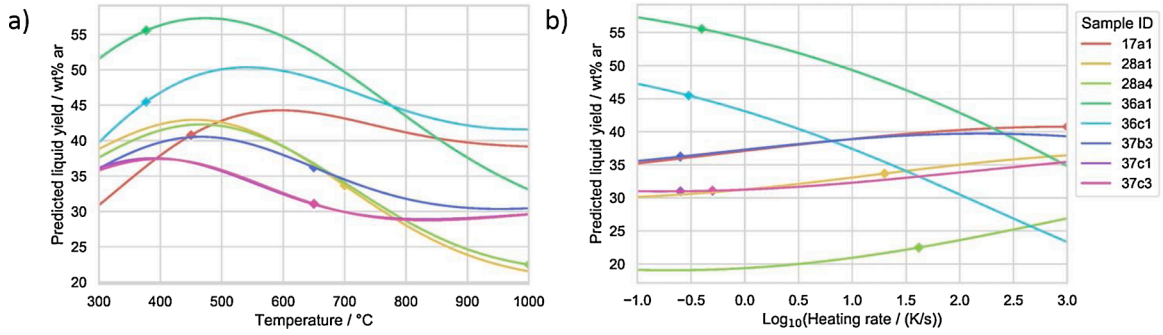

Fig. 6. Predictions of the full liquid ANN for varying values temperature (a) and heating rate (b) for specific test samples.

worst performing ones among the three, the loss in generalization performance by the addition of the extra inputs in the full model was compensated by the amount of information added. The same kind of analysis as in the case of the reduced char model presented above, was also conducted for the full liquid model, using the same samples from the database. As can be seen in Fig. 6, the full liquid ANN was able to learn correctly the correlation between temperature and liquid product yield. For each of the samples tested, the liquid product maximum yield was obtained in the temperature range 400–600 °C. The behaviour of the heating rate was diverse on the other hand. Fig. 6b shows that all the samples apart from 36a1 and 36c1 point to a positive correlation between heating rate and liquid yield. Similar results were obtained also for the rest of the parameters used as inputs for the liquid model, with possible overfitting being encountered for some of them.

Regarding the gas prediction models, the reduced version (temperature, heating rate, moisture content, gas residence time and particle size) produced a RMSE of 5.6 wt% ar (Fig. 7), which was slightly better compared to the full version (RMSE of 6 wt% ar). In Fig. 7, for the reference with ID 36, the variation of the gas yield values due to the heating rate alternating between 0.4 Ks^{-1} and 0.8 Ks^{-1} was correctly predicted. However, this behaviour was not successfully generalized as apparent from reference ID 37. For this reference, data points a1, a2, a3, b1, b2, b3, c1, c2, d1 and d2 correspond to a heating rate of 0.25 Ks^{-1} while the rest relate to 0.5 Ks^{-1}. From the results, it can be concluded that the heating rate variation does not affect the prediction significantly. Furthermore, by observing Fig. 8b, it is apparent that while for slow heating rates the positive correlation with gas yields is properly established, the trend stops and reverses for faster heating rates. This probably indicates the need for the inclusion of more fast pyrolysis experiments in the database. Another interesting observation can be made for the poor performance of samples 30b1 and 30c1, which correspond to pure cellulose and lignin pyrolysis experiments, respectively. This

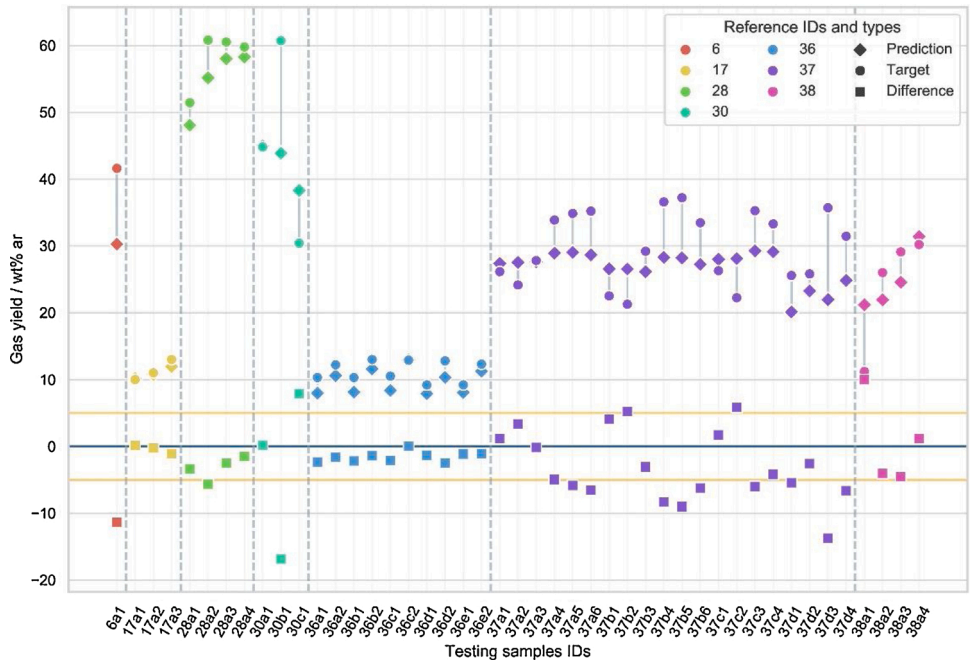

Fig. 7. Performance of the reduced gas ANN over the test set. Predictions of the networks are shown alongside the targets for each single sample in the test set. Indicative boundary lines are shown ±5 wt% ar around the zero line.

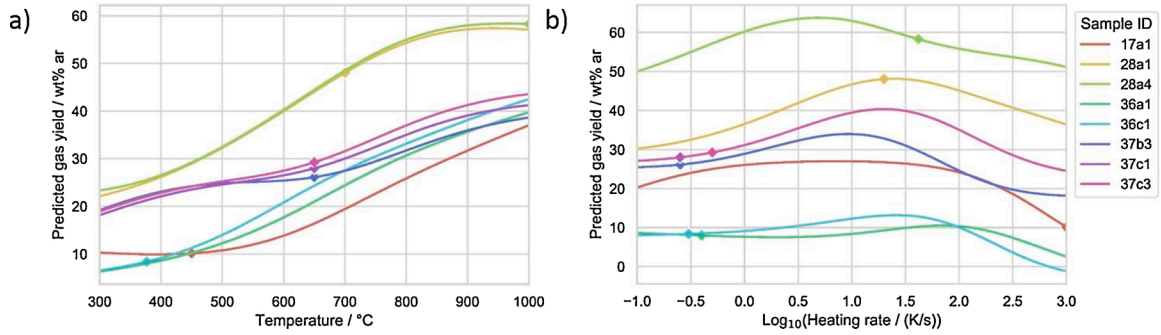

Fig. 8. Predictions of the reduced gas ANN for varying values temperature (a) and heating rate (b) for specific test samples.

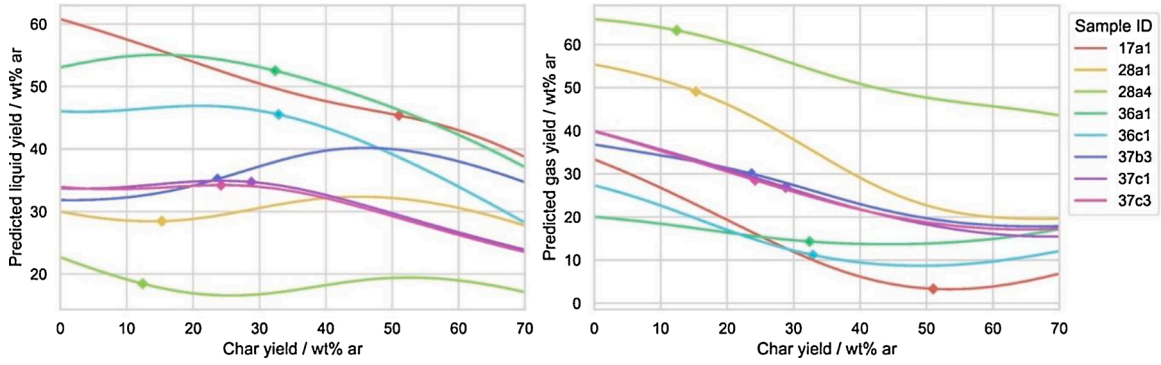

Fig. 9. Predictions of the full liquid (left) reduced gas (right) ANN for varying char values for specific test samples.

poor prediction stems from the fact that lignocellulosic content is not an input for the reduced gas network. For sample 30a1 (pure xylan), the good prediction can be attributed partly to chance and also to the fact that hemicellulose in general is not predominantly linked to the formation of particular product classes, contrary to cellulose and lignin [73]. It is interesting to note, that despite the fact that the full network performed slightly worse overall, it was more successful at the prediction of the ID 30 samples. This observation shows that despite the reduced accuracy of the full gas model, the inclusion of certain parameters leads to correct learning behaviour. Finally, through Fig. 8a, it is possible to affirm that the expected behaviour of the gas yield rising for increasing temperatures was correctly predicted, at least qualitatively.

On a general note, the superior performance of the char models can be attributed to the higher reliability of the char yield measurement from a slow or fast pyrolysis lab scale experiment. The char yield typically consists of the residual mass in the reactor after the completion of the experiment, along with what is captured in a particle separator, cyclone or filter if one of this methods is employed [74]. It can be therefore argued, that there is a higher consistency and intrinsic accuracy in the measurement of the char yield compared to the gaseous and liquid yields, for which several different methods are employed in the literature. Especially in the measurement of the liquid products, several methods exist in the literature for its quantification. The various methods employed include different sampling train configurations, solvents (and solvent evaporation methods) used, temperatures under which the sampling takes place, as well as different types of detectors used for the detection and quantification of certain compounds [74,75]. The lack of robust guidelines for the measurement in the liquid product from small scale pyrolysis experiments, as is the tar protocol for larger setups [76], can lead to significant discrepancies between studies. Additionally, the previously mentioned approach of calculating one of the product classes' yield by difference can lead to similar results. Lastly, it should be mentioned, that the networks that have been obtained in this work, are mutually independent and possess no information regarding the mass balance over the three products. Therefore, the sum of the predictions of the three models do not add up to 100 %. However, it is possible to add the average mass closure of the training set in the model, by normalizing the results of each product with it. This can lead to marginal improvement of the predictions for the liquid and gas products, but not for the char. The description of these ANNs was omitted for brevity.

3.2.2. Char as an input feature

From the previously presented results, it became obvious that the char models were the best performing ones among the ANNs developed. This fact, along with the higher inherent accuracy of char measurements from pyrolysis experiments, led to the decision of the inclusion of char as an input to the liquid and gas ANN models. For this purpose, the full liquid and the reduced gas ANN were trained with char (experimentally derived) as an additional input. It should be mentioned, that for the generalization and refinement of the conclusions derived from this particular approach the powerset and sequential tests would have to be repeated. Furthermore, correlations between the char yield and inputs such as the temperature and the heating rate might exist that make the use all of them redundant in the context of the information fed into the ANN models. However, such an investigation was outside the context of the present work.

This move led to significantly improved predictions for both models. More specifically the RMSE of the full liquid ANN improved from 6.9 wt % ar to 5.5 wt% ar and the reduced gas ANN from 5.6 wt% ar to 4.9 wt% ar. As it can be seen in Fig. 9, the variation of both yields over the char yield, shows a negative correlation between them. This was certainly expected, since increasing char yields are usually accompanied by decreasing volatile production in thermochemical processes in general. The results obtained from those models fall very consistently within ± 25 % accuracy boundaries and the difference between the measured and predicted yields is also consistently less than 10 wt% ar, making them comparable to the results of Neves et al. [74]. In the aforementioned work, a model for the prediction of pyrolytic volatiles was developed employing a system of equations where elemental and energy balances are combined with empirical parameters. For this work char was also used as an input parameter, however only the results of one study were used for the testing of the model.

3.2.3. Single study ANNs

In general, pyrolysis regression ANN models for single sets of experimental results are described in the literature (e.g. [5,18,24,38]). In order to investigate the behaviour of the ANN models for single studies, references with ID 34 and ID 12 were examined. The first one, which is a study by Nik-Azar et al. [69] with beech wood, has a significant amount of data points (97) and only particle size, heating rate and temperature were varied experimentally. The second study by Aysu and Küçük [52] had a smaller amount of data points (27) and the temperature, the heating rate and the gas residence time were varied. Therefore, two ANN models for each reference were developed, with only the corresponding data points constituting the training and testing sets in each case. The figures containing the results of these models are presented in the Appendix C. The char ANN for ID 34 resulted in an RMSE of 1.9 wt% ar and the liquid ANN an RMSE of 1.5 wt% ar. The results for ID 12 were even better (RMSEs of 0.43 wt% ar for char and 0.63 wt% ar for gas), showing that not many data points are required from the model, especially for narrower ranges of experimental conditions. It should be mentioned that optimization of the hyperparameters was not performed for either case. From this brief analysis, it can be shown that ANN models can deliver very good predictions when it comes to a limited range of inputs in terms of experimental parameters. However, these models are not generalizable; they are reactor and biomass type specific. Furthermore, any variation of the input parameters beyond the limits of each study would constitute an extrapolation on behalf of the model.

4. Conclusions

The ANN models proposed within this work for the estimation of solid, liquid and gaseous pyrolysis product yields focus on generalizability and aim to achieve the best possible results over different reactor systems, conditions and biomass types. This was made possible through the creation of a unique, large database, consisting of a variety of small-scale experimental pyrolysis studies. It can be argued that the implementation of the ANN models was successful, given the quite reasonable values of RMSE of the predictions. However, the ANN models cannot be compared to ones obtained from single or in general more limited studies. The models developed in this work appeared to be able to consistently reproduce the expected behaviours for the respective yields, especially in relation to temperature variation. However, a difficulty in extracting useful information from inputs such as gas residence time and holding time was also noted. Furthermore, a reduction of the input parameters was attempted, based on an evaluation of the most effective parameters. The increased generalization capabilities achieved through

this method were observed in terms of prediction quality improvement for the char and gas ANNs, while in the case of the liquid ANN the loss of information led to worse performance. Finally, it was shown that the inclusion of the experimentally derived char yield as an input parameter in the ANN models, can lead to improved predictive capabilities.

For the cases of the char and gas ANNs, the reduced input networks performance was only slightly better compared to the full ones. The liquid product ANN was the worst performing one, with the reduced version being also considerably less accurate (RMSE of 9.3 wt% ar) than the full one (6.9 wt% ar). Among the three product classes, the char models were the best performing ones, largely due to the higher accuracy of char yield experimental measurements compared to the ones for the liquid and gaseous products. The wide variety of methods employed for pyrolysis liquid product determination as well as the calculation of either the liquid or the gaseous product by difference add to that effect. Considering the lower reliability of the gas and liquid yields measurement from pyrolysis experiment, the reason for the significantly better performance of the gas models in the present work can be sought in the actual numerical values of the yields. In the present database, the standard deviation of the gas yield values (10.9 wt% ar), is significantly lower compared to the ones of the char (15 wt% ar) and liquid (14.7 wt % ar). This means that there is a lower variability in the reported gaseous yields and therefore their prediction, which falls within a smaller interval, entails a smaller error.

In general, the maximum achievable accuracy for the models obtained in this work is limited due to a number of factors. That of course does not exclude the possibility of improvements for example by further optimization of the ANNs, the inclusion of continuous reactors in the database by making the necessary adaptations in the models, the reduction of the models' scope (e.g. focus on specific pyrolysis regime) or the introduction of stricter criteria for the induction of data in the database. Furthermore, the feature reduction method, could be further refined, by utilizing hypothesis – testing methods for the derivation of correlations within the dataset. Additionally, the reported lack of fast pyrolysis samples could be addressed by the removal of some input parameters and/or by focusing on specific regimes, that would allow the expansion of the database to include studies previously left out due to incomplete information. In any case however, the limitations induced through discrepancies in the literature are still significant. Firstly, the composition of biomass samples can be measured using different methodologies of which the results might differ significantly. The standards that are used are often not mentioned in the literature. Furthermore, fundamental parameters are also sometimes omitted, such as the lignocellulosic composition, the gas residence time, even in some cases the heating rate. Finally, the implications of the employment of different methods for products measurement, the calculation of product yields by difference and the ambiguity in definition of units of measurement have already been discussed thoroughly in the present work. In a world that is rapidly shifting its focus towards the realm of big data, it is essential to provide high amounts of quality data that can be easily used and compared by these types of models. Therefore, the pyrolysis scientific community needs to be aware of using higher standards in terms of reported data quality.

Author statement

C. Tsekos: Conceptualization, Methodology, Resources, Writing - Original Draft, Writing - Review & Editing, Visualization. **S. Tandurella:** Methodology, Software, Formal analysis, Investigation, Data Curation, Writing - Review & Editing. **W. de Jong:** Writing - Review & Editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A

Table A1
Studies from literature included in the database, along with the amount of data points.

ID	Biomass Type	Data points	Reference
2	Wood mixture, reed	12	[77]
3	Hazelnut, almond, walnut and sunflower shells	32	[46]
4	Cotton cocoon shell, tea factory waste, olive husk	12	[47]
5	Torrefied and non – torrefied ash wood	25	[78]
6	Leaucaena leucocephala	1	[79]
7	Coffee waste	6	[48]
10	Switchgrass	12	[80,81]
11	Pine needles	23	[82]
12	Giant fennel	27	[52]
13	Laurel extraction residue	23	[53]
14	Safflower seed cake	19	[83]
15	Hazelnut cupula	12	[84]
16	Euphorbia rigida, sesame stalk	4	[85]
17	Rice straw	3	[86]
18	Maple fruit	12	[54]
19	Miscanthus X Giganteus	27	[55]
22	Rice straw	5	[43]
23	Geodae – Uksae 1	7	[87]
24	Bagasse, coco peat, paddy straw, palm kernel shell, umbrella tree stem, umbrella tree bark	6	[44]
26	Sugarcane bagasse	15	[88]
27	Rice husk	18	[89]
28	Spruce wood	4	[49]
29	Xylan, cellulose, hemicellulose and mixtures	6	[73]
30	Xylan, cellulose and hemicellulose	3	[90]
31	Lignin	7	[91]
33	Cotton seed cake	12	[92]
34	Beech wood	97	[69]
35	Beech and fir wood, agricultural residues	18	[93]
36	Beech wood	10	[94]
37	Wheat straw, almond shell, olive stone, grape refuse	20	[95]
38	Pine wood	4	[96]

Appendix B. Hyperparameters values

Table B1, Table B2

Table B1
Hyperparameter values used in the powerset and sequential tests.

Parameter	Powerset test	Sequential test
Hidden layers	1	1
Neurons in hidden layers	15	15
Batch size	30	30
Epochs	1250	1500
Learning rate	0.001	0.001
Noise (σ)	0	0.02
Dropout probability	0	0.2

Table B2
Hyperparameter values for the ANN models developed in the present study.

Parameter	Full char	Reduced Char	Full liquid	Reduced liquid	Full gas	Reduced gas	Full liquid with char input	Reduced gas with char input
Hidden layers	1	1	1	1	1	1	1	1
Neurons in hidden layers	9	9	18	9	9	9	18	9
Batch size	30	30	30	30	30	30	30	30
Epochs	500	750	1500	1500	750	1500	750	750
Learning rate	0.01	0.0001	0.001	0.01	0.01	0.001	0.003	0.003
Noise (σ)	0.3	0.2	0.3	0.3	0.1	0.2	0.3	0.2
Dropout probability	0.2	0	0.2	0.2	0.2	0	0.2	0

Appendix C. Additional figures

A) Full char ANN

Fig. C1

B) Reduced liquid ANN

Fig. C2

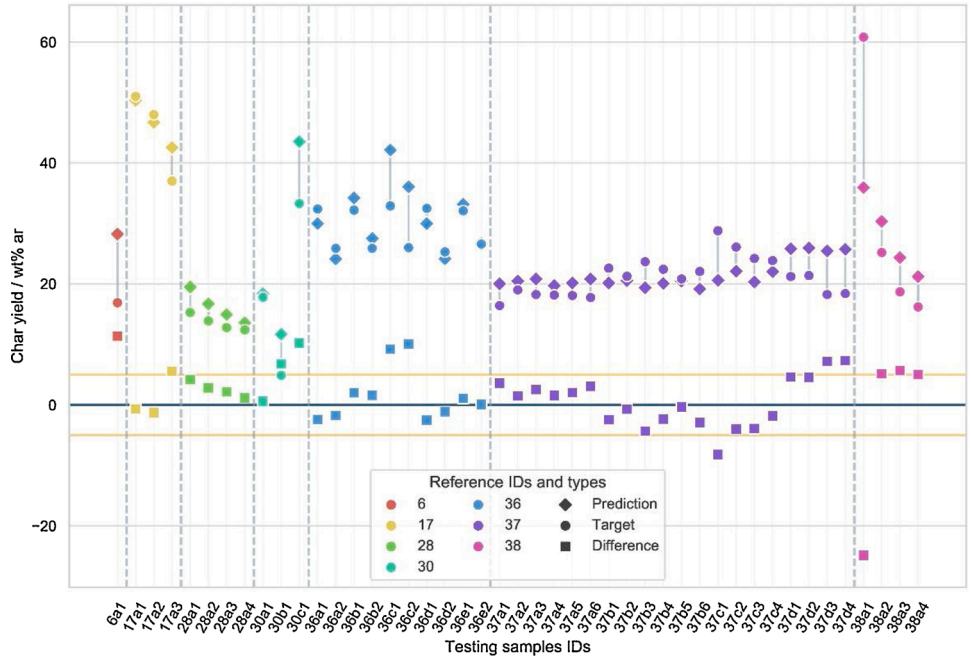

Fig. C1. Performance of the full char ANN over the test set. Predictions of the networks are shown alongside the targets for each single sample in the test set. Indicative boundary lines are shown ±5 wt% ar around the zero line.

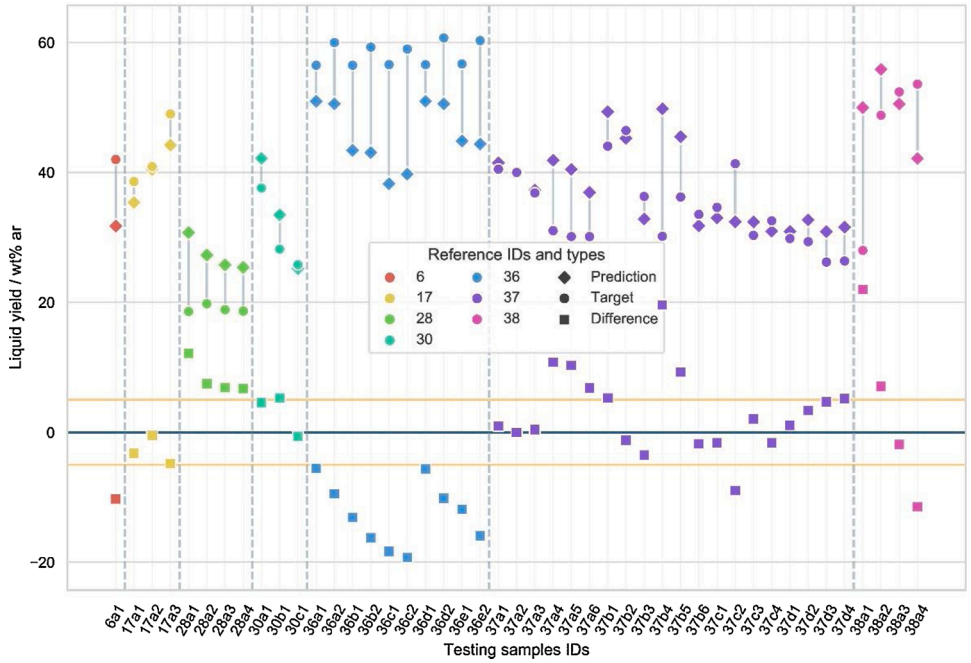

Fig. C2. Performance of the reduced liquid ANN over the test set. Predictions of the networks are shown alongside the targets for each single sample in the test set. Indicative boundary lines are shown ±5 wt% ar around the zero line.

C) Full gas ANN
Fig. C3

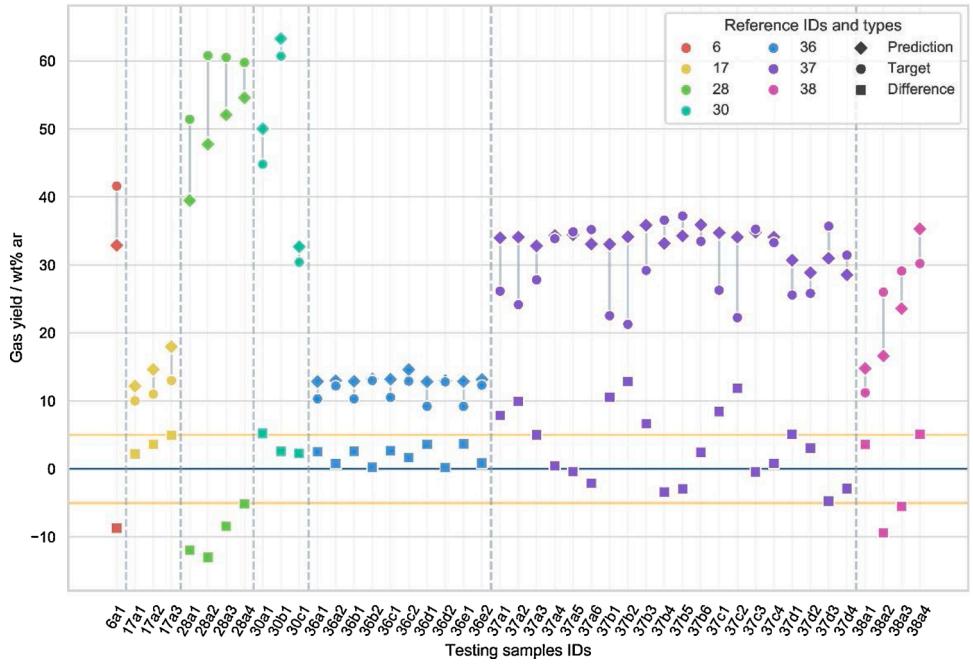

Fig. C3. Performance of the full gas ANN over the test set. Predictions of the networks are shown alongside the targets for each single sample in the test set. Indicative boundary lines are shown ±5 wt% ar around the zero line.

D) Full liquid with char as an input ANN
Fig. C4

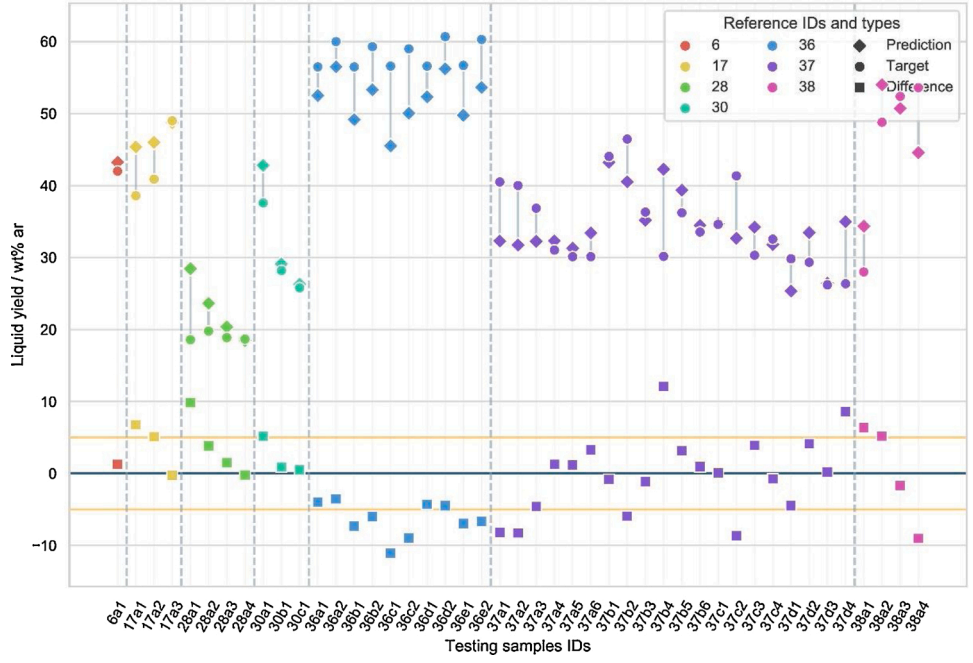

Fig. C4. Performance of the full liquid ANN with char as an input over the test set. Predictions of the networks are shown alongside the targets for each single sample in the test set. Indicative boundary lines are shown ±5 wt% ar around the zero line.

E) Reduced gas with char as an input ANN
Fig. C5

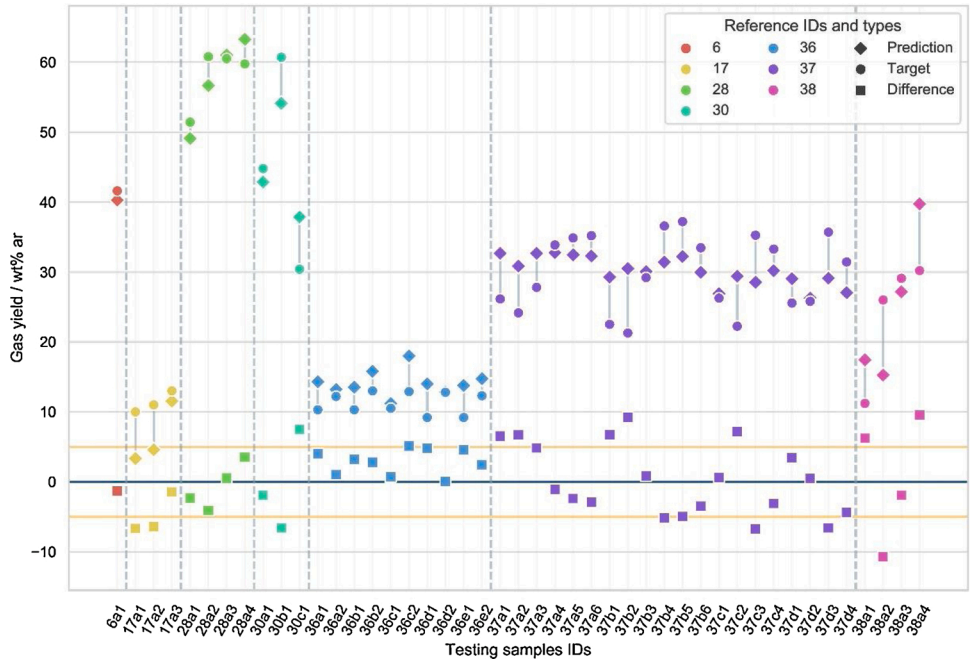

Fig. C5. Performance of the reduced gas ANN with char as an input over the test set. Predictions of the networks are shown alongside the targets for each single sample in the test set. Indicative boundary lines are shown ±5 wt% ar around the zero line.

F) Single study ANNs
Fig. C6

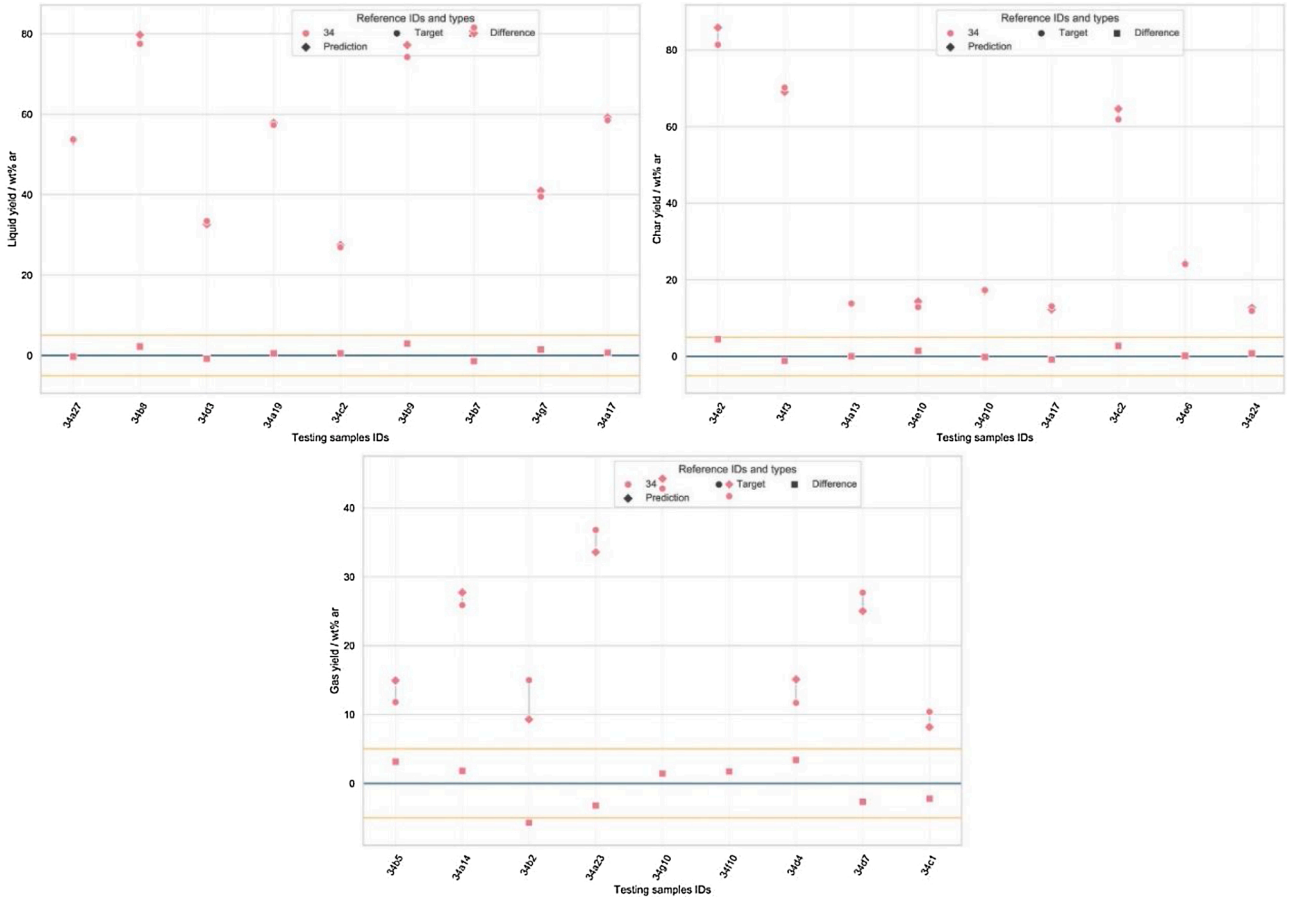

Fig. C6. Performance of the liquid, char and gas ANN over the test set for reference ID 34. Predictions of the networks are shown alongside the targets for each single sample in the test set. Indicative boundary lines are shown ±5 wt% ar around the zero line.

Fig. C7

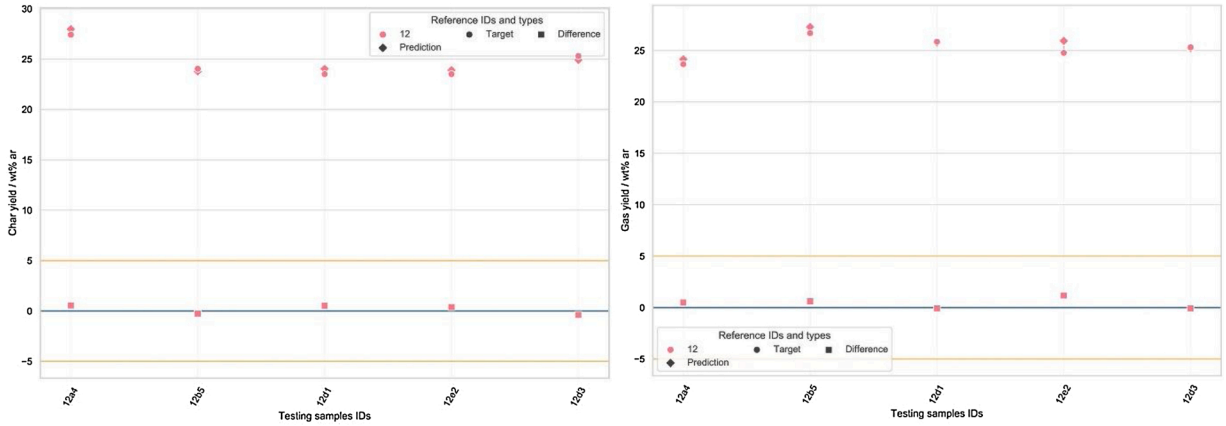

Fig. C7. Performance of the char and gas ANN over the test set for reference ID 12. Predictions of the networks are shown alongside the targets for each single sample in the test set. Indicative boundary lines are shown ±5 wt% ar around the zero line.

Appendix D. R^2 values of the ANNs

Table D1

Table D1
Correspondence between RMSE and R^2 values for the ANN models developed within the present study.

ANN	RMSE (wt% ar)	R^2
Reduced Char	5.1	0.75
Reduced Gas	5.6	0.86
Full Liquid	6.9	0.7
Full Liquid w/ char	5.5	0.81
Reduced Gas w/ char	4.9	0.89
Full Char	5.9	0.66
Reduced Liquid	9.3	0.47
Full Gas	6	0.84
Char ID 34	1.9	1
Liquid ID 34	1.5	0.99
Char ID 12	0.43	0.91
Gas ID 12	0.63	0.62

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