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Predicting FTS products through artificial neural network modelling

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Abstract

Fischer-Tropsch synthesis is essential for converting CO_2 into hydrocarbons, creating sustainable fuels and olefins. However, challenges in production yield and reaction kinetics remain. This study introduces an artificial neural network (ANN) to predict FT synthesis products from specific inputs, including temperature, pressure, GHSV, H_2/CO_2 ratio, and catalyst composition (Fe weight and K as a promoter). The ANN's ability to predict outputs like CH_4, C_{2-4}, C_{5+}, CO_2 conversion, and CO selectivity, without detailed reaction mechanisms, is a key innovation. This approach circumvents complex kinetic models. The network architecture is optimized for minimal error, and results are validated against a comprehensive database.

Keywords: Fischer-Tropsch, Neural Network, Optimization, Modelling.

1. Introduction

Addressing climate change, reducing CO2 emissions from fossil fuels is crucial. The shift towards sustainable initiatives like 'energy transition' presents both environmental and economic opportunities for businesses. Strategies like Carbon Capture and Storage (CCS) and Carbon Capture Utilization (CCU) are pivotal, with CCU gaining attention for converting CO2 into valuable chemicals and fuels (Chung et al. 2023). Power-to-Liquid (PTL) approaches in CCU are significant for producing high-energy-density fuels like methanol, gasoline, and diesel, which are easier to store and transport. Fischer-Tropsch Synthesis (FTS), since 1925, has been effective in generating hydrocarbons like alpha-olefins and linear paraffins from various feedstocks, crucially without sulfur, nitrogen, and aromatic compounds (Mohajerani et al., 2018). The adaptation of CO2-based FTS for fuel production is a notable advancement under stringent environmental regulations (Martín & Cirujano, 2022). Artificial Neural Networks (ANN) play a vital role in the process industry, enhancing equipment failure prediction, maintenance (Nadai et al., 2017), and system optimization. Their application in conventional FT synthesis for process optimization and kinetic modeling has been successful (Adib et al., 2013; Chakkingal et al., 2022; Sharma et al., 1998). This study applies ANN to FT synthesis with CO2 feedstock, aiming to predict the selectivity of key species like CO, CH4, C2-4, and C5+, using Fe-based catalysts promoted with K. To enhance predictions, five networks were developed for each output, based on parameters like catalyst composition, surface area (BET), temperature, and pressure, identified through Kendall correlation coefficient analysis. The ANN's architecture was optimized using a mixed-integer genetic algorithm methodology. Modelling

2.1 Experimental set-up

In the continuous mixing setup employed, the flow rates of hydrogen (H_2, 30 Nml min^{-1}), carbon dioxide (CO_2, 10 Nml min^{-1}), and nitrogen (N_2, 5 Nml min^{-1}, internal standard) were regulated using three Brooks mass flow controllers. These gases were introduced from the top into a packed bed catalytic reactor, which had an internal diameter of 6 mm and was charged with 1 gram of catalyst. The catalyst was held in position by two disks of quartz wool. To ensure the reactor's internal surface was inert, a blank test was conducted. The process of catalyst activation took place at a temperature of 623 K and a pressure of 0.4 MPa over a duration of four hours. During this phase, the reagent flow rate was maintained at 45 Nml min^{-1}, employing the CO_2/H_2 mixture. Following the reaction, liquid products, including water and heavy hydrocarbons (C_{5+}), were condensed in a cold trap equipped with an external cooling jacket set to 278 K. The condensed liquids were then subjected to gas chromatographic analysis. Pressure within the system was kept constant at 2.0 MPa by means of a pneumatic back pressure regulator. To compute the CO_2 conversion rate and product selectivies , an Agilent 3000A micro gas chromatograph was utilized. This device measured the peak areas of N_2 and CO_2 (AN_2 and ACO_2), their respective relative response factors (k), and the inlet flow rates of N_2 and CO_2 (Fin N_2, and Fin CO_2).Samples of the effluent were collected every two hours for analysis, using the chromatograph equipped with molsieve and QPLOT columns.

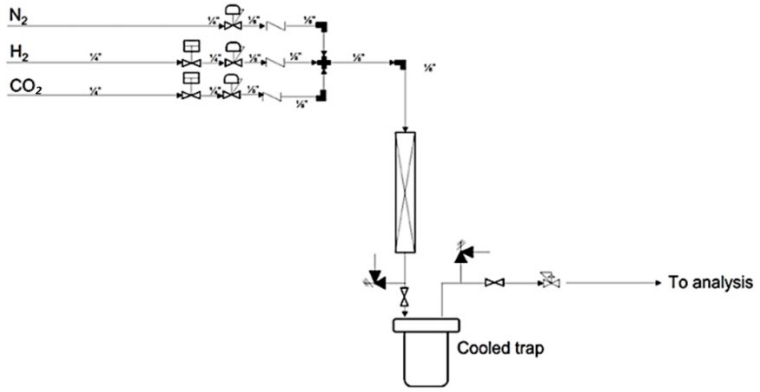

Figure 1*: simplified experimental plant set-up for FT reaction.*

2.2 Neural Network Architecture

The architecture of the ANN is based on the relations between the biases and weight of each node, the neuron activation function, and the training function. Firstly, cascade forward network has been considered, since it relates the output layer weights with an additional weight evaluated from the values of the input variables. It has been seen that it helps to better identify and exploit all the dependences between the input and output variables, given the nature of the system (Zimmermann and Mattedi, 2022). The other network characteristics have been chosen by optimizing the performance of the network. This was done through a genetic algorithm, which selected through a random generation of points (i.e., generation), the best one that minimize the mean square error (MSE) or the network. Both activation functions (AF) and training functions (TF) have been labeled with integers numbers, to be successfully read from the optimizer. Thus, a mixed-integer approach has been used; and the hidden layer have been constrained between 1 and 10 layers. In fact, the variability and quantity of data in the dataset considered is not enough

to achieve good performances with high hidden layers number (Ogunbo et al., 2020). Table 1 shows the list of the activation and training functions. The modeling and optimization have been performed through MATLAB©, from which it has also been chosen the type of activation and training function.

Table 1. Labeling of activation and training functions selected for the mixed-integer optimization.

Label	Activation function	Training function	Abbreviation
1	Pure linear	Levenberg-Marquardt	LM
2	Log-sigmoidal	Bayesian regularization	BR
3	Tan-sigmoidal	Quasi-Newton BFGS	QN-BFGS
4	-	Resilient Back Propagation	RBP
5	-	Scaled conjugate gradient	SCG
6	-	Conjugate gradient with Powell/Beale restarts	P/B-CG
7	-	Fletcher-Powell conjugate gradient	F/P-CG
8	-	Polak-Ribiére conjugate gradient	P/R-CG
9	-	One-pass secant	OPS
10	-	Gradient drop-down variable learning rate	GDVLR
11	-	Gradient disc with momentum	GDM
12	-	Gradient Discess	GD

2.2.1 Input variable definition

The input variables to the model have been chosen accordingly to the nature of the catalyst and of the process. Since the aim of the model is to predict the kinetic results and performances of the process, the catalyst composition has been addressed, in terms of density and (ρ_{cat}) and specific surface (BET). Since the active phase and promotor have been fixed *a priori*, the density gathers the information of the catalyst intrinsic composition. Finally, the Kendall correlation coefficients evaluation (Figure 1) confirms the goodness of the dependences between catalyst features and products, which shows that at higher catalyst density, higher chain products are preferred, but at higher BET, lighter hydrocarbons are favored, since increase the selectivity of the catalyst itself in terms of pore dimension and tortuosity. Moreover, two more input variables have been selected: temperature (T) and pressure (P). By defining the state of the system, these are important information since highlights both the sensitivity to the process to produce a certain group of species and the catalyst operational window. At higher temperature, lower chain hydrocarbons are expected, and at higher pressure higher chain hydrocarbons are favored (Chen and Yang, 2019).

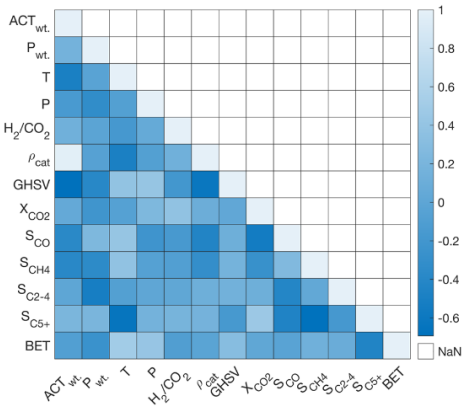

Figure 2: *Heatmap of the correlation coefficients of the dataset features*

2.3 Dataset Compilation for Artificial Neural Network Training

To facilitate the modeling process through an artificial neural network (ANN), a comprehensive dataset was necessary. This dataset was compiled from a combination of 12 articles (Qingxin Yang, 2021) and experimental results. From these articles, a variety of data points were extracted, encompassing reaction conditions such as temperature, pressure, gas hourly space velocity (GHSV) and ratios of reactants. Additionally, reaction outputs were included, such as: CO_2 conversion and selectivities towards products. The nature of the catalysts used in these studies was also a critical component of the dataset, represented by their densities, which were calculated (Eq. 1)based on the amounts of active metals, promoters and the porosity (φ). The latter was calculated as the average between the experimental values of the catalysts used and literature values taken as standard case (Yulan Zhang, 2015).

$$\rho_{cat} = \varphi \cdot \left(\frac{\%\,K}{100} \cdot \rho_K + \frac{\%\,Fe}{100} \cdot \rho_{Fe} + \frac{100-\%\,K-\%\,Fe}{100} \cdot \rho_{Ti_2O}\right) \quad (1)$$

In total, literature review yielded data for 70 different reaction conditions, providing a robust foundation for the ANN. To complement this, experimental data reflecting similar parameters were incorporated into the dataset. This experimental contribution added 25 unique data sets, ensuring a diverse and comprehensive pool of information for training the neural network. This amalgamation of literature-derived and experimental data forms the backbone of the ANN model, ensuring its relevance and applicability in the context of Fischer-Tropsch synthesis.

2. Results and Discussion

The best architecture for the five networks is found from the optimization (Table 2). Two activation functions, one for the hidden layers (HL) and one for the output layer (OL) are selected. It must be said that the learning rate and normalization of input/output variables are done automatically by the MATLAB© algorithm used for the modeling. The performances of these networks are assessed with the value of the MSE (Table 3). These values are in line with the ones obtained in literature (Fernandes, 2006). As it is possible to notice, the highest performances are reached for X_{CO2} and S_{C2-4} predictions, while the worst one came from the modeling of the S_{C5+}.

Table 2. optimization architecture from the genetic algorithm solution

Output	Symbol	N° HL	AF HL	AF OL	TF
CO_2 conversion	X_{CO2}	9	Log-sigmoidal	Pure linear	P/B-CG
CO selectivity	S_{CO}	2	Pure linear	Tan-sigmoidal	F/P-CG
CH_4 selectivity	S_{CH4}	9	Log-sigmoidal	Pure linear	OPS
C_{2-4} selectivity	S_{C2-4}	4	Log-sigmoidal	Tan-sigmoidal	OPS
C_{5+} selectivity	S_{C5+}	8	Tan-sigmoidal	Tan-sigmoidal	BR

However, despite the MSE gives to this the highest value, the mean prediction error (MPE), evaluated as the relative error between the experimental data and the network calculations, has its highest value on the prediction of the CO selectivity. This is principally due to the intrinsic nature of the ANN when applied on chemical processes.

Table 3. Performance indicators of the networks.

Network	Total epochs	Epoch at minimum MSE	MSE	MPE
CO_2 conversion	16	10	92.87	0.30
CO selectivity	28	22	118.4	0.82
CH_4 selectivity	12	6	112.3	0.58
C_{2-4} selectivity	20	14	81.62	0.19
C_{5+} selectivity	45	44	167.3	0.37

On the other hand, other algorithms have been used for comparison; with particular focus on S_{CO} evaluation. To make the comparisons, MSE has been used as performance indicator. Firstly, Multiple Linear Regression (MLR) and Decision Tree Regression (DTR) are tested, using as independent variable the same used in ANN. Results are shown in table 4.

Table 4. Performance indicators and comparison with other algorithm.

Algorithm	Average MSE	STD.DEV	S_{CO} MSE
ANN	114.5	33.00	118.4
MLR	157.3	36.75	193.1
DTR	138.6	44.30	172.5

As it possible to notice, ANN outperformance the other algorithm tested; MLR, the simplest one, has the lowest score, and this is reasonable since the behavior of the species, including CO, is strongly nonlinear, depending on the thermodynamic of the process. On the other hand, DTR has better score with respect to MLR, but still not performing enough well. This because decision tree can be overwhelmed from the variability of the data, which led to a drastically change in the tree structure during the regression. In conclusion, it is recommended to still use ANN as primary algorithm for the prediction of these parameters and, if possible, evaluate the CO selectivity as a complementary to the other parameters.

3. Conclusions

The application of artificial neural networks (ANN) in this Fischer-Tropsch synthesis study demonstrates a balance of success and challenges. The ANN's ability in predicting CO_2 conversion and C_{2-4} hydrocarbon selectivity, in line with existing literature (Fernandes, 2006), underscores its effectiveness in modeling specific aspects of the synthesis process. However, the model's struggles with accurately predicting longer chain hydrocarbons (SC_{5+}), as reflected by a higher Mean Square Error (MSE), reveal limitations in its capacity to handle the complexities of these reaction pathways. This could stem from data variability, limitations in the network architecture, or insufficient training data. The most significant Mean Prediction Error (MPE) in predicting CO selectivity highlights a critical area of improvement. It suggests the model's limited sensitivity to subtle variations in reaction conditions, a crucial aspect for precise chemical process modeling. This finding calls for a deeper exploration into refining the ANN architecture, possibly integrating more diverse and complex datasets or adopting more sophisticated machine learning techniques. Overall, the study presents a promising yet incomplete picture of ANN's capability in chemical process optimization. Future research

should focus on enhancing the model's accuracy across a broader range of outputs and delving into more complex reaction dynamics. Such advancements are essential for realizing the full potential of ANN in this field.

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