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Direct neural network modeling for separation of linear and branched paraffins by adsorption process for gasoline octane number improvement

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HIGHLIGHTS

- ANN was used for hydrocarbons breakthrough curves in separation of linear and branched paraffins.
- Concentration at t time over initial concentration was simulated as output variable.
- ANN was successfully trained with experimental database and validated with another database.
- ANN enables the implementation of sensors for on-line quality determination C/C_o in the process.
- Density and octane number were the most influential parameters in adsorption system.

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ABSTRACT

An artificial neural network (ANN) approach was used to develop a new predictive model for the calculation of hydrocarbons breakthrough curves in separation of linear and branched paraffins by adsorption process. Three-layer ANN architecture was trained using an experimental database and the concentration at t time over initial concentration (C/C_o) was calculated as output variable. Experimental temperature (T), times of adsorption (t), octane number (ON) and the density (ρ) of the hydrocarbons were considered as main input variables for the model. For the ANN optimization process, the Levenberg–Marquardt (LM) learning algorithm, the hyperbolic tangent sigmoid transfer-function and the linear transfer-function were applied. The best fitting training data set was acquired with an ANN architecture composed by 22 neurons in the hidden layer (4-22-1), which made possible to predict the C/C_o with a satisfactory efficiency ($R^2 > 0.96$). A suitable accuracy of the ANN model was achieved with a mean percentage error (MPE) of ~5%. All the C/C_o predicted with the ANN model were statistically analyzed and compared with the "true" C/C_o experimental data reported in the experiments carried out in the lab. With all these results, we suggest that the ANN model could be used as a tool for the reliable prediction of the breakthrough curves obtained during the separation of linear and branched paraffins by adsorption processes.

1. Introduction

In a world with environmental problems, it is necessary to develop answers based in research that can provide maximum energy efficiency. The end of cheap oil will drive the refining industry to optimize the performance of their carburant even more, increasing the efficiency of vehicle motors [1]. Particularly, in the case of gasoline, the combustion quality is measured by the octane number (ON). We are aware that when the ON is high combustion occurs as a smooth explosion instead of a detonation and the performance of the motor is improved.

In accordance with [1], in the past 20 years, methyl tertiary butyl ether (MTBE) has been used in gasoline to replace lead as an octane enhancer. However, controversy has surrounded its use, most recently because of concern over contamination of drinking water supplies, leading to calls for restrictions on its use.

Consequently, developing a new process for producing high octane gasoline from complex mixtures of light distillates was performed. The latter is based in the separation of C5–C8 linear and branched alkanes depending on their adsorption properties, chain length, and number of branches [2]. As a rule, multibranched

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alkanes are related with high octane numbers. Isomerization process generates a mixture of isomers (linear alkanes, monobranched alkanes like methyl and ethyl-alkanes, and multibranched alkanes) that usually require separation and recycle of the non-isomerized components. Therefore, to find materials with such adsorption capabilities to selectively separate highly branched alkanes from the gasoline mixture, with substantial regeneration and reutilization properties is highly desirable. These PVDC-based CMS materials seem promising for octane boosting separation technologies because of their adsorptive and molecular sieve discrimination capabilities between linear and branched alkanes [3].

In this case, the whole research process is carried out in laboratories operating under different experimental conditions. However, due to the complexity of these various operating conditions, the need arises to develop mathematical models based in experimentation to achieve an optimal orientation of these complex processes [4–7].

Therefore, empirical models based on the ANN training with actual experimental data are proposed as alternative model for separation of linear and branched paraffins by adsorption processes. ANN are typically recognized as suitable tools for dynamic modeling and have been suggested as practical computational implements that do not consider complex physical and mathematical models for the industrial process monitoring [8]. Within this context ANN have been extensively applied in the solution of engineering problems associated with petrochemical industry, for example: (a) Optimization of the energy efficiency for a petrochemical plant [9]; (b) The Classification of premium and regular gasoline by gas chromatography/mass spectrometry [10]; (c) Performance and exhaust emissions of a gasoline engine [11]; (d) Prediction of torque and specific fuel consumption of a gasoline engine [12]; (e) Determination of octane numbers of gasoline compounds from their chemical structure [13], among others.

The aim of this study is to develop a computational model using ANN to predict the behavior of breakthrough curves from the experimental parameters. Details of the computational methodology, as well as the numerical validation, and the comparative statistical analysis are fully described.

2. Materials and methods

2.1. Adsorption process

Adsorption process is the adhesion of the molecules from a mixture in a gaseous or liquid state to a solid surface. This process creates a film of the adsorbate on the surface of the adsorbent. In this work the adsorbent used was a carbon molecular sieve (CMS) that have been of great industrial interest for many years due to their uniform pore structure and appropriate selective adsorptive properties [14,15]. The CMS-IMP12 material was prepared from the pyrolysis of poly(vinylidene chloride-co-vinyl chloride) (PVDC–PVC, Saran^{TM}) following the technique described by Jiménez-Cruz et al. [16]. The surface properties that were calculated according to the *t*-plot analysis [17–19] are shown in Table 1. A pore diameter distribution between 0.5 and 0.8 nm was obtained based on the method described by Horváth and Kawazoe [20]. The material was characterize by scanning electronic microscopy (SEM) using a Philips ESEM XL30 instrument at 30 kV and transmission electronic microscopy (TEM) using a TECNAI F30 instrument equipped with a field emission gun at 300 kV, as shown in Fig. 1.

Table 1
Adsorbent properties as calculated by the *t*-plot analysis [17–19].

BET surface area, m^2/g	968
Micropore area, m^2/g	873
External surface, m^2/g	95
Total pore volume, mL/g	0.40
Micropore volume Dubinin–Radushkevich, mL/g	0.36
Macro-mesopore volume, mL/g	0.04
Micropore volume de Boer, mL/g	0.34

To understand the different behaviors that occurs in a CMS uses the breakthrough curves, which are a form of experimentally evaluating the evolution of the concentration of the solution, since they serve to determine the time of adsorption with respect to the inlet concentration adsorbed (*time vs* C/C_o) [21].

2.2. Experimental set-up

Experiments were performed in the vapor phase by pumping upwards (5 mL/min) the naphtha from the bottom of a column filled with approximately 90 g of CMS-IMP12 already sieved to 80/120 mesh, set at the temperature of the experiment (175–325 °C). The adsorption column consists of 26.6 mm i.d. stainless steel column 395 mm in length (220 mL). Due to the bulk density of the adsorbent tested (0.68 g/ml) the rest of the volume was filled with an inert (bed porosity = 0.43). Pressure was in the range of 262–289.6 kPa. The adsorption vessel was followed by a heat interchanger column consisting of stainless steel condensation column with 30 mm i.d. and 150 mm of length, cooled with an 80/20 water/propanol mixture. Time was set to zero at the beginning of the pumping procedure and recorded when the first drop

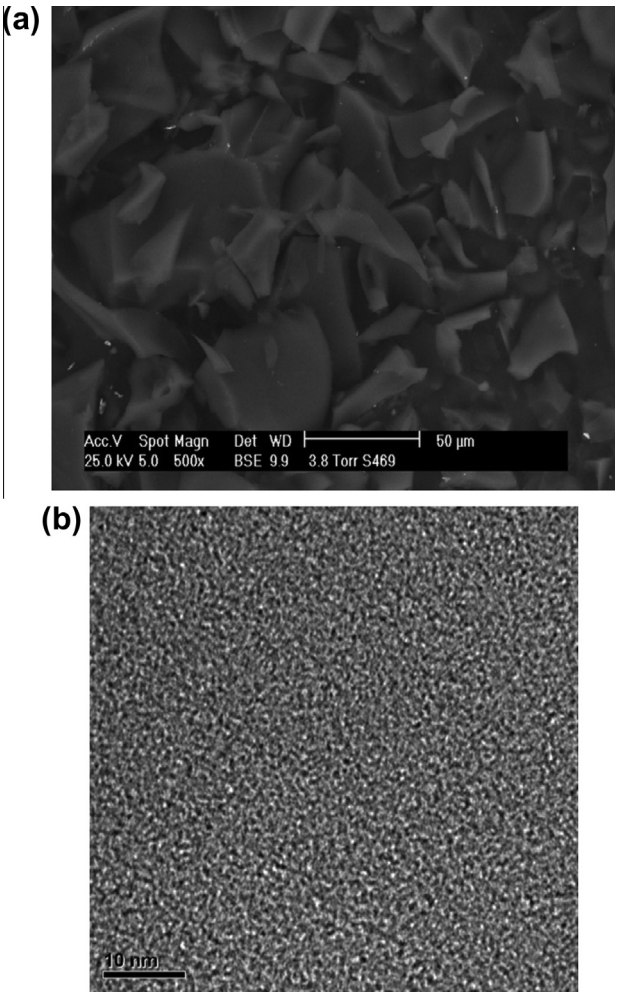

Fig. 1. (a) SEM micrograph of the CMS-IMP12 material at a magnification of 500X, and (b) TEM micrograph of the CMS-IMP12 material.