A Soft Computing Technique applied to Industrial Catalysis

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Abstract. A Soft Computing technique based on the combination of neural networks and a genetic algorithm has been developed for the discovery and optimization of new catalytic materials when exploring a high-dimensional space.
One possible application of this technique is the optimization of the catalytic performance of new solid materials by exploring simultaneously a big number of variables as elemental composition, manufacture procedure variables, etc. Another application is the optimization of process conditions in catalytic reactors at industrial scale. Considering the high temporal and financial costs required for synthesizing and empirically testing potential solid catalysts, the application of Soft Computing techniques in this field seems really interesting, as the number of experiments could be reduced. The proposed system has been validated using two hypothetical functions, based on the modelled behaviour of multi-component catalysts explored in the field of combinatorial catalysis. Moreover, this Soft Computing technique has been applied to an industrial problem, being possible to obtain an optimize Ti-silicate catalyst for the epoxidation of olefins.

1 INTRODUCTION

One of the main objectives of the chemical industry consists of the production of highly efficient catalysts that allow reactions to be produced in better conditions from the economic, safety and versatility point of view. The financial benefits of an efficient catalyst are enormous: lower operating costs, higher purity products, safer operating conditions, etc. However, the discovery of new catalysts by the traditional method is an arduous and rather unpredictable trial-and-error process [15].

The application of new technologies like automation, micromecanics, microelectronics, etc. in chemistry and materials science has increased exponentially the throughput of experiments, being possible at present to screen libraries of hundreds of materials in a single day under realistic test conditions.

In the field of catalysis, these new experimental tools for materials synthesis, catalytic testing and physico-chemical characterisation enable to explore simultaneously a large number of variables like multi-component catalyst formulation, synthesis conditions, catalyst activation conditions, etc. The growth of those accelerated tools was accompanied with the development of software techniques for data management, multi-variable experimental design and data mining. The research in catalysis applying accelerated experimental tools combined with powerful computational techniques constitutes the so-called combinatorial catalysis.

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An important issue in combinatorial catalysis is how to design the experiments in order to explore and optimize the high-dimensional solution space minimising the number of trials to achieve a solution. The most suited procedure for the optimization of multi-dimensional problems are the stochastic procedures, being the genetic algorithm (GA) specially useful for their application in the field of combinatorial catalysis, since (i) GA uses a population of points to conduct the search, being this approach appropriate for high-throughput tools, (ii) the objective is to find an approximate global maximum and (iii) GA tolerates noisy experimental data.

A promising novel approach [4], [9] is the combination of powerful data mining tools with high-dimensional optimization algorithms, in such a way that the knowledge extracted from all the previous experimentations can be applied in the design of the new subset of catalysts to be experimentally screened in the next optimization step. In the present work, we describe a new optimization architecture employing a Soft Computing technique [18], [2] based on a genetic algorithm (GA) coupled with an artificial neural network (ANN).

2 AIMS OF THE WORK

The discovery and optimization of new catalytic materials is a huge process, due to its high temporal and economical costs. The main purpose of this work is to develop a method that could reduce the number of samples to be empirically tested, and also explore efficiently the whole multi-variable space. Specifically, our approach is based on the combination of neural networks and a genetic algorithm. The genetic algorithm, based on real codification, allows to deal with different problems in chemical engineering. Also, the neural network simulates the reaction process and allows to calculate the fitness functions used by the genetic algorithm. Thus, the developed architecture would be applied in the optimization of catalytic performance of new solid materials by exploring simultaneously a big number of variables as elemental composition, manufacture procedure variables, etc. On the other hand, this technique would be employed in the optimization of process conditions in catalytic reactors at industrial scale.

Moreover, this proposed Soft Computing technique seems suitable to be used in the combinatorial catalyst field. On the one hand, artificial neural networks are suitable tools for modelling and prediction of complex catalytic systems and have been applied in catalysis, including different applications like the design of solid catalysts [5], [7], [8], [12] for different reactions of interest. It has also been described [4] the employment of ANNs for modelling experimental data derived from high-throughput experimentation, namely from evolutionary strategies in material discovery. Another application of ANN in catalysis deals with the modelling experimental kinetic data

[1], [13], being possible to obtain kinetic models for prediction of catalytic reactor performance.

On the other hand, the GA is an effective optimization technique, among other aspects, because it is a stochastic algorithm. It relies on random elements in parts of its operations rather than being determined by specific rules. Some recent applications of this kind of algorithms in catalysis field are [16], [17]. Hence, the combination of GA with an ANN seems suitable [11].

3 METHODOLOGY

A new optimization architecture based on the combination of a neural network and a genetic algorithm has been followed. In figure 1, a scheme of the architecture is shown.

Initially, a setting up process for establishing the Soft Computing parameters and the initial population is carried out. Next, samples of actual population are experimentally tested and then a training process of the ANN is taken. After that, the genetic algorithm is applied in order to obtain the next generation of samples, employing the ANN in its crossover operator. Then, the generation is empirically tested in the reactor to obtain its empirical results. The whole process is repeated again, starting from the ANN retraining with these new empirical values.

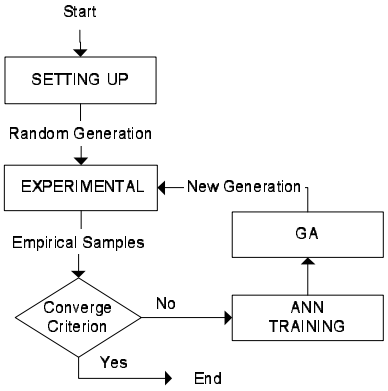

Figure 1. Soft computing architecture applied to experimental design in catalysis

In the setting up process, the GA parameters are established. Moreover, an initial set of individuals is obtained following a process that guarantees enough diversity to start with. In this process, several random generations are created and a statistical population study is done in order to select the most diverse initial population.

In the experimental process, the current generation is tested empirically in the reactor. Therefore, experimental results of the behaviour of the samples are obtained. Those results will be lately used by the GA to calculate the fitness value of each sample. In the case of a simulated study, hypothetical functions can be used replacing experimentation at lab scale.

Regarding the ANN training process, the results of the initial generation are used for training different neural network topologies, employing several training algorithms, in order to determine which one can better model the reaction behaviour. If needed, more generations can be used for selecting a suitable neural network. Lately, each subsequently generation that has been empirically tested is divided into training and test samples. The training set is used to retrain the best neural network stored, whereas the test samples are employed to compare the stored and the retrained neural networks. The one with the lowest MSE error is selected and stored. Finally, the GA provides a new generation of samples based on its mutation and crossover operators. During the crossover process, the GA uses the ANN to simulate the reaction process. So, the ANN allows to predict the information necessary to calculate the fitness function of each sample. This genetic algorithm is detailed in the following section.

3.1 Genetic algorithm

The genetic algorithm attempts to find the optimal solution to the problem by investigating many possible solutions simultaneously. Over a number of generations, goods traits dominate the population, resulting in an increase of the quality of the solutions. The efficient working of the genetic algorithm requires a quick feedback of the fitness values of the samples.

3.1.1 Genetic algorithm codification

Genetic algorithms are a very powerful tool, but they could be dangerous if the problem codification is not appropriate. If the selected codification for the problem was wrong, it would be possible that the algorithm would solve a different optimization problem from the one under study. In the problems faced in this paper, each variable belongs to a continuous domain so it has been decided to adopt real codification [6], [10].

In the codification, not only the element values are studied (such as chemical concentrations, kinetic values, etc.), but also there are some rules that guide and restrict the genetic algorithm. Specifically, the maximum and minimum quantities for each element, subset and set of elements are taken into account. Moreover, the number of elements and subsets of them that can be selected in each moment is determined. The maximum and minimum values are required both because of the rules of the nature and economical reasons (for example, there are good materials but very expensive, which should not exceed some composition limits as the final catalyst would be very expensive and not productive).

Concretely, each sample or chromosome is formed by zero or more compounds and conditions. The compounds include those elements whose chemical value must sum up 100%. On the other hand, a condition represents a set of elements that have some properties in common or have to be studied all together (but the chemical values of their elements do not have to sum up 100%).

A compound can have one or more sections. Each section groups together those elements that follow specific characteristics. Moreover, sections are divided into subsections, which contain the elements of the sample.

Regarding conditions, they are split into types, subtypes and the final elements. In figure 2 a chromosome formed by only one condition is shown.

All samples can be represented by the array of values of all possible elements that belong to the final sample. Not selected elements will have zero value.

3.1.2 Genetic algorithm operators

The GA designs the new generations of samples using mutation and crossover operators. Mutation operator modifies randomly genes with a new value. The number of genes to mutate in each individual is a parameter of the GA. Thus, the mutation is an explorer operator which looks for new solutions and prevents system to converge quickly on a local maximum, avoiding loss of genetic diversity.

CONDITION			
TYPE: ***CONTENTS OF THE GEL*** Min:1 Max:18 Selec:1 Value: 9.2			
SUBTYPE: *Contents of CTMA in gel* Min:0.15 Max:0.4 Value: 0.22	SUBTYPE: *Relation TMA/(CTMA+TMA)* Min:0 Max:0.72 Value: 0.68	SUBTYPE: *Contents of [OH-] in gel* Min: 0.15 Max: 0.6 Value: 0.3	SUBTYPE: *Contents of titanium in gel* Min: 1 Max: 18 Value: 8
ELEMENTS	ELEMENTS	ELEMENTS	ELEMENTS
Contents of CTMA in gel	*Relation TMA/(CTMA+TMA)*	*Contents of [OH-] in gel*	*Contents of titanium in gel*
Min:0.15 Max:0.4 Value: **0.22**	Min:0 Max:0.72 Value: **0.68**	Min: 0.15 Max: 0.6 Value: **0.3**	Min: 1 Max: 18 Value: **8**

Figure 2. Example of a chromosome codification formed by one condition

On the other hand, the crossover operator employed is based on confidence intervals [10]. This operator is associated with the capacity of interpolation (*exploitation*), related to the belonging of an individual to a confidence interval built from the best individuals of the population (parents). It is also associated with the capacity of extrapolation (*exploration*), derived from its *not* belonging to the same confidence interval. To obtain that confidence interval, three new individuals formed by the lower ends, upper ends and means of the parent samples are calculated. When an individual is crossed, the new genes are obtained from the original ones, their belonging to the confidence interval and the fitness values of the three confidence interval individuals. In order to calculate this fitness value, it is required to predict their catalytic results by means of the ANN, which simulates the reaction process.

4 EXPERIMENTAL

The proposed system has been validated using two hypothetical functions, based on the modelled behaviour of multi-component catalysts explored in the field of combinatorial catalysis. Lately, this Soft Computing technique has been applied to an industrial problem.

4.1 GA parameters optimization

An analysis of the different parameters of the GA has been carried out. In this study the GA was used separately from the rest of the architecture to avoid possible interferences. Therefore, the GA is employed alone and no ANN retraining process is taken. However, the GA makes use of the predictions of a modelled ANN for its crossover operator. Therefore, an initial generation was used for training and testing several neural networks in order to find the most suitable ANN topology for the problem under study. This ANN turned out to be a multi-layer perceptron with 5 input nodes, 10 hidden nodes and 2 output nodes, trained with Backpropagation Momentum (learning factor=0.8, momentum term=0.8).

All generations provided by the genetic algorithm were validated by a hypothetical function previously used in [17] with another optimization approach. This hypothetical function (1) describes the dependency of the catalyst composition with the final catalytic performance in the oxidative dehydrogenation of propane and it replaces the experimental process. This function was selected to allow comparison between [17] approach and our proposed method.

The catalyst variables considered in this model are the content of five different elements: V, Mg, Mo, Mn and Fe. The objective function (1) to be maximized is the propylene yield (Y%), which absolute maximum is around 7.5%.

$$Y = Y_1 Y_2 \tag{1}$$

$$Y_1 = [66 x_V x_{Mg}(1 - x_V - x_{Mg}) + 2x_{Mo} - 0.1(x_{Mn} + x_{Fe})] \tag{2}$$

$$Y_2 = [66 x_V x_{Mg}(1 - x_V - x_{Mg}) - 0.1 x_{Mo} + 1.5(x_{Mn} + x_{Fe})] \tag{3}$$

$$\sum x_i = 1, x_i \geq 0 \tag{4}$$

In all the following studies, five runs of the algorithm were made for each combination of parameter values, starting from the same initial generation.

4.1.1 *Study of mutation parameters*

The aim of this study was to determine the best parameters for the mutation process. The mutation probability (MP) and the number of genes to mutate (Gen) were modified with the values: MP=5%, 10%, 15% and 20%; Gen=1, 2, 3, 4 and 5. The rest of parameters were fixed to: α=0.5, population=50, parents=20%.

The evolution of the mean quality of each generation for the combinations of the mutation parameters is shown in figure 3. The combination MP=5% and Gen=1 was chosen, as it allowed the GA to obtain a good evolution of the quality through all generations.

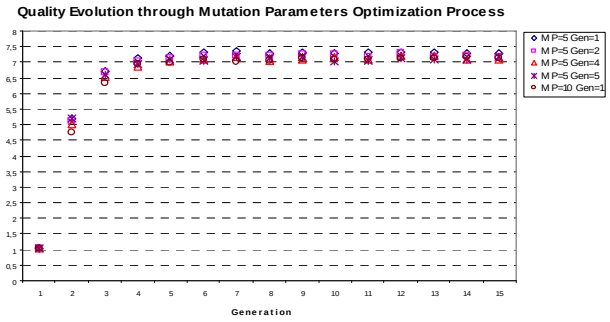

Figure 3. Mean quality evolution in the study of mutation parameters

4.1.2 *Study of crossover parameters*

The α parameter (which determines the size of the confidence interval used by the crossover operator) and the parents parameter were modified with: $\alpha = 0.3$, 0.5, 0.7 and 0.9; parents=10%, 20%, 30% and 40%. The other parameters were set to: population=50, MP=5%, Gen=1. In figure 4 the evolution of the quality average for each combination of these parameters is shown. The combination α=0.9, parents=10% is chosen.

4.1.3 *Study of population parameter*

The number of samples in each population is modified as follows: population=25, 50, 75 and 100. The other parameters were set to: PM=5%, Gen=1, α=0.9, parents=10%. In figure 5 the evolution of the quality average is shown. All combinations were very similar, so population=50 was chosen as this value is nearer to the real capacity of the reactor.

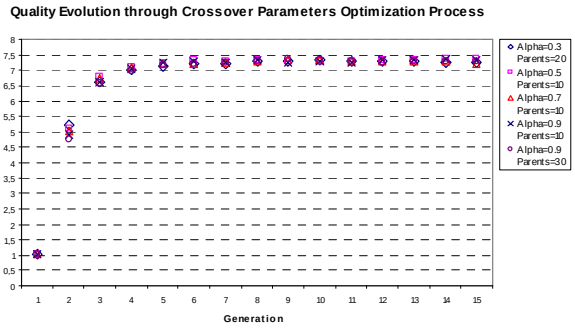

Figure 4. Mean quality evolution in the study of crossover parameters

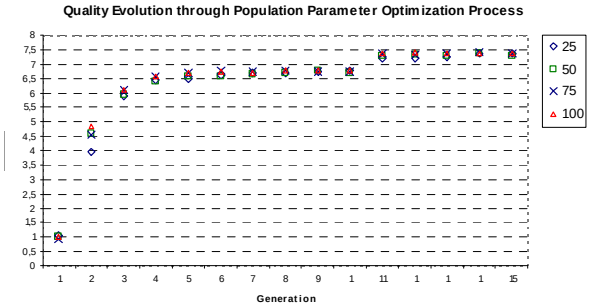

Figure 5. Mean quality evolution in the study of population parameters

4.1.4 Discussion

The proposed Soft Computing technique has provided better results for the hypothetical function (1) comparing to those results obtained in [17]. In that paper the maximum quality value found was 7.5% and six generations were needed with a population of 100 individuals. In our case, only one generation is needed to obtain the maximum, with a population of 25 individuals (figure 6). Moreover, the mean quality of the samples evolves rapidly to the maximum, reaching near values from the 4th generation, whereas in [17] the mean quality comes closer to those values from the 10th generation, employing in both cases a population of 50 samples. Furthermore, that optimization algorithm is more sensitive to the number of samples of the population. Thus it needs more than 100 samples to reach the maximum quality value whereas our approach obtains good results with only 25 samples.

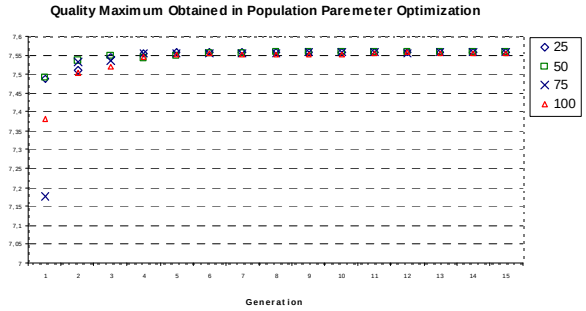

Figure 6. Maximum quality evolution in the study of population parameters

4.2 Soft computing technique validation

Another hypothetical function (5), based on the modelled behaviour of multi-component catalyst explored in the field of combinatorial catalysis, has been applied to validate the whole proposed method.

$$Y(x_1,x_2,x_3,x_4,x_5) = z_i(x_1,x_2)+z_j(x_2,x_3)z_k(x_3,x_4,x_5) \quad (5)$$

where:

$$\sum x_i = 100, x_i \geq 0$$

$$z_i(u,v) = 0.6g(100u-35,100v-35) + 0.75g(100u-10,100v-10) + 1g(100u-35,100v-10)$$

$$z_j(u,v) = 0.4g(100u-10,100v-30)$$

$$z_k(u,v,w) = 5+25(1-(1+(u-0.3)^2+(v-0.15)^2+(w-0.1)^2)^{0.5})$$

$$g(u,v) = 100-(u^2+v^2)^{0.5} + 50(sin(1(u^2+v^2)^{0.5}))/((u^2+v^2+0.001)^{0.5})$$

In figure 7, a representation of this hypothetical function is shown. The maximum values are in the lighter areas (values closer to 550).

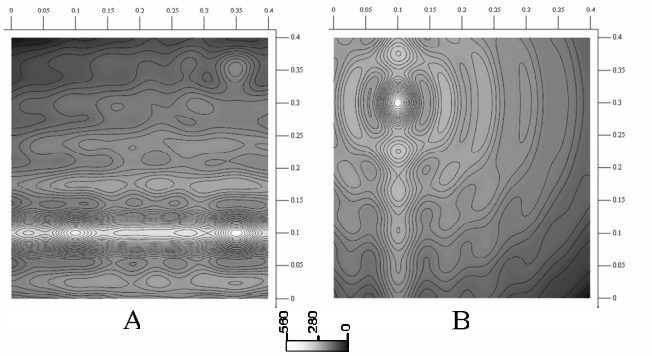

Figure 7. Representation of the hypothetical function in the planes containing the absolute maximum of the function: A) Varying x1 and x2 with (x3,x4,x5)=(0.3,0.15,0.1); B) Varying x2 and x3 with (x1,x4,x5)=(0.11,0.15,0.1)

A suitable ANN model of this function was obtained, training and testing several ANN topologies with different training algorithms. A multi-layer perceptron with 5 input nodes, 4 nodes in the 1st hidden layer, 3 nodes in the 2nd hidden layer and 1 output node, trained with Backpropagation algorithm with momentum (learning factor=0.8, momentum term=0.8) was selected.

An initial generation was obtained in the setting up step of our proposal (figure 1). Then, the rest of the Soft Computing technique (configured with the best GA parameters obtained in the previous studies) was applied with the same initial generation, making five runs. In figure 8 the evolution of the mean quality values and the maximum values achieved in each generation for the five runs are shown. It can be observed that from the 6th generation good quality results are obtained. In all tests, the ANN only used samples from about five generations in its retraining process.

4.3 Application to industrial catalysis

The Soft Computing technique was finally applied to a real industrial problem, trying to optimize Ti-silicate catalysts for the epoxidation

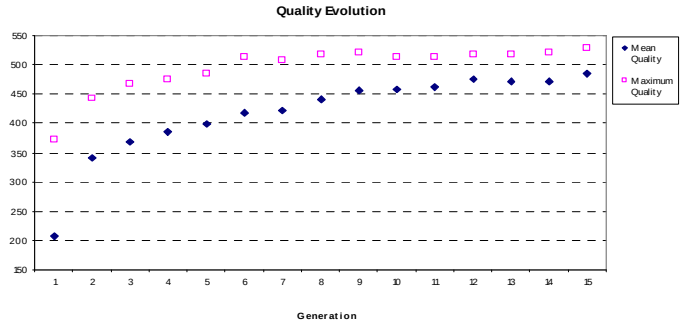

Figure 8. Mean Quality evolution and maximum values achieved

of olefins. In this case, it is needed to establish the value of four variables.

An initial random generation of 37 samples was used to determine an ANN model, studying several topologies and training algorithms. In this case, a multi-layer perceptron with 4 input nodes, 2 nodes in first hidden layer, 1 node in second hidden layer and 2 output nodes, trained with Backpropagation algorithm with Momentum (learning factor=0.8 and momentum term=0.5) was selected. This ANN model was combined with the GA in order to develop new industrial catalysts, following the Soft Computing method proposed. Thus, three generations of 37 samples have been synthesised and tested.

Through the NN-GA optimization process, an important improvement in the activity and selectivity of the starting materials has been achieved as it can be observed in figure 9. This figure shows the cyclohexane epoxide yields for the 3 evolved generations (3x37 samples). Moreover, the best catalyst found (2th generation, sample 32) improves in a 15% the catalytic performance (epoxide yield) with respect to the best previously reported catalyst [3].

To summarize, a highly active and selective catalyst for the epoxidation of cyclohexene has been found, that can be applied to the epoxidation of other olefins, specially propylene. Epoxides are starting materials for commodity products like plastics or drugs [14]. The best materials have low titanium contents, and were extracted and silylated. These materials have a Ti-MCM-41 structure and a very hydrophobic surface.

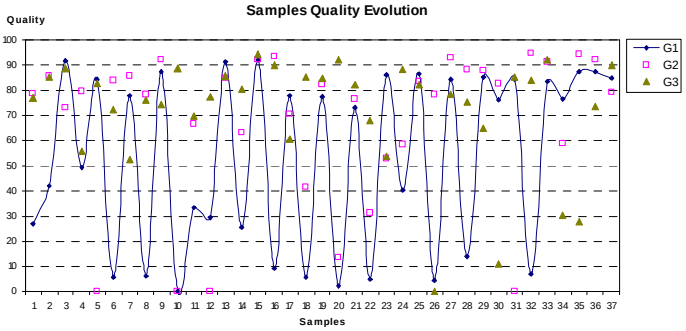

Figure 9. Quality evolution of samples of the Ti-silicate catalyst for the epoxidation of oleofins

5 CONCLUSIONS

The high-speed catalysis experimentation was guided by artificial intelligent techniques, i.e., a hybrid algorithm consisting of a GA coupled with a neural network. Specifically, this Soft Computing algorithm seems to be a new useful tool for the intelligent discovery of new catalytic materials, since it has appropriate tools for high-dimensional optimization but maintains in memory the whole ”history” of the search. Summarizing, in the future this method could be used to reduce the screening of statistically-poor active materials.

Although we have applied our technique to catalysis, our proposed codification is general enough to be applied to other chemical fields. Moreover, the codification enables to carry out more deeper studies, not only optimizing the configuration of the samples, but also allowing the analysis of the elements that compose the samples (for example, identifying the elements that appear in the best samples more frequently, in which percentage, etc.).

ACKNOWLEDGEMENTS

This paper is partially funded by grants TIC2003-07369-C02-01, CICYT DPI2002-04434-C04-02, FPU AP2001-1516 and FPU AP2003-4635 of the Spanish government.

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