

Neural Network Modeling of Methanol to Propylene over P-ZSM-5 in a Fluidized Bed

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Abstract

P-ZSM-5 catalyst selectively converts methanol to propylene (MTP) and other olefins at moderate temperatures (325–550 °C). Between 250–325 °C, the catalyst dehydrates methanol to dimethyl ether (MTD) reaching 87% at low gas velocities in a fluidized bed. A carbon pool forms in the catalyst pores from which propylene and other hydrocarbons are derived. Propylene selectivity varied between 20–41% at temperatures between 400–550 °C and weight hourly space velocities (WHSV) of 0.20–0.39 h⁻¹. Two multilayer feed forward artificial neural network (ANN) models represent the methanol conversion and propylene selectivity very well ($R_{MTD}^2 = 0.973$ and $R_{MTP}^2 = 0.999$, respectively). Temperature is the most significant factor: conversion increases from 42% at 300 °C to 63% at about 500 °C. The rank of importance for conversion and selectivity are: catalyst weight > argon flow > methanol flow and water flow > catalyst weight > methanol flow > argon flow, respectively. ANN is an alternative to kinetic and hydrodynamic modeling to optimize reactor performance particularly for complex systems such as MTP in fluidized beds.

Introduction

Steam cracking and fluid catalytic cracking (FCC) of heavy oil feedstocks produce light olefins (C₂ = – C₄ =), which are the most important petrochemical monomers [1]. Alternative feedstocks are desirable to substitute crude oil for the petrochemical industry because of supply concerns and price fluctuations [2]. The catalytic conversion of methanol is an option to produce high value products because it can be derived from coal, natural gas or biomass all of which are readily available and relatively inexpensive.

Dimethyl ether (DME), which is produced from methanol, is a low cost and clean fuel, propellant, and refrigerant. Furthermore, it is a precursor for various chemicals, such as dimethyl sulphate, acetic acid and olefins (dimethyl ether to olefins — DTO). Lurgi has constructed MTD/MTP plants in Iran and Norway [3] with multi-tubular fixed beds. In the first step, a fraction of the MeOH dehydrates to DME and in the second step, the mixture reacts to form paraffins, olefins and aromatics. The main factors that influence methanol conversion to propylene include catalyst type, temperature, feed concentra-

tion (including water), space velocity and pressure [4,5]. Besides the catalyst type (ZSM-5, SAPO, etc.), other factors related to the catalyst that influence hydrocarbon yield are: catalyst acidity, topology, and crystallite size [6-8]. ZSM-5 zeolite is more selective towards ethylene and propylene compared to other hydrocarbons and its selectivity may be altered by varying the operating conditions [8-10]. Models save time and cost when generating basic data for new facilities, during the design and start-up stages, as well as while the plant is operating.

Recently, researchers have applied ANN to diverse fields including pattern recognition, organization, parameters estimation, and fault-tolerance [11]. ANN develops a model based on raw data and uses these data to generate an initial network (training). We test the network with new data but can continually input data to refine the model. Compared to theoretical models, ANN is a black box technique: it only requires data. Inputs into the model include operating conditions — temperature, flow rate, pressure, catalyst inventory, and concentration — and response variables such as conversion, selectivity, product distribution, etc. Ideally, we need fewer experiments to derive a working model that adequately represents multiparameteric systems behavior compared to fundamental physico-chemical modeling, where we derive the heat and mass balance equations from first principles together with a detailed

kinetic model (DFT - density functional theory, for example). Several research teams have applied ANN to characterize complicated engineering systems over a wide scope of applications [12-14].

Among various neural network architectures, the multi-layer feed forward neural network with a back propagation training algorithm, typically called back propagation neural network (BPNN), is the most common to predict and organize systems [15]. Several studies on catalytic conversion of methanol, including deactivation, reaction rates, catalyst design, optimization of operational conditions are already available (Table 1). Adib et al. (2013) applied ANN to predict the molar percentage of CH_4 , CO_2 and CO for the Fischer-Tropsch process. They found that 5-8-1, 4-7-1 and 4-9-1 ANN topologies are optimal to predict of molar percent of CH_4 , CO_2 and CO . The results of the ANN agreed well with the experimental data ($R_{\text{CH}_4}^2 = 0.94$, $R_{\text{CO}_2}^2 = 0.93$ and $R_{\text{CO}}^2 = 0.96$). Oliveira et al. (2009) reported that ANN is a powerful modeling tool to characterize the selective catalytic reduction (SCR) process [17]. They predicted NO_x conversion of three SCR catalysts (CuZSM-5, CuMORD and a commercial SCR catalyst — CATCO). The ANN with three neurons and one hidden layer provided the best agreement with the experimental data ($R_{\text{CATCO}}^2 = 0.73$, $R_{\text{CuMORD}}^2 = 0.85$ and $R_{\text{CuZSM-5}}^2 = 0.85$). Valeh-e-Sheyda et al. (2010) proposed a multilayer feed forward neural network to model methanol dehydration to dimethyl ether over $\gamma\text{-Al}_2\text{O}_3$ in a fixed bed reactor [18]. The ANN included one hidden layer with six neurons and a scaled Bayesian regularization (BR) algorithm to predict the reaction rate with a minimum error (MSE — mean square error = 8.89×10^{-7} and $R^2 = 0.992$). A single hidden layer ANN including seven neurons and conjugate gradient (SCG) algorithm gave MSE = 1.08×10^{-7} and $R^2 = 0.991$. The ANN with 3-10-1 topology and the Levenberg-Marquardt (LM) algorithm gave MSE = 2.02×10^{-7} and $R^2 = 0.982$. The gradient descent adaptive (GDA) algorithm with eight neurons in a hidden layer gave MSE = 4.97×10^{-8} and $R^2 = 0.996$.

Kito et al. [19] proposed an ANN model to characterize how methanol deactivates H-mordenite zeolite catalyst in a fixed bed reactor. They reported good agreement between experimental data and the ANN prediction but did not focus on the selection of an optimum structure.

Omata et al. [20] implemented radial basis function networks (RBFNs) to optimize i) physical properties and life time of modified ZSM-5 catalyst with additives ii) the zeolite composition for dimethyl ether to olefins (DTO) in a fixed bed reactor. The proposed optimum ANN included one hidden layer with 9 neurons.

We focus on the capacity of BPNN for MTD and MTP reactions over P-ZSM-5 catalyst in a fluidized bed reactor. In particular, we concentrate on predicting methanol conversion and propylene selectivity as function of effective operating parameters — temperature, flow rate and feed composition.

Artificial neural network

ANN creates a mathematical structure that can predict outputs based on experimental inputs. A neural network is a non-

linear data modeling method which comprises a set of simple interrelated analog signal processors. “Training” the network optimizes the non-linear relationship between inputs and outputs. A feed forward network is the second category of ANNs. The signals go in only one direction — there are no loops in this network. The error function evaluates the difference between the target and the predicted data, as well as the ability of the models to generalize. We use MSE and root mean squared error (RMSE) equations to evaluate the performance of the ANNs.

$$MSE = \frac{1}{n} \sum_{i=1}^n (d_i - D_i)^2 \quad (1)$$

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (d_i - D_i)^2} \quad (2)$$

Data set

In ANN applications, we normalize data to train the process. In fact, normalizing the input data eliminates the effect of outliers and considers each input data has equal significance.

$$d'_i = \alpha \frac{d_i - d_{\min}}{d_{\max} - d_{\min}} + \beta \quad (3)$$

where d'_i is the normalized data, d_i is the original data, d_{\max} and d_{\min} are the maximum and minimum, respectively. The two positive constants (α , β) determine the limits of the interval for the normalized data. In our case, α and β are 0.8 and 0.1, respectively. Therefore, the normalized input/output data are in the range of [0.1, 0.9]. We trained the ANN with 65% of the data and 10% and 25% of the data, validated and tested the model, respectively.

Experimental

Methanol reacts over a phosphorus promoted ZSM-5 catalyst in a glass fluidized bed reactor. The reactor was 46 mm ID and about 1.60m long (the catalyst bed height of catalyst was generally lower than 300mm). An electric furnace controlled the temperature within $\pm 5^\circ\text{C}$ of the set-point. The furnace temperature would drift at times so the final conditions deviated slightly from the original experimental plan. The reactor operated at atmospheric pressure and temperatures from 250–550 $^\circ\text{C}$. The composition of the catalyst precursor was 10% CBV28014 (Zeolyst), Levasil 100s/30%, and kaolin 60%. After spray-drying, the catalyst calcined at 550 $^\circ\text{C}$ for 4h in air. The microspheres then underwent an ion-exchange treatment with an aqueous solution of $(\text{NH}_3)_2\text{HPO}_4$ under continuous agitation. The P-ZSM-5 catalyst included 1.5% phosphorus. The average particle size of catalyst was 108 μm . It was placed on top of glass beads in the reactor and heated to the desired reaction temperature in a stream of argon gas. (The total height of glass beads resting on the glass distributor was about 20cm, which brought the catalyst higher into the heated zone.) We maintained the gas velocity below the minimum fluidization velocity of the glass beads to minimize mixing between the beads and the catalyst.

MTD experiments

The design of experiments (DOE) for the methanol conversion

References	Year	Catalytic process	ANN application
Liu et al. [21]	2001	CO ₂ hydrogenation	Catalyst design as a function of the catalyst composition and reaction conditions
Corma et al. [22]	2002	Oxidative dehydrogenation of ethane	Modeling catalytic data and predicting new potential catalyst compositions
Kito et al. [19]	2004	Methanol to olefin	Prediction of catalyst deactivation
Akcayol et al. [23]	2005	Catalytic converter	Prediction of catalyst temperature, hydrocarbon emissions and CO emissions
Moliner et al. [24]	2005	Catalyst synthesis	Prediction of the occurrence and crystallinity of zeolite beta and competing phases
Omata et al. [20]	2009	Dimethyl ether to olefin	Optimization of physicochemical properties and life time of catalyst
Oliveira et al. [17]	2009	Selective catalyst reduction (SCR)	Prediction of NO _x conversion
Valeh-e-Sheyda et al. [18]	2011	Methanol dehydration	Prediction of reaction rate
Arcotumapathy et al. [25]	2011	Methane Steam Reforming	Catalyst design and reactor operation
Ehsani et al. [26]	2013	Oxidative Coupling of Methane	Optimization of operation conditions
Maity et al. [27]	2013	Oxidation of benzothiophene	Prediction of conversion of benzothiophene oxidation
Alavi et al. [28]	2013	Methanol to dimethyl ether	Optimization of feed conditions to maximize methanol conversion
Adib et al. [16]	2013	Fischer-Tropsch process	Prediction of molar percentage of CH ₄ , CO ₂ and CO
Betiku et al. [29]	2014	Transesterification	Prediction of optimal operation conditions
Badday et al. [30]	2014	Ultrasound-assisted transesterification	Prediction of fatty acid methyl ester (FAME) yield

Table 1: Recent literature concerning ANN modeling for catalytic processes

Temperature(°C)	Catalyst weight(g)	MeOH flow(ml min ⁻¹)	Ar flow(ml min ⁻¹)
250	25	50.5	154
275	50	309	613
290	100	792	1580
325	200	1250	2560

Table 2: Variable levels for MTD reaction [32]

experiments included four each levels for temperature, catalyst loading, methanol flow and argon flow (Table 2). The feed included various mole percent of methanol in argon (5, 15, 30, and 33%mol). The superficial gas velocity varied between 4.5–84 mm s⁻¹ for catalyst loadings of 25, 50, 100, and 200g. The temperature was 250, 275, 290 and 325 °C. Kaarsholm et al. report the details of the experiments [32].

MTP experiments

The operating temperatures were 400, 450, 500 and 550 °C. We injected the feed — pure methanol, mixture of methanol/water or methanol/argon — after reaching steady-state conditions. The total feed rate varied between 0.5–3.6 Lmin⁻¹ for superficial gas velocity from 13mm s⁻¹ to 100 mm s⁻¹ and catalyst loading of 50, 110, 220 and 330g (Table 3). The run length was 4–5h. A detailed explanation of the experimental set up and the products analysis are reported by Kaarsholm et al [31].

Temperature (°C)	Catalyst weight(g)	MeOH flow (ml min ⁻¹)	Argon flow (ml min ⁻¹)	water flow (ml min ⁻¹)
400	50	0.92	0	0
450	110	1.84	139.5	0.92
500	220	2.5	1144	1.5
550	330	3.68	2288	1.84

Table 3: Variable levels for MTP reaction [31]

Results and Discussion

Modeling

ANN topology, training algorithms and transfer functions influence the ANN predictive ability. However, a method to

identify the optimal combination of these factors is lacking. We optimized the factors by trial and error. For each case, we completed more than 20 runs by changing the initial weights of the connections.

MTD network

We tested many different ANN topologies and algorithms to characterize the methanol de-hydration experiments with varying degrees of success (Table 4). Increasing the number of neurons in the hidden layers decreases ANN efficiency. The optimum ANN had two hidden layers with 10 neurons in each layer ($R_{MTD}^2 = 0.973$). The optimum topology (4-10-10-1) includes tangent sigmoid (TS) and piecewise linear (PL) transfer functions in the hidden layers and the output layer, respectively (Figure 1). Increasing the number of neurons or number of hidden layers had no effect on the performance. After optimizing the ANN topology, we investigated the effect of various algorithms on how well the model predicted the experimental data (Figure 2). GDA, resilient back propagation (RP) and gradient descent (GDX) algorithms deviate from the experimental data significantly ($R_{GDA}^2 = 0.561$, $R_{RP}^2 = 0.647$, $R_{GDA}^2 = 0.598$). The LM algorithm predicts the methanol conversion best ($R_{LM}^2 = 0.973$).

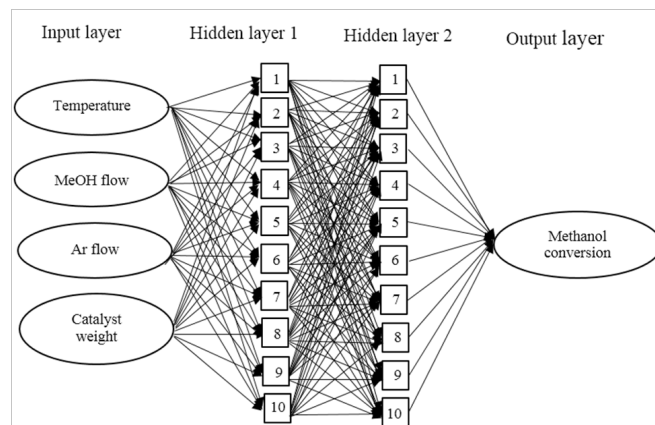


Figure 1: MTD ANN schematic

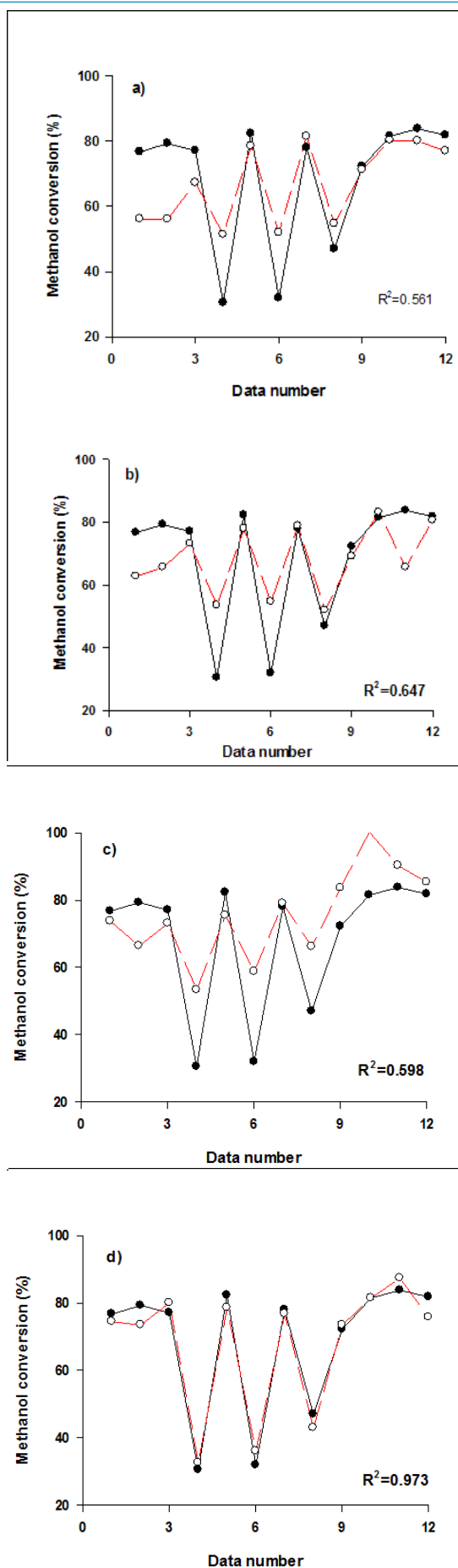


Figure 2: Methanol conversion parity plot for a) GDA b) RP c) GDX d) LM with optimal ANN structure. (-●-experimental data and -○-predicted data)

Structure	Transfer Function	R2	RMSE
4-5-1	TS-PL	0.961	0.016
4-10-1	TS-PL	0.9	0.007
4-15-1	TS-PL	0.918	0.003
4-20-1	TS-PL	0.82	0.097
4-50-1	TS-PL	0.66	0.026
4-5-1	TS-TS	0.899	0.048
4-5-1	LS-PL	0.799	0.048
4-5-1	PL-PL	0.89	0.012
4-5-10-1	TS-TS-PL	0.89	0.041
4-5-20-1	TS-TS-PL	0.82	0.079
4-10-10-1a	TS-TS-PL	0.973	0.012
4-15-50-1	TS-TS-PL	0.82	0.062
4-10-10-1	LS-LS-PL	0.93	0.061
4-10-10-10-1	TS-TS-TS-PL	0.85	0.067

Table 4: Details of the various examined MTD ANNs with LM algorithm. Most of the data predicted by the model is in excellent agreement with the experimental data.

Several authors have characterized the MTD process based on detailed engineering models. They derive a kinetic model taking into consideration the underlying hydrodynamics of the reactor. Kaarsholm et al [32] tested the Bercic and Levec model against their experimental data collected in a bubbling fluidized bed. A simple n-CSTR (continuous stirred tank reactors) model characterized the experimental data equally well as a detailed two phase fluidized hydrodynamic model. They modified the kinetic model and were able to account for 94% of the variance in the data with the n-CSTR (Table 5). The n-CSTR hydrodynamic model including the kinetic model of Bercic and Levec [33] accounted for 92.5% of the data. The MTD ANN gives the best performance and predicts the experimental data better ($R^2 = 0.973$). The results confirm the potential of the ANN modeling approach to characterize chemical reactions in fluidized bed reactors.

MTP network

Increasing neurons in the hidden layer to more than 20 and also the number of hidden layers decrease the MTP ANN efficiency (Table 6). A suitable topology is an ANN structure with one hidden layer including 20 neurons. The LM algorithm provides better agreement with the selected ANN topology ($R^2 = 0.999$). Therefore, the feed-forward BPNN with one hidden layer (5-20-1) including TS and PL transfer functions and the LM algorithm is an optimum ANN for modeling the propylene selectivity of the MTP reaction (Figure 3). We characterized the ANN prediction ability with the test data set, which was not used for training. The ANN model accounted for $R^2 = 0.999$ of the propylene selectivity (Figure 4). Kaarsholm et al [31] developed fluid-bed and kinetic models for the MTP reaction. They assumed that gas rose through the bed in bubbles and the reaction the MeOH reacted in the emulsion surrounding the fast rising bubbles. Interphase mass transfer characterized the exchange of products and reactants between the bubble phase and emulsion phase. The models accounted for 80 % of the variance in the data whereas $R_{MTP}^2 = 0.999$. This is a remarkable difference.

Kinetic model	Reactor model	R2
Kaarsholm et al. [32]	Fluidized bed	0.901
	6 CSTR's	0.94
Bercic and Levec [32]	Fluidized bed	0.884
	6 CSTR's	0.925
MTD ANN		0.973

Table 5: Comparison of different models for MTD reaction

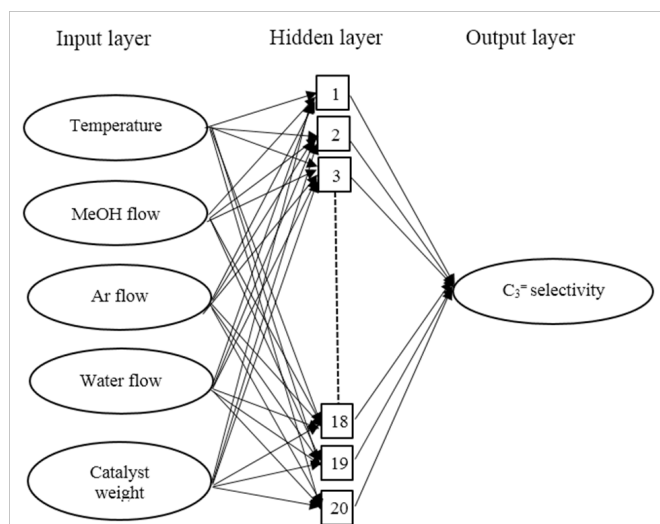


Figure 3: MTP ANNSchematic

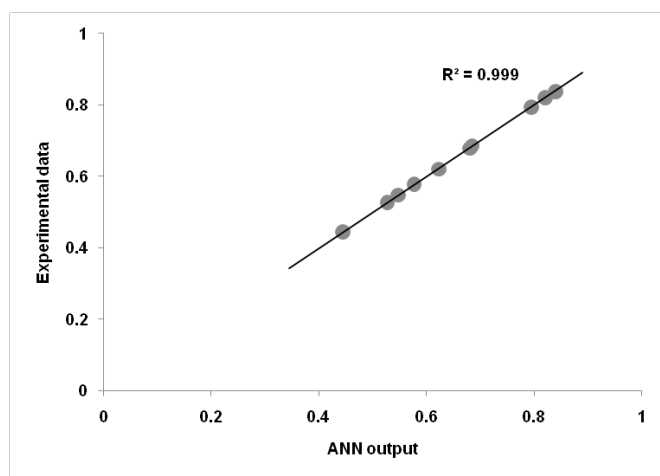


Figure 4: Propylene selectivity parity plot

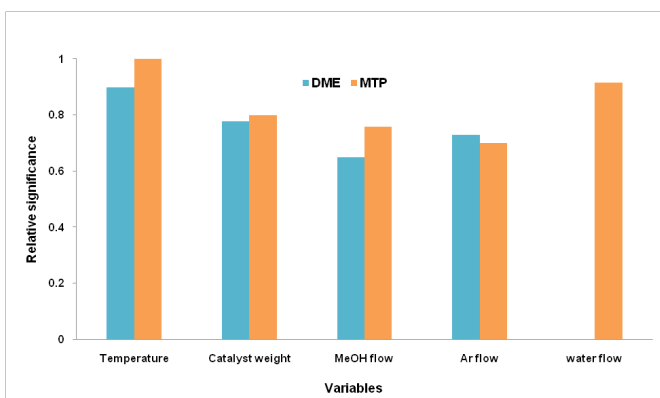


Figure 5: Relative significance of the factors on methanol conversion (MTD) and propylene selectivity (MTP).

Sensitivity analysis

We tested the strength of the relationship between response variable and input factors with the cosine amplitude method (CAM). Data array, X , involves the entire data pairs as a general X -space.

$$X = \{X_1, X_2, \dots, X_n\}$$

where, each component (X_i) is a vector of length of m .

$$X_i = \{X_{i1}, X_{i2}, \dots, X_{im}\}$$

A specific point in m -dimensional space, represents each data pair. The calculated r_{ij} , is a pairwise evaluation between two components (x_i and x_j) of the X -space (Eq. 4) [34].

$$r_{ij} = \frac{\sum_{k=1}^m x_{ik} x_{jk}}{\sqrt{\sum_{k=1}^m x_{ik}^2} \sqrt{\sum_{k=1}^m x_{jk}^2}} \quad (4)$$

MTD reaction

Methanol conversion depends on all of the factors (Figure 5). Temperature is the most significant parameter, which agrees with literature [35,36]. Bjorgen et al [37] reported that methanol conversion continually increased with temperature up to 310 °C. The catalyst weight and argon flow are the next most significant parameters, both of which relate to reactant (and product) residence time. Wang et al. [38] found that methanol conversion decreased at high gas hourly space velocity (GHSV) due to the short contact time between the methanol and catalyst. The methanol flow is the least effective factor on methanol conversion, which is intuitively obvious [39]: less methanol reacts as we feed more.

MTP reaction

The reaction temperature affects propylene selectivity most whereas the argon flow rate is the least significant factor (Figure 5). The next most significant factor is water flow rate. Water competes with hydrocarbon molecules for the acid sites [39]. At high temperature, water inhibits side reactions and increases propylene selectivity by decreasing cracking rate of light olefins. The catalyst weight and methanol flow have a minor effect on the propylene selectivity through the MTP reaction.

ANN generalization

The optimum MTP ANN predicts propylene selectivity for different inputs in the domain of the training data set. The high propylene selectivity (38%) is at low methanol flow (< 1 ml min⁻¹) and a catalyst inventory of (> 150g) (Figure 6a) which corresponds to a low weight hourly space velocity (WHSV). The C₂-C₄ olefins are intermediate components in the conversion of methanol to propylene. Increasing the methanol WHSV favors paraffins and aromatics. This phenomena is attributable to hydride transfer and cyclization of olefinic carbenium ions. Low methanol partial pressure results in high olefin selectivity [40]. Water is a good diluent for MTP because it has a high heat capacity and carries away the heat of reaction with the effluent gases. Based on the equilibrium thermody-

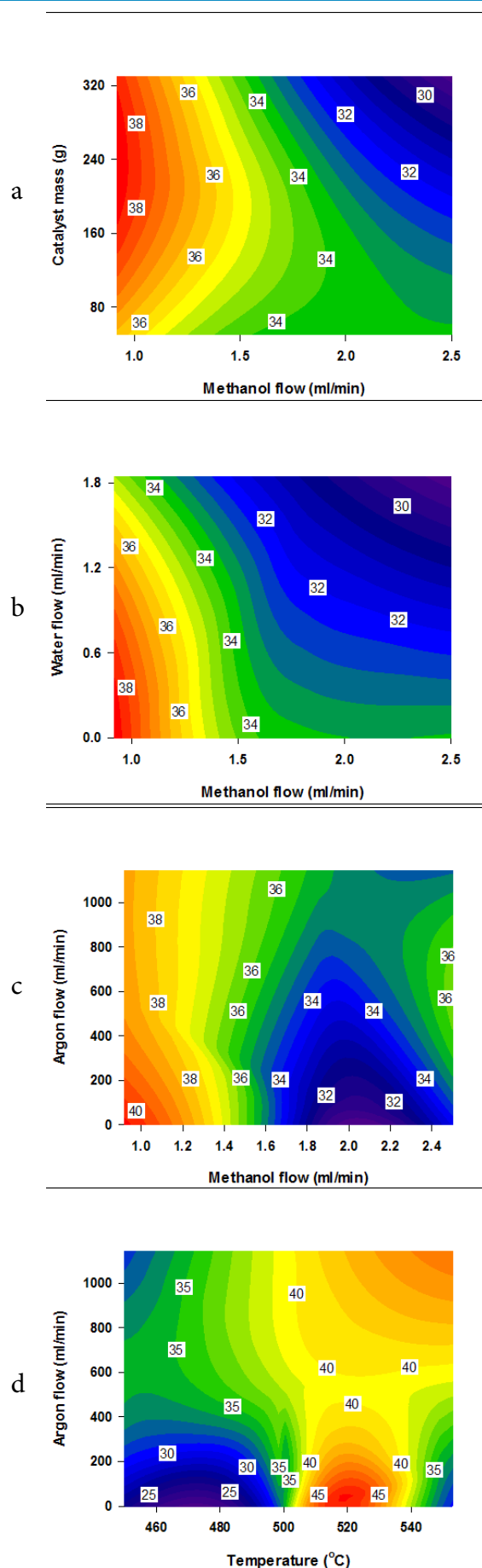


Figure 6: Propylene selectivity as function of operating condition: a) Catalyst mass and methanol flow b) Water flow and methanol flow c) Argon flow and methanol flow d) Argon flow and temperature

Structure	Learning Algorithm	Transfer Function	R2	RMSE
5-5-1	LM	TS-PL	0.639	0.076
5-15-1	LM	TS-PL	0.976	0.012
5-20-1 ^a	LM	TS-PL	0.999	0.0007
5-25-1	LM	TS-PL	0.915	0.025
5-30-1	LM	TS-PL	0.827	0.032
5-50-1	LM	TS-PL	0.934	0.022
5-20-1	GDX	TS-PL	0.354	0.065
5-20-1	RP	TS-PL	0.562	0.064
5-20-1	BR	TS-PL	0.279	0.076
5-20-10-1	LM	TS-TS-PL	0.565	0.06
5-20-20-1	LM	TS-TS-PL	0.408	0.071
5-20-50-1	LM	TS-TS-PL	0.208	0.094
5-20-10-1	LM	TS-LS-PL	0.329	0.125
5-10-10-1	LM	LS-LS-PL	0.552	0.062

Table 6: Details of the various examined ANNs for MTP a) Optimum MTP ANN topology

namics between dimethyl ether and the reactants, co-feeding water reduces dimethyl ether conversion to methanol, which favors olefin formation [40]. However, propylene selectivity was highest (38%) when the water co-fed with the methanol was low ($< 0.6 \text{ ml min}^{-1}$) (Figure 6b). In fact, the high water concentration hinders methanol molecules adsorption on zeolite acid sites due to the competitive adsorption between water and methanol molecules. Co-feeding argon with the methanol reduces propylene selectivity when the methanol flow rate was low (Figure 6c). At the low methanol concentration, argon addition decreases the residence time so less reactants adsorb on active sites. The high reaction temperature increases the molecular velocity and the collision frequency between the reactants and the active surface. Several authors studied the effect of temperature on the MTP reaction over ZSM-5 catalyst [37,42]. It is generally accepted that the propylene selectivity increases with temperature (Figure 6d). At the low end of the temperature range, the MTP reaction rate is slow and the formed heavy hydrocarbons block the catalyst pores. In other words, less reactants reach the active sites and the propylene selectivity drops. High temperature enhances methanol conversion and cracking reactions which favors light olefin production. The highest propylene selectivity (45%) is at a high temperature (520°C —Figure 6d). High argon flow in the feed limits the temperature effect on the propylene selectivity. This behavior results from the energetic molecules and the low WHSV.

Conclusions

We propose powerful ANNs to model P-ZSM-5 catalyst performance in a bubbling fluidized bed for both the MTD and MTP processes. Two multilayer feed-forward BPNNs with two and one hidden layers are optimum ANN topologies for the MTD and MTP reactions, respectively. The ANNs characterize the relationship between propylene selectivity and methanol conversion better than the first principles model that combines the kinetics and fluidized bed hydrodynamics. The sensitivity analysis reveals that temperature is the most significant factor for both methanol conversion and propylene selectivity.

The ANNs are applicable to model and optimize the MTP process over P-ZSM-5 catalyst in fluidized bed. The technique is applicable to complex reactions and multi-phase reactors for which the theoretical understanding is incomplete. In these systems, it will be important to estimate the minimum number of experiments required in order to interpolate over the variable space — temperature, pressure, feed rates. Future work will also use the ANNs to generate experimental designs that can be used to estimate kinetic parameters and hydrodynamics.

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