Proceedings of the 6th World Congress on Mechanical, Chemical, and Material Engineering (MCM'20)
~~Prague, Czech Republic~~ Virtual Conference – August, 2020
Paper No. ICCPE 119
DOI: 10.11159/iccpe20.119

Control Properties of a Reactors System to Produce Magnetic Nanoparticles by Thermal Decomposition

K. J. Delgado – Carrillo[1], J. de J. Ibarra–Sánchez[2], C. Molina–Guerrero[1], A. H. Sámano[2], M.E. Cano[2]
[1]Departamento de Ingenierías Química, Electrónica y Biomédica, División de Ciencias e Ingenierías, Universidad de Guanajuato – Campus León
Loma del Bosque 103, Lomas del Campestre, C.P. 37150, León, Guanajuato, México
delgadock2015@licifug.ugto.mx; cmolina@fisica.ugto.mx
[2]Centro Universitario de la Ciénega, Universidad de Guadalajara
Avenida Universidad 1115, Linda Vista, C.P. 47820, Ocotlán, Jalisco, México
chuy_lindo3@hotmail.com; h.s.alfonso@gmail.com; meduardo2001@hotmail.com

Abstract **–** During the last years, the study of magnetic nanoparticles (MNPs) is progressing due to the potential of their applications. The purpose of this work is to present a design methodology for a plant production of MNPs which are obtained through a thermal decomposition route. The analysis is carried out by proposing a pilot plant for MNPs production in the non–stationary state. A main part of the work is focused in the study of the dynamics and control of the reaction systems. The modelling of this reactions systems is done in the non–stationary state through the mass and energy balance. In addition, dynamic closed–loop behavior is analysed using a feedback control scheme. For the closed – loop study, the algorithm of Simulated Annealing is used to find the optimal parameters of PI controller. The design, modelling and simulation of the pilot plant for MNPs production is done by using MATLAB 2017a.

Keywords**:** Magnetic Nanoparticles; Thermal decomposition; Process Simulation; Optimization; Process Control.

1. Introduction

The field of nanotechnology has had a remarkable advance since the 1990s studying materials of nanometric size. Within these materials are magnetic nanoparticles, which exhibit interesting physical and chemical properties. A first important advantage that MNPs offer is that they have sizes comparable to that of proteins, cells, viruses and DNA, and it is possible to manipulate them at a distance by applying an external magnetic field, which opens a wide field for applications [1].

MNPs have demonstrated immense potential in biomedical applications such as hyperthermal therapy (HT) for cancer treatment, magnetic resonance imaging (MRI), drug administration and radiotherapy due to their properties to work both at the cellular and molecular level [2]. Some of the properties that allow this complete set of applications are the abnormally high magnetocaloric effect, giant magnetoresistance, the general magnetic moment and highly saturated magnetization [3].

The use of MNPs as heavy metal adsorbents has also become a trend, because it has a larger surface area that allows a greater number of active sites. Iron oxide nanoparticles attracted great interest in the field of environmental remediation because these superparamagnetic materials can be easily dispersed and quickly recovered from water by turning off and lighting an external magnetic field, which cannot be done with other materials typically used [4]. All the previously mentioned applications make MNPs have a promising future in research and industry, so it is the main material of study in this work.

It is known that the preparation of nanoparticles can be classified in two categories: subdivision of massive or macroscopic materials (top–down) and growth from molecular precursors (bottom–up). Recently, studies have been conducted on the bottom–up method using organic precursors of the atoms of which the particles are composed, organic solvents of high boiling point and in the presence of surfactants. This method is known as thermal decomposition.

A reported method in 2009 starts with an organometallic precursor of iron III, a reducing agent (a diol) to produce iron II and surfactants to reduce the surface tension of the particles. The decomposition temperature is given by the solvent, where long chain aliphatic hydrocarbons with double bonds are typically used. In this way, the decomposition temperature will be as high as possible, and the nucleation and growth phases are appreciably separated. However, this synthesis route

is highly sensitive to changes in its material balance, as well as to operational changes in the reaction [5]. Ibarra – Sánchez (2011) studied the key parameters for the synthesis of MNPs through thermal decomposition. The results showed that the stirring speed is key to controlling the particle size, where the value of 100 rpm determines the maximum size that the MNPs can reach (10 nm), and this is an important parameter to determine the maximum yield of the reaction [6].

The demand for MNPs have increased in recent years, however, there is little reported information on industrial production [7]. Therefore, it is necessary to use systematic methodologies for the elaboration of a process design in which MNPs of controlled size are obtained.

For any design and modelling purpose, the goal is to obtain enough information about the system of interest to provide more accurate predictions and better designs. In this way, computational optimization, modelling and simulation form an integrated part of modern design practice in engineering and industry [8]. Due to the technological development in speed and computational availability, the implementation of optimization methods to solve robust problems provides greater scope in process design. Therefore, the objective of this work is to model and design a process to obtain MNPs through thermal decomposition analysing the dynamics of reaction systems, in addition to optimizing the process using stochastic algorithms. The synthesis of MNPs is proposed through a process consisting of two conventional continuous stirred–tank reactors connected in series, based on kinetic data obtained in previous experiments.

2. Methodology

The proposed process diagram for the MNP production plant is shown in Fig. 1. First, the reactors are modelled from the kinetic data of the growth phase at the temperature of 473.15 K (R–101) and nucleation phase at 588.15 K (R–102) and the mass and energy balance in a non–stationary state.

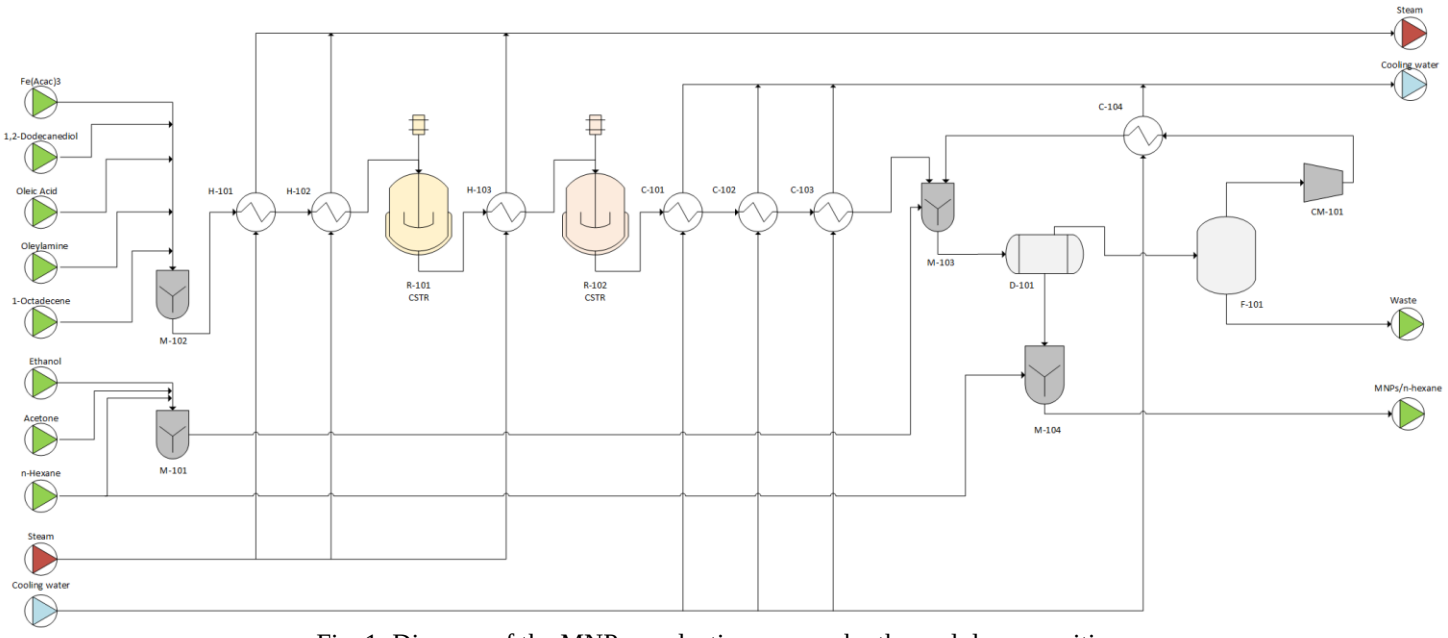

Fig. 1: Diagram of the MNPs production process by thermal decomposition.

Subsequently, the PI controller for each reactor is tuned by disturbing the initial concentration of the precursor, the jacket temperature and the reaction temperature, which are the optimization variables, by +5%, in order to obtain the optimum values of K_c and τ that minimize the IAE (Integral Absolute Error) using the Simulated Annealing stochastic algorithm. The optimized parameters were used to simulate the operation of the reactors.

For the heat exchange process necessary to bring the currents to the reaction temperatures and subsequent cooling, this design is carried out using the Kern methodology in conjunction with the minimization of the total cost of each equipment, including pumping, steam and cooling water costs. The optimization of heat exchangers is carried out using the Simulated Annealing algorithm also programmed in the MATLAB 2017a software.

3. Results and Discussion

Table 1 shows the optimal parameters of the PI controller obtained, both for the R-101 reactor (where nucleation occurs) and for the R-102 reactor (where the growth of the MNPs is carried out).

Table 1: Optimized parameters for the tuned PI controller for reactors R–101 and R–102.

	K_c	τ	IAE
R–101	100.000	0.9597	7067.98
R–102	99.980	0.0200	23184.84

Using the parameters of the previously optimized PI controllers, the reactors in operation were simulated. Result of the simulations, in Fig. 2 the profiles of initial precursor concentration (Ca), temperature in the reactor (T) and temperature in the jacket (Tj) are shown as a function of time. For the case of the R-101 reactor, the target temperature of 473.15 K was reached in 120 minutes, and a reduction in the precursor concentration ($Fe(Acac)_3$) of 64.70% is observed during this period, which suggests that the nucleation reaction is carrying out, even if the reactor temperature has not reached its optimum point (473.15 K). This may be due to the large amount of energy supplied by the steam to the rector and the low heat of reaction that this reaction possesses.

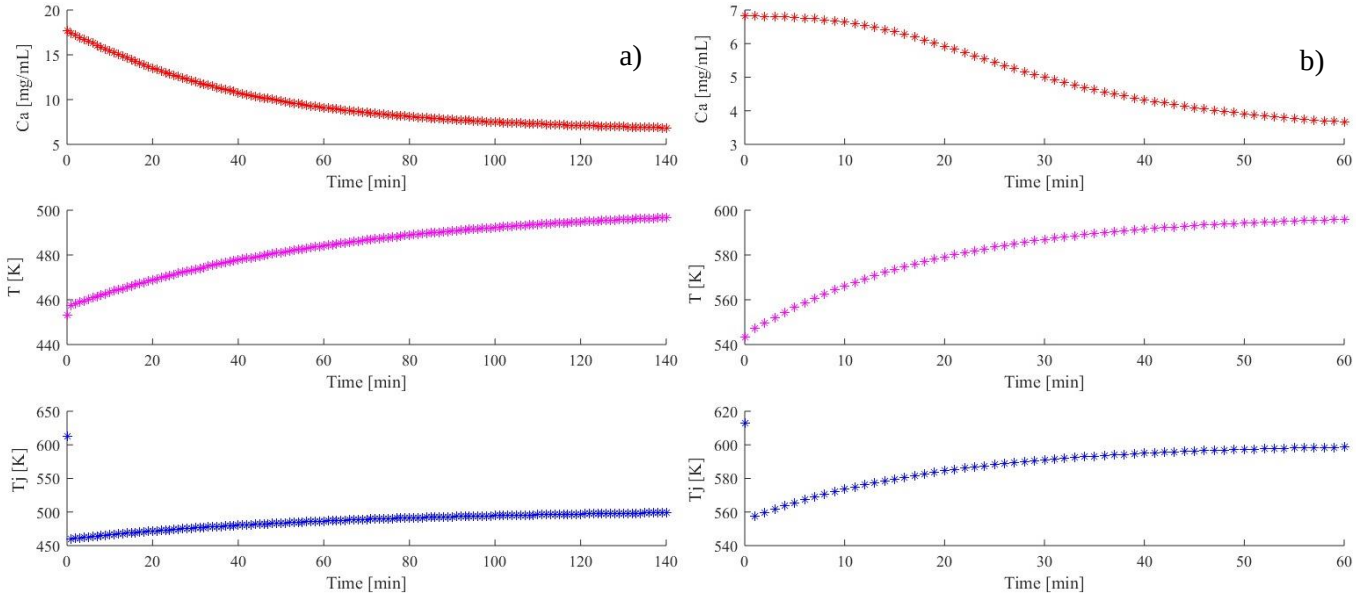

Fig. 2: Dynamic response of the reaction system at the start of the production of the MNPs. a) Nucleation phase (R-101), b) Growth phase (R-102).

On the other hand, it is observed that in the R-102 reactor there is a decrease in the concentration of the precursor of 42.85% in a period of 60 minutes, which is less than in the previous stage, this is congruent, because a large part of the precursor was consumed in the nucleation stage, since in the growth stage the reacting precursor contributes to the growth of the particle. In addition, at this stage the target temperature of 588.15 K is reached within 60 minutes. Unlike the nucleation stage the reaction lasts another 30 minutes extra, because it is where the particle growth occurs, this means that

for the first part of the reaction it is only enough to reach the temperature of 473.15 K at startup and at that time the entire precursor reacts because its concentration does not show considerable changes. Once the temperature has been reached, the reaction time of the precursor will last the residence time of 120 minutes, otherwise with the second stage, where in 60 minutes the last remaining precursor reacts, so in this stage the crucial part is the particle growth, which has nothing to do with the kinetics of the reaction, since much of the precursor has already reacted.

Finally, the plant's cooling and heating system was optimized. For all cases, the Simulated Annealing algorithm was used. The results showed that for the heating system: H – 101, H – 102 and H – 103, the transfer area was 9.2903 m^2 in all exchangers. In this case, outlet temperatures of 353.15, 453.15 and 543.15 K respectively were used, and steam was used as heating medium. In the case of the plant's cooling system: C – 101, C – 102 and C – 103, the transfer area was 9.2903 m^2 in all cases. For this system, outlet temperatures of 453.15, 353.15 and 308.15 K were used respectively and as a means of cooling water. An additional equipment is needed in the purification stage to cool the stream from 505 K to 303.15 K. The Table 2 shows the heating/cooling loads of the described heat exchangers.

Table 2: Heating/cooling loads for process heat exchangers.

Equipment	T [K]	W_{cp} [W/K]	Q [W]
H-101	298.15 - 353.15	0.1353	7.4460
H-102	353.15 - 453.15	0.1498	14.9864
H-103	473.15 - 543.15	0.1719	12.0347
C-101	588.15 - 453.15	0.1719	-23.2100
C-102	453.15 - 353.15	0.1498	-15.1363
C-103	353.15 - 308.15	0.1353	-6.0922
C-104	505.00 - 303.15	4.1166	-830.9400

4. Conclusion

The results showed that in the first part of the reaction (nucleation phase) the temperature is not a crucial point for the reaction, however, it is necessary to establish a control system because the temperature of the nucleation and growth phases must be separated to obtain homogeneous MPNs. On the other hand, for the growth stage, both the temperature and the retention time are key parameters which will allow a specific particle size.

For the heating and cooling system, the results suggest the use of energy integration to reduce costs, because the heating temperatures are very similar to the cooling temperatures. In addition, the specific heat of the reactor effluent does not change significantly with respect to the reaction mixture, because the concentrations of the precursors are relatively low. Furthermore, the total heating / cooling load of the plant is -840.90 W, which means that, using energy integration, the steam stream can be eliminated.

References

[1] Q. Pankhurst, N. Thanh, S. Jones, J. Dobson, “Progress in applications of magnetic nanoparticles in biomedicine,” *Journal of Physics D: Applied Physics*., vol. 42, no. 22, pp 1–15, 2009.

[2] T.E. Torres and A. G. Roca, “Magnetic properties and energy absorption of $CoFe_2O_4$ nanoparticles for magnetic,” *Journal of Physics: Conference Series 200.*, pp. 1–4, 2010.

[3] P. Tartaj, M. Morales, S. Veintemillas and T. González, “The preparation of magnetic nanoparticles for applications in biomedicine,” *Journal of physics D: Applied physics.*, vol. 36, no. 13, pp. R182–R197, 2003.

[4] P. Yuan, D. Liu, M. Fan, D. Yang, R. Zhu, F. Ge, “Removal of hexavalent chromium [Cr(VI)] from aqueous solutions by the diatomite–supported/unsupported magnetite nanoparticles”, *J. Hazard. Mater*., vol. 173, pp. 614–621, 2010.

[5] A. Gomez–Roca, R. Costo, A. Rebolledo, S. Tartaj, P. González–Carreño, T. Morales, M. P. Serna, “Progress in the preparation of magnetic nanoparticles for applications in biomedicine,” *Journal of Physics D: Applied Physics*., vol. 42, no. 22, pp. 1–11, 2009.
[6] J. Ibarra–Sánchez, “Escalado y Análisis de los Parámetros en la Síntesis de Nanopartículas Magnéticas para Aplicaciones Biomédicas,” Master Thesis, Guanajuato Univ., Guanajuato.
[7] C. Zhi, X. Lee, Y. Ling, Y.S. Yien, Y.B. Kah and N.M. Mubarak, “Pilot study of magnetic nanoparticles via SuperPro simulation using catalytic hydrothermal carbonization process,” *Journal of Environmental Chemical Engineering*., vol. 7, no.1, pp. 1–11, 2019.
[8] X. Yang, S. Koziel and L. Leifsson, “Computational Optimization, Modelling and Simulation: Recent Trends and Challenges,” *Procedia Computer Science*., vol. 18, pp. 855–860, 2013.