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Pd/SBA-15 MESOPOROUS CATALYST FOR ETHANOL STEAM REFORMING. A NEURAL NETWORK APPROACH

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A Pd/SBA-15 catalyst with 1% Pd was prepared by impregnation method. The catalyst was characterized by X-ray diffraction, N_2 adsorption-desorption, thermogravimetric analyses. For this study the artificial neural network was used to identify the optimum parameters in the case of Pd/SBA-15 catalyst for the production of hydrogen by catalytic reforming of ethanol. Specifically the neural network was used to determine the optimum conditions for obtaining maximum hydrogen production.

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1. Introduction

Alcohols, like ethanol and methanol are considered as potential carriers of hydrogen by different techniques for use in fuel cells application. Polymer electrolyte fuel cells are considered for applications as power supplies for vehicles and small generators, pointing same advantages as compact size, easy start-up and shut down and high power density [1]. From non-fossil feedstock, such as ethanol, methanol and so on, ethanol has several advantages as chemical H_2 source for fuel cells thanks to its storage facilities, handling and transport safety [2] but on the other hand, vegetable oils have remarkable lubrication properties, high flash point, very high biodegradability and are renewable [3].

In spite of the apparent simplicity of the stoichiometry reaction for maximum hydrogen production $C_2H_5OH+H_20 \rightarrow 6H_2+2CO_2$, ethanol steam reforming for hydrogen production involves a complex reaction system, where several products can be obtained such as CO, CO_2, CH_4, ethylene, acetaldeldehyde and hydrogen. Therefore the production of hydrogen is affected by many undesirable side reactions which involves first off all the properties of the catalysts used [4].

Noble, metal-supported catalysts have exhibited catalytic ability in steam reforming process. Supported palladium catalysts have been shown to have excellent activity toward oxidation and PdO is considered the active species [5,6]. Recently, mesoporous silica SBA-15 which has a highly ordered hexagonal structure with high surface area (500-1000 m^2g^{-1}) and wall thickness of 3.1-6.4 nm has attracted wide attention as a new material for catalysts and especially as catalyst supports.

Pd-based catalysts supported on SBA-15 have been reported to exhibit excellent activity in different types of reactions. Eswaramoorthi et al. [7] tested Pd-Zn supported SBA-15 catalysts varying Pd and Zn content for hydrogen production from methanol by partial oxidation and steam reforming. The authors found that catalyst with 4.5%Pd and 6.7% Zn on SBA-15 showed better H_2 selectivity with limited CO formation due to the enhanced Pd dispersion as well as larger Pd metallic surface area.

Wang et al. [8] confirm that the SBA-15 supported Pd catalyst is also good for CO oxidation. The preparation condition has a significant influence on the catalyst activity. The authors concluded that because of the importance of the Pd catalysts, the Pd-SBA-15 catalysts

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prepared will have many other applications beyond CO oxidation, like the three way catalysts, sensors, drug delivery and optoelectronic.

Pudukudy et al. [9] investigated the Ni/SBA-15 catalyst promoted with Pd for the thermo catalytic decomposition of methane into CO_x-free hydrogen. The catalyst characterization techniques used, indicated that the addition of Pd increased the crystalline of NiO, allowing for the fine dispersion of NiO on the SBA-15 support and increasing the surface area of Ni/SBA-15 catalyst.

The aim of the present study is the preparation and testing of Pd/SBA-15 catalyst regarding ethanol conversion and hydrogen selectivity in ethanol steam reforming process. The purpose of better understanding the performance of Pd/SBA-15 catalyst for steam reforming process, neural networks were applied in the present study.

A class of estimation methods is based on the flexibility and accuracy of the artificial neural networks (ANN). The neural networks represent a branch of the artificial intelligence, which is accepted as a new computing technology. The principle behind the neural network is to simulate the structure and functioning of the biological neural networks [10].

Umegaki et al. [11] proposed to develop a Cu-based catalyst for steam reforming of methanol using an artificial neural network. The authors applied ANN to improve the performance of the Cu-Pr-Ti catalyst by optimizing the catalyst composition and the preparation conditions.

Omata et al. [12] used artificial neural network in the oxidative reforming of methane, as a kind of function considering that the inputs are physicochemical properties of elements and outputs are catalytic activities.

Song et al. [13] use the artificial neural network to design an optimum catalyst for the production of hydrogen by the reforming of ethanol based on determining the inter-relationship between catalyst-preparation methods, metal loading catalyst characteristics and catalyst performance. Specifically ANN was used to determine the optimum catalyst conditions for obtaining maximum hydrogen production performance of a Ni/Al_2O_3 catalyst.

Horiguchi et al. [14] optimized $K\text{-}Ni/Al_2O_3$ catalyst to attain high activity for reforming of methane. The catalyst parameters such as the calcinations temperature of Al_2O_3 and the amounts of NiO and K loading were designed by a radial basis function network. The results of their work suggests that the combination of radial basis function network and the conventional multivariate analysis can be used to find the optimum conditions of the catalyst preparation for the highest activity.

The present paper studies mainly utilization of artificial neural network to determine the interrelationships for Pd/SBA-15 catalyst in the catalytic ethanol steam reforming process.

2. Experimental

2.1. Chemicals used

The following chemicals were used for catalyst synthesizing: for SBA-15 support we used poly-(ethyleneglycol)-block-poly-(propyleneglycol)-block-poly-(ethyleneglycol) ($EO_{20}PO_{70}EO_{20}$, Pluronic P123), 1,3,5trimethylbenzene (TMB) and tetraethylortho-silicate (TEOS) purchase from Sigma Aldrich and hydrochloric acid, potassium chloride, ethanol from Carl Roth. The palladium chloride salt used for the impregnation process was purchased from Fluka.

2.2. Catalyst synthesis

The synthesis of SBA-15 support was carried out by using the following procedure [15]. Briefly a mixture made of Pluronic P123 and potassium chloride is dispersed in deionized water and acid hydrochloric. For stirring several hours, TEOS was added drop wise, and continue stirring. The obtained mixture was kept at 300 K in an oven for 24 h then transferred to an autoclave and heated under static condition for 24 h. The solid product was separated by filtration, washed with deionized water several times. In order to remove the organic-template, the sample was calcinated under air flow conditions at required temperature.

Supported catalyst was prepared by pore volume impregnation method using hydrochloric acid. The mixture obtain was added to a known quantity of support under continuous stirring. After Pd loading (1%) the sample was dried for 48 h at 373K.

2.3. Catalyst characterization

The Pd/SBA-15 catalyst was characterized by means of X-ray diffraction (XRD), N_2 adsorption-desorption, thermo gravimetric analysis (TGA).

X-ray powder diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer with CuKα radiation in the 2θ range of 0^0-60^0 at scanning rate of 10°/min.N_2 sorption isotherms at 77 K were recorded with an automatic Quantachrome Autosorb Gas Sorption system. TGA measurements of catalyst were performed on TGA/SDTA 851 Mettler Toledo instrument in the temperature range from ambient to 700^0C.

2.4. Catalytic activity tests

The feed for this process was ethanol and distillated water. The reactor used to obtain experimental data was made of a stainless steel tube equipped with a control pane which provides: control and registration of the reactor temperatures and indicates the temperature along the catalytic bed. The raw material was delivered to the reactor chamber by means of a HPLC pump able to control the flow rates at the desired flow rates. Prior to reaction the catalyst was reduced in situ by treatment with H_2 at 550^0C for 6h. The reactions were carried out at atmosphere pressure and different reaction temperatures (300-500^0C). The product mixture during reaction was passed through a condenser and gas-liquid separator to separate the gaseous and liquid products for analysis.Theliquid product was analyzed using a Carlo Erba chromatograph and the composition of the output gas stream was analyzed on line by gas chromatography Varian CP 3800 with helium as carrier gas. The catalyst was evaluated for itsperformance in the steam reforming of ethanol. The evaluation criteria used were ethanol conversion and hydrogen selectivity.

Ethanol conversion was define according to eq (1) while hydrogen selectivity was outline according to eq (2)

Ethanol conversion

$$X_{EtOH} = \frac{n_{EtOH_{in}} - n_{EtOH_{out}}}{n_{EtOH_{in}}} \times 100 \quad (1)$$

Hydrogen selectivity

$$S_{H_2} = \frac{g_{H_2}}{g_{mp}} \cdot 100 \quad (2)$$

Where:
X_{EtOH}- ethanol conversion
n_{EtOHin} – moles of ethanol fed
$n_{EtOHout}$ – moles of ethanol produced
S_{H2}- hydrogen selectivity
g_{mp}–raw material mass, g
g_{H2}- hydrogen gas mass, g

2.4 Neural network

For this case study we use the artificial neural network (ANN) to estimate the optimal operating conditions of the process for maximum ethanol conversion and hydrogen selectivity.

Because, basically, the neural network is a computer algorithm, it has input and output data. In this paper, the input data that will be used are temperature (°C), ethanol proportion (% vol.) and weight hour space velocity (h^{-1}) whilethe output data are ethanol conversion (%) and hydrogen selectivity (%).

The correct use of an ANN is a two-step process:

1. Training the ANN.

2. Creating and configuring the neural network.

Training the neural network is a step thatuses data obtained beforehand, data which are gathered into a database called *training database*. This database has the same input and output data (called *target data*) as the ones that will be used when the neural network will be exploited. The training processadjustssome parameters of the neural network algorithm so as, when it will be used for estimation, it will offer the best approximations possible, relative to the data used in the training database.

An important parameter regarding training the neural network is *training efficiency*. A high training efficiency of the neural network means that the future estimations will be very accurate, relating to the data f-rom the training database. Training efficiency depends a lot of the correlation degree of the data from the training database.

Among the existent tools to determine the neural network's training efficiency there are: the error histogram and data regression.

Creating and configuring the neural network was made using the Neural Fitting app of the MATLAB R2015a program. MATLAB R2015a is a wide-known software program developed by Mathworks [16]. The Neural Fitting app is an interface wrapper of the MATLAB neural network functions, making the creation and the use of the neural network much easier.

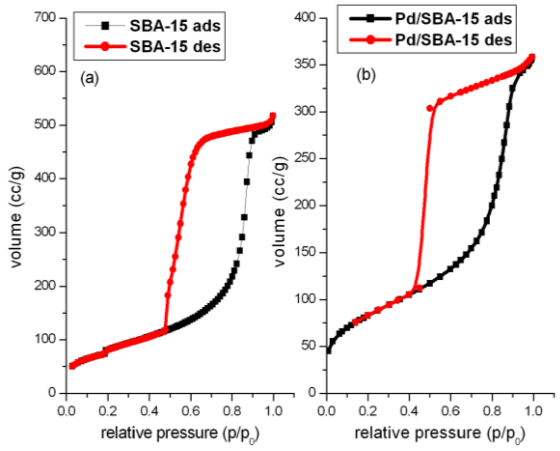
The process of properties estimation using the neural network has a random factor attached to it. This is because a part of the training process requires randomly distributing the data from the training database into three separate categories: the training data, the validation data and the testing data. The proportions in which these data are distributed vary, but a common practice is to distribute 70% of the data to training data and the rest of the 30% being distributed equally between the remaining two categories. To offset theinfluence of the random factorfrom database training, the estimation process used in this paper will have two steps:

1. Three distinct estimations using the neural network, for the same input data will be made. Between the estimations, the neural network will be trained using the same training database, presented in table 1;
2. The final output which will be considered will be the average of the three estimations.

3. Results and discussion

3.1. Catalyst characterization

The nitrogen adsorption/desorption isotherms for pure SBA-15 and Pd/SBA-15 catalyst are presented in figure 1a and b. The isotherm for SBA-15 is a type IV adsorption-desorption isotherms, which is characteristic of this mesoporous material. The hysteresis loop is regular type H_1. An interesting feature of SBA-15 regarding this type of analysis is the microporosity [17]. The adsorption/desorption isotherm of Pd/SBA-15 catalyst is also type IV. This shows that the uniform pore structure remains even after palladium loading. The surface of the Pd/SBA-15 catalyst is 601.44 m^2/g pore volume 0.55 cm^3/g and 6.2 nm pore diameter.



(a) (b)

Fig 1. The nitrogen adsorption-desorption isotherms for SBA-15 (a) and Pd/SBA-15 catalyst (b)

Figure 2 show the XRD patterns of the Pd/SBA-15 sample at low and high diffraction angle respectively. It is observed, that the sample exhibit one intense peak at 0^0 which correspond to 100 reflection plane characteristic to mesoporous SBA-15. The results indicated that the pore structure of SBA-15 is preserve in Pd/SBA-15 catalyst suggesting that the anchoring of Pd during impregnation process has no significant effect on the mesoporous structure.

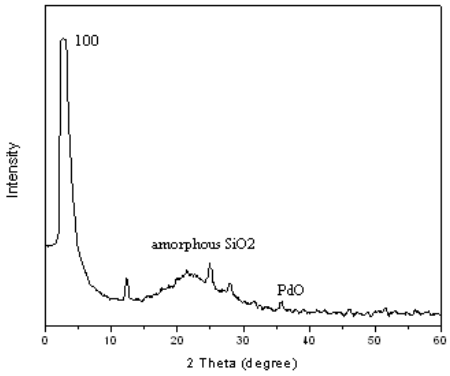


Fig. 2. The X-ray diffraction of Pd/SBA-15 catalyst

The results obtain suggest the presence of a broad diffraction peaks 2θ~ 15-30^0 ascribed to the amorphous framework of SBA-15 involving SiO_2. A relatively sharp diffraction peak at 2θ degree~36^0 can be assignable to the PdO this suggests that relatively Pd species were formed in the impregnated sample.

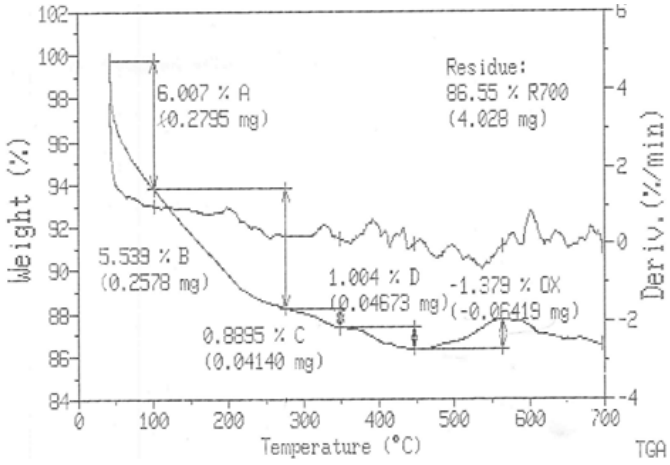


Fig. 3.TGA profile of Pd/SBA-15 catalyst

For Pd/SBA-15 catalyst the TGA measurements (figure 3) were performed to determine the minimum temperature required for removal of the surfactant.

In the case of Pd/SBA-15 catalyst the TGA measurements were performed to determine the minimum temperature required for removal of the surfactant. The catalyst was heated from 50 to 700^{o}C. The first 6.007 wt% of total weight loss is assigned to removal of absorbed water and a part of bound water. The surfactant was removed in the range of 200 to 360^{0}C which covered 5.539 wt% of total mass loss. The remaining carbon species were removed in the range of 360-600^{0}C, with 3.272 wt% of total mass losses.

3.2. Hydrogen production and the neural network approach

In this paper, the data that will be used for the training database are the results obtained from the catalytic test and are presented in table 1. The input and the output data have been specified earlier.

Table 1.Data that will be used in the training database.

Temperature (^{0}C)	**Ethanol 5%, w=3h^{-1}**		**Ethanol 5%, w=9h^{-1}**		**Ethanol 5%, w=15h^{-1}**	
	X	**S**	**X**	**S**	**X**	**S**
300^{0}C	67.32	87.42	63.63	78.08	59.01	73.58
350^{0}C	68.31	86.33	64.46	77.08	60.02	72.92
400^{0}C	71.28	85.83	65.02	77.08	63.00	72.50
450^{0}C	72.32	82.25	67.00	71.17	65.00	66.75
500^{0}C	79.70	80.33	77.28	71.00	71.07	66.25
Temperature (^{0}C)	**Ethanol 10%, w=3h^{-1}**		**Ethanol 10%, w=9h^{-1}**		**Ethanol 10%, w=15h^{-1}**	
	X	**S**	**X**	**S**	**X**	**S**
300^{0}C	69.13	88.17	68.19	83.42	58.76	82.00
350^{0}C	70.37	87.17	69.48	82.17	63.95	76.67
400^{0}C	73.00	80.17	73.54	77.25	63.95	75.92
450^{0}C	81.48	70.42	79.01	70.25	66.17	75.83
500^{0}C	88.00	67.42	82.00	68.42	78.12	67.08
Temperature (^{0}C)	**Ethanol 15%, w=3h^{-1}**		**Ethanol 15%, w=9h^{-1}**		**Ethanol 15%, w=15h^{-1}**	
	X	**S**	**X**	**S**	**X**	**S**
300^{0}C	61.64	88.17	50.57	87.17	36.00	87.00
350^{0}C	66.78	88.17	56.44	86.50	54.39	85.75
400^{0}C	68.06	81.17	60.98	85.25	57.19	85.00
450^{0}C	71.68	62.17	67.30	60.17	63.96	65.67
500^{0}C	75.45	58.75	74.97	64.17	69.23	64.08

The notations from table 1 have the following meaning:

1. X — ethanol conversion (%);
2. S — hydrogen selectivity (%)

In this paper, the database training creation and the neural network creation and training was made according to the procedure specified in the MATLAB R2015 manual [18]. The parameters used for neural network creation and training is:

1. Data distribution proportions into the three categories: 70% training data, 15% validation data and 15% testing data;
2. Number of neurons: 10;
3. Training algorithm: Levenberg-Marquardt

The neural network's architecture is represented in figure 4.

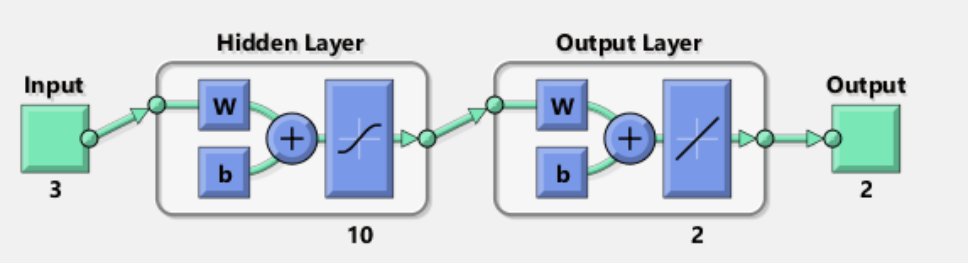


Fig. 4. Neural network architecture

The neural network created with the parameters specified above was trained using the training database presented in table 1. After the training was complete, its efficiency was checked, using the error histogram and the data regression analysis. The resulting error histogram is presented in figure 5.

In figure 5, it can be observed that most of the data are gathered around the mean, having errors between -2.258 and 1.409. Concluding from these results, according to the error histogram, the neural network training was efficient.

The regression analysis of the data is presented in figure 6.

From figure 6, it can be seen that the training and the validation data have a high correlation, with R above 0.93. The target data are less correlated than validation data, with R=0.89758. However, the authors think that the lower R values for validation and test data are due to a low number of data available for both of these categories. This assumption is backed by the fact that the correlation of the training data is very good (R=0.99), this category having the most data available in the training database. Because of these considerations and because of the value of R overall (close to 0.95), the authors conclude that, according to the data regression analysis, the neural network training was also efficient, the error histogram confirming this fact.

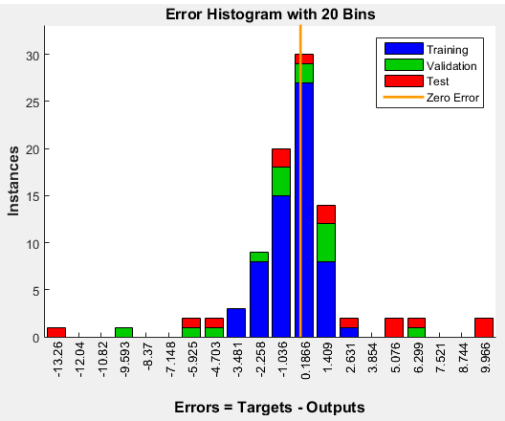


Fig. 5. Error histogram of the neural network training

To test the estimation accuracy of the newly created neural network, it will be tested on a set of input data, which are already known, determined values for output. The test consists in estimating the ethanol conversion and hydrogen selectivity at 300°C, w=3h^{-1} and 5% ethanol. The determined ethanol conversion and hydrogen selectivity for this case is presented in table 1.
The obtained estimations using the neural network are presented in table 2.

Table 2. Estimations using the neural network

	Estimation 1	Estimation 2	Estimation 3	Mean
Ethanol conversion (%)	66.8157	66.8023	64.1807	65,9329
Hydrogen selectivity (%)	87.8093	87.2794	86.5173	87,202

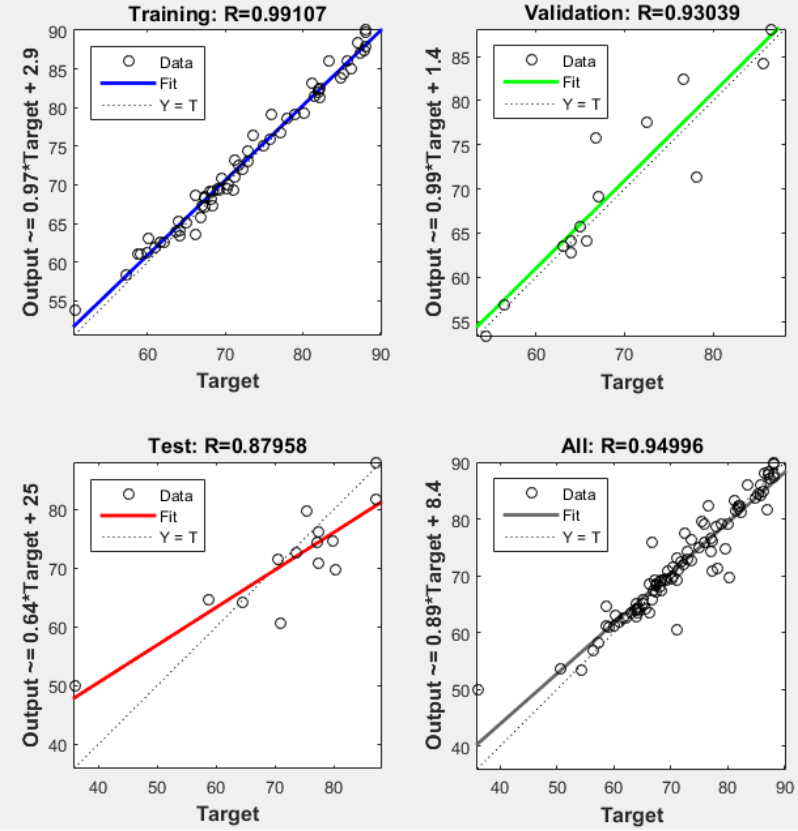


Fig. 6. Data regression analysis

The obtained estimations for ethanol conversion and hydrogen selectivity, rounded to 2 digits, were compared to the experimental values. The results are presented in table 3.

Table 3. Comparison between the determined and the estimated values for the two properties

	Obtained values		Difference (D-E)
	Determined (D)	Estimated (E)	
Ethanol conversion (%)	67.32	65.93	1,39
Hydrogen selectivity (%)	87.42	87.2	0,22

In table 3 it can be noticed that the difference between the determined and the estimated values for the two studied properties is 1.39% for ethanol conversion and 0.22% for hydrogen

selectivity. These differences are low, proving the efficiency of the estimations of the neural network. The neural network devised based on experimental data allows for other parameters, using the same type of catalyst, in the same chemical process to estimate results.

4. Conclusions

The aim of the present study is to predict the performance of a Pd/SBA-15 catalyst with good performance in the ethanol steam reforming process using an artificial neural network. The catalyst has been synthesized by impregnation method. The catalyst presents a surface area of 610.44 m^2/g and average pore diameter of 6.2 nm.

The neural network was used to determine the optimum catalyst conditions for obtaining maximum hydrogen production performance of Pd/SBA-15 catalyst for the production of hydrogen by the steam reforming of ethanol.

To be able to correctly use the neural network, it had to be trained using a training database, which was presented in table 1. The data from the training database had a high degree of correlation, meaning that the training was highly efficient, relating to the data from the database. Because of its high efficiency, the differences between the estimated and the determined properties of the example taken into account were less than 1.5%.

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