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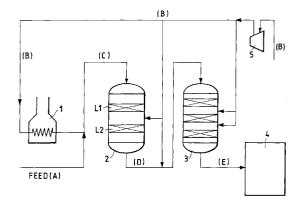
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(54) Process for determining the nitrogen content of the effluent of the pretreatment reactor in a catalytic hydrocracking plant

- (57) Process for determining the nitrogen content of the effluent of the pretreatment reactor in a catalytic cracking plant with hydrogen, the above reactor consisting of at least one fixed catalytic bed, which comprises the following steps:
 - 1) collecting the process and laboratory historical data relating to a high number of runs effected by the pretreatment reactor;
 - 2) selecting from the data of point (1) a subset of data to be used as input for a first neural network (NN1);
 - 3) calculating the NABT (NABT = normalized average catalytic bed temperature) for each series of historical data using the data of point (2) and correlations available in literature;
 - 4) constructing a first neural network (NN1) using the data of point (2) and the NABT of point (3);
 - 5) selecting a first set of training data of the first neural network NN1, comprising the data of point (2) and the corresponding calculated NABT values of point (3), generating a set of NABT predictive data of point (5);
 - 6) selecting a second set of training data comprising the data of point (2) and the set of NABT predictive data of point (5);
 - 7) constructing a second neural network NN2 using the data of point (6), generating a set of nitrogen predictive data in the effluent and the configuration parameters of the network NN2;
 - 8) applying the predictive data of points (5) and (7)

to continuous process data, thus estimating the NABT of NN1 and the corresponding nitrogen content of the outgoing effluent without effecting laboratory analyses.

Fig.1



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[0001] The present invention relates to a process for determining the nitrogen content of the effluent of the pretreatment reactor in a catalytic cracking plant with hydrogen.

[0002] The catalytic cracking process with hydrogen (hydrocracking) treats fractions and/or petroleum residues, particularly heavy Vacuum and Visbreaker distillates, to transform them into lighter products with a greater added value.

[0003] The above plant consists of two main sections, a reaction section and a fractionation section.

[0004] The reaction section, in turn, consists of two reactors in series, the first of which is for hydrotreatment with hydrogen which transforms sulfur and nitrogen mainly into hydrogen sulfide and ammonia, and the second for hydrocracking in which, again in the presence of hydrogen, the heavier products are transformed into lighter products with a greater added value.

[0005] In refineries the nitrogen content at the outlet of the first reactor (which for the sake of simplicity is herein called pretreatment) is normally determined by the removal of samples which are subsequently analyzed in the laboratory. It is very important to know the nitrogen content at the outlet of the pretreatment reactor. Nitrogen in fact forms a temporary poison of the catalyst of the subsequent hydrocracking reactor. A nitrogen content which exceeds certain levels (indicatively but not necessarily, over 60 ppm) causes a consequent decrease in the yields with evident economic damage.

[0006] A first drawback of this procedure consists in the difficulty of effecting the sampling of the stream leaving the pretreatment reactor; the pressure in fact is very high (about 105-110 Kg/cm²).

[0007] A second, but not minor, disadvantage is due to the fact that the laboratory data are not constantly available.

[0008] It is therefore necessary to predict the nitrogen content in the stream leaving the pretreatment reactor. Only a nitrogen datum obtained in real time would allow suitable measures to be taken immediately, i.e. to change the operating conditions (particularly the temperature), of the first reactor. In this way it would be possible to avoid the temporary deactivation of the second reactor and consequent drop in yield.

[0009] The present invention overcomes the above drawbacks as it allows the nitrogen content of the stream leaving the pretreatment reactor to be predetermined in real time.

[0010] In accordance with this, the present invention relates to a process for determining the nitrogen content of the effluent of the pretreatment reactor in a catalytic cracking plant with hydrogen, the above reactor consisting of at least one fixed catalytic bed, preferably two, which comprises the following steps:

1) collecting the process and laboratory historical

data relating to a high number, preferably at least 50 and under different operating conditions, of runs effected by the pretreatment reactor;

- 2) selecting from the data of point (1) a subset of data to be used as input for a first neural network (NN1);
- 3) calculating the NABT (NABT = normalized average catalytic bed temperature) for each series of historical data using the data of point (2) and correlations available in literature;
- 4) constructing a first neural network (NN1) using the data of point (2) and the NABT of point (3);
- 5) selecting a first set of training data of the first neural network NN1, comprising the data of point (2) and the corresponding calculated NABT values of point (3), and correlating the data of point (2) with the NABT values of point (3), generating a set of NABT predictive data and the configuration parameters of the network NN1;
- 6) selecting a second set of training data comprising the data of point (2) and the set of NABT predictive data of point (5);
- 7) constructing a second neural network NN2 using the data of point (6), generating a set of nitrogen predictive data in the effluent and the configuration parameters of the network NN2;
- 8) applying the configuration parameters of points (5) and (7) to continuous process data, thus estimating the NABT of NN1 and the corresponding nitrogen content in the outgoing effluent without effecting laboratory analyses.

[0011] A brief outline of the structure and functioning of the neural networks is provided hereunder.

[0012] Neural networks are an attempt to simulate the architecture and functioning of the human brain; in these, as in the nervous system, the capacity of processing and learning derive from the co-operation of a large number of elements which carry out an elementary function (neurons) capable of exchanging information with each other (exciting other neurons by sending out electric impulses) and which have the property of inhibiting or increasing the amplitude of the signal transmitted. The capacity of neural networks to learn from examples and memorize what has been learnt lies in this possibility of modifying the intensity of the signal transmitted.

[0013] The set-up and means of interconnection (interaction) between the neurons determine the type of network.

[0014] A typical neural network is one in which each neuron (node) of the network is connected to all nodes of the following level by means of a connection which is associated with a value (significance), through which the outgoing signal of the node is modified (learning).

[0015] Each node of the network is therefore characterized by the significances of all the input connections (to that node) and its own transfer function (the same

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for all the nodes).

[0016] The information is supplied at the first layer of nodes (input level), sent forward (feedforward) towards the intermediate nodes (hidden levels), where it is processed; the result is finally sent back from the nodes of the last level (output level).

[0017] Neural networks are capable of identifying any relation, either linear or not, or of reproducing any function of any degree and type without the necessity of programming complex or particular algorithms, but only by modifying the geometry of the network in terms of the number of hidden levels and nodes in these levels. In addition, their application is particularly effective when the relations which link the data under examination are not completely known or when these data are affected by measurement uncertainties (noise) or are incomplete.

[0018] The functioning of a neural network is characterized by two distinct phases, i.e. a learning phase during which the network behaves like an adaptive system modifying its own internal structure (connection significances) so as to minimize the error between the network output and the known result vis-à-vis a certain input value; a prediction phase in which the network structure is not modified and the network, receiving an input for which it was not instructed, reacts by supplying the output it retains correct.

[0019] The learning phase of a neural network consists in determining the significances, associated with the single connections, which minimize, for all the examples used, the shift between the output value determined by the network and the real value.

[0020] There are many algorithms for minimizing the error function but in most applications the iterative algorithm called "backpropagation" is used, in which the interconnection significances are modified in reverse, starting from the nodes of the output level. For the output nodes the error variation rate is calculated with respect to variations in the connection significances. An analogous iterative method is applied for the intermediate nodes.

[0021] In the prediction phase, when a new input x which does not belong to the set of examples supplied in the prediction phase, is given and the connection significances have been set, the network calculates the output of all the nodes of the intermediate levels and finally the value of the output level.

[0022] The performances of a neural network can be quantified by the error committed in the prediction phase. This error greatly depends on the procedure and criteria used, in the learning phase, by the programmer; more specifically:

** Number of hidden levels and number of neurons in the hidden levels. These numbers define the complexity of the network and its capacity of effecting complex and extremely non-linear functions. An undersized network is not capable of "learning" the

function under examination, whereas an oversized network is not very reliable in the prediction phase even though it has excellent capacities in the "learning" phase. Algorithms and methods for determining the optimum number of levels and nodes are available in literature.

** Selection of the set of examples and training duration. The set of data used in the learning phase must be representative for the function under examination and the learning duration must be sufficient to guarantee a final error below a certain threshold. ** Selection of the input variables. Variables which give an essential informative contribution for the function under examination must be selected. The use of input variables which do not entirely relate to the problem in question can jeopardize the capacity of the network.

** Initialization of the significances. The significances are initialized at random using algorithms existing on the market, there are particular criteria however for selecting the initial values which accelerate and optimize the training phase of the network.

[0023] As far as the catalytic cracking plant is concerned, a typical, but non-limiting, configuration is illustrated in figure 1, where (1) is the heating oven of the recycled gas, (2) is the desulfuration and denitrification reactor, (3) is the conversion (cracking) reactor, (4) represents the separation units, (5) is the compressor.

[0024] Again in figure 1, (A) is the feed, (B) is the recycled gas, (C) is the feed to the reactor (2), (D) is the stream leaving the reactor (2), (E) is the effluent of the reactor (3) which goes to the separation section (4).

[0025] The functioning of the plant of catalytic cracking with hydrogen is described hereunder with reference to figure 1.

[0026] The charge (A), normally consisting of a vacuum or visbreaker heavy distillate, is brought to a pressure of 112-118 kg/cm² by means of a pump and to a temperature of about 380°C, heat being recovered from the stream leaving the reactor. The above stream (A) is mixed, before entering the reactors, with a stream of recycled hydrogen (B), heated in turn in the oven (1) to a temperature of about 490°C. The combined charge (C) then enters the hydrotreatment reactor (2) consisting of two catalytic beds (L1) and (L2), normally based on Nickel and Molybdenum. The stream (D) leaving the reactor (2) then enter the cracking (conversion) reactor (3) with hydrogen. The reactor (3) consists of a series of catalytic beds, in this specific case 3, based on zeolites. The stream (E) leaving the reactor (3) is finally sent to the fractionation section. All the reactions are exothermic and consequently cooling with fresh recycled hydrogen (60°C) between the various catalytic beds is provided, which allows temperature control at the inlet of the beds themselves.

[0027] For the running of the plant, the measurement of the total nitrogen content in the stream (D) leaving the

hydrotreatment reactor (2) is fundamental; nitrogen in fact is a temporary poison for the catalyst of the reactor (3). As already specified, this analysis is carried out in the laboratory on samples taken occasionally, normally according to the method ASTM D-4629. Following periodic evaluations of the deactivation state of the catalysts of the two reactors, the refinery technical office gives a target of the nitrogen content which the operating staff must maintain, by acting on the operating parameters of the plant.

[0028] If the nitrogen content measured is higher than the value to be followed (for example 60 ppmwt), this means that the reactor (2) is not working enough (with a consequent low deactivation of the catalyst), whereas the reactor (3) will have difficulty in maintaining the desired conversion levels (with a consequent high deactivation of the catalyst). As a result, with the aim of balancing the deactivation values of the two reactors and maintaining a high conversion, the operating staff will have to increase the temperature of the reactor (2) to obtain a lowering of the nitrogen content in the effluent, an increase in the deactivation of the catalyst of the reactor (2) and a decrease in the deactivation of the reactor (3). Viceversa, if the nitrogen content measured is lower than that to be followed, the operating staff will have to decrease the temperature of the reactor (2).

[0029] The process of the present invention is illustrated hereunder assuming, for the sake of simplicity, that the reactor (2) consists of 2 catalytic beds.

[0030] The first step of the process of the present invention consists in collecting the historical data of the plant (for example, flow-rates, pressures, temperatures) and of the laboratory (for example nitrogen, sulfur, density of the charge; nitrogen of the effluent) of runs effected in the plant itself. The term "plant data" does not only refer to the data measured directly, but also to the relative combinations, for example (see figure 2):

- (a) $\Delta T1 = T2-T1$; temperature difference of the 1st 40 catalytic bed;
- (b) ABT1L1 = (T2+T1)/2; average temperature of the 1st bed;
- (c) $\Delta T2 = T4-T3$; temperature difference of the 2nd catalytic bed;
- (d) ABT1L2 = T4+T3)/2; average temperature of the 2nd bed;
- (e) ABT = average temperature of the reactor;
- (f) ΔT = temperature difference between the inlet and outlet of the reactor.

[0031] The ABT parameter measured in the plant may refer to the project conditions using correlations available in literature. The data thus transformed are called NABT (i.e. normalized ABT) and are an index of the deactivation of the catalyst of the reactor (2).

[0032] Using the laboratory analyses and plant operating data, a first neural network (NN1) estimates the

relative NABT, for each set of process data.

[0033] The network NN1 estimates the NABT parameter only when it receives new laboratory data relating to the nitrogen in the stream (d).

5 [0034] The estimated NABT data thus obtained from NN1 are used by a second neural network NN2. The latter, not only on the basis of the NABT but also on the basis of the relative plant data and laboratory analyses, predicts the nitrogen content of the effluent (D) in real time.

[0035] The estimated nitrogen data thus obtained can be visualized; in any case they are used in the operative running as described above.

[0036] The following example provides a better understanding of the present invention.

EXAMPLE

[0037] About 200 historical data were collected deriving from 4 years of running of the pretreatment reactor of a hydrocracking plant. In addition the corresponding NABT was calculated for each of these data.

[0038] The data thus obtained are divided into 2 subsets, a training subset and a test subset.

[0039] The following procedure is then followed:

- (1) the training of the first neural network NN1 is effected, using the training subset, minimizing the error between the calculated NABT and NABT predicted by NN1;
- (2) using the test subset, the best fit of the NABT prediction is verified in the presence of data not known "a priori" by the network NN1;
- (3) repeating operations (1) and (2) several times, the architecture and inputs of the network are varied until the best configuration is found, which minimizes the error between the predicted and calculated data:
- (4) about 600 nitrogen data of the outgoing stream, the relative predicted NABT previously obtained and the corresponding process and laboratory data are subdivided into 2 subsets, a training subset and a test subset:
- (5) the training of the second neural network NN2 is effected, using the training subset, minimizing the error between the nitrogen measured in the laboratory and the nitrogen predicted by NN2;
- (6) using the test subset, the best fit of the nitrogen prediction is verified in the presence of data not known a priori by the network NN2;
- (7) repeating operations (5) and (6) several times, the architecture and inputs of the network NN2 are varied until the best configuration is found, which minimizes the error between the predicted and calculated data;
- (8) the two networks (NN1 and NN2) thus defined (architecture and significances) are used to predict the nitrogen value in relation to the process data

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and laboratory analyses taken in real time from the plant.

[0040] Figure 3 indicates the trend of the NABT prediction effected by the first neural network on 15 new samples (set of plant data) compared with the NABT actually measured. The particularly limited average error and standard deviation provide a further confirmation of the capacity of the network NN1 of predicting the NABT. [0041] Figure 4 indicates the trend of the nitrogen prediction in the outgoing reactor effluent effected by the second neural network NN2 on 33 new samples (set of plant data) compared with the nitrogen actually measured in the laboratory. The average error obtained (9.9) is particularly low considering that the reproducibility (error between two laboratory analyses on the same sample using similar analyzers) of the analysis carried out in the laboratory is indicated as 10 ppm.

Claims

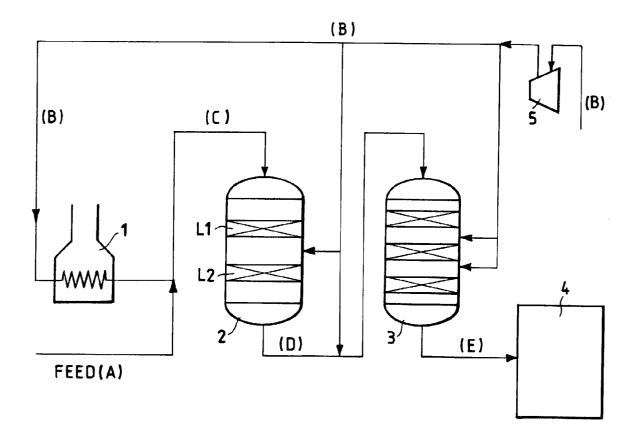
- A process for determining the nitrogen content of the pretreatment reactor in a plant of catalytic cracking with hydrogen, the above reactor consisting of at least one fixed catalytic bed, which comprises the following steps:
 - 1) collecting the process and laboratory historical data relating to a high number of runs effected by the pretreatment reactor;
 - 2) selecting from the data of point (1) a subset of data to be used as input for a first neural network (NN1);
 - 3) calculating the NABT (NABT = normalized average catalytic bed temperature) for each series of historical data using the data of point (2) and correlations available in literature;
 - 4) constructing a first neural network (NN1) using the data of point (2) and the NABT of point (3);
 - 5) selecting a first set of training data of the first neural network NN1, comprising the data of point (2) and the corresponding calculated NABT values of point (3), generating a set of NABT predictive data and the configuration parameters of the network NN1;
 - 6) selecting a second set of training data comprising the data of point (2) and the set of NABT predictive data of point (5);
 - 7) constructing a second neural network NN2 using the data of point (6), generating a set of nitrogen predictive data in the effluent and the configuration parameters of the network NN2;
 - 8) applying the configuration parameters of points (5) and (7) to continuous process data, thus estimating the NABT of NN1 and the corresponding nitrogen content of the outgoing ef-

fluent without effecting laboratory analyses.

- 2. The process according to claim 1, characterized in that the pretreatment reactor consists of two fixed catalytic beds.
- 3. The process according to claim 1, characterized in that the process operating data are selected from the charge flow-rate and temperature, temperatures and pressures of the reactor and the relative calculated variables.
- 4. The process according to claim 1, characterized in that the laboratory analyses are selected from nitrogen, sulfur and the density of the plant charge and nitrogen in the reactor effluent.
- 5. The process according to claim 1, characterized in that the number of runs of the plant according to point 1 is at least 50, carried out under different operating conditions.

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Fig.1



<u>Fig.2</u>

