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MODELING, SIMULATION, AND OPTIMIZATION OF A FRONT-END SYSTEM FOR ACETYLENE HYDROGENATION REACTORS

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Abstract - The modeling, simulation, and dynamic optimization of an industrial reaction system for acetylene hydrogenation are discussed in the present work. The process consists of three adiabatic fixed-bed reactors, in series, with interstage cooling. These reactors are located after the compression and the caustic scrubbing sections of an ethylene plant, characterizing a front-end system; in contrast to the tail-end system where the reactors are placed after the de-ethanizer unit. The acetylene conversion and selectivity profiles for the reactors are optimized, taking into account catalyst deactivation and process constraints. A dynamic optimal temperature profile that maximizes ethylene production and meets product specifications is obtained by controlling the feed and intercoolers temperatures. An industrial acetylene hydrogenation system is used to provide the necessary data to adjust kinetics and transport parameters and to validate the approach.

Keywords: optimization, selective hydrogenation, acetylene reactor, front-end system.

INTRODUCTION

The cracking of petrochemical naphtha with vapor produces a stream composed mainly of ethylene and also of paraffins, diolefins, aromatics, and a small amount of acetylene. The ethylene is mainly used in the production of polymers, especially polyethylene (Peacock, 2000).

Small amounts of acetylene, on the order of parts per million, are harmful to the catalysts used in polymerization (Schbib et al., 1996). Therefore, the acetylene in the ethylene stream must be hydrogenated aiming at reducing its concentration with a minimum loss of ethylene to ethane. The inadequate operation of an acetylene hydrogenation reactor in a petrochemical plant can result in a loss of up to five million dollars per year (Huang, 1979; Brown et al., 1991; Kalid, 1999). In the petrochemical industry there are two different routes for ethylene production: tail-end and front-end (Schbib et al., 1994). For acetylene removal, the difference between them is very significant, as discussed later in this paper.

Despite the commercial importance of acetylene hydrogenation, few papers have been published on the kinetics of the reactions for the front-end system, the subject of the present work. The majority of the studies (Huang, 1979; Näsi, 1985; Brown et al., 1991; Bos and Westerterp, 1993) deal with the tail-end system, using pure reactants and operating conditions not even close to those in industrial plants. The difficulties in reproducing industrial operating conditions are due to the high temperature, above 100 °C; the high pressures, above 3 MPa; and the multicomponent feed gas, resulting from the pyrolysis of naphtha.

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According to Brown et al. (1991), the following reactions can occur inside hydrogenation reactors:

$C_2H_2 + H_2 \rightarrow C_2H_4$ (Acetylene hydrogenation)

$C_2H_4 + H_2 \rightarrow C_2H_6$ (Ethylene hydrogenation)

$nC_2H_2 + 1/2nH_2 \rightarrow (C_2H_3)n$ (Oligomerization, formation of green oils)

In the case of front-end reactors, hydrogenation of methylacetylene, propadiene, propylene, and 1,3 butadiene also occurs:

$C_3H_4 + H_2 \rightarrow C_3H_6$ (Methylacetylene or propadiene hydrogenation)

$C_3H_6 + H_2 \rightarrow C_3H_8$ (Propylene hydrogenation)

$C_4H_6 + H_2 \rightarrow C_4H_8$ (1,3Butadiene hydrogenation)

Only two articles dealing with the kinetics of front-end systems were found in the literature. Using atmospheric pressure; a temperature range of 40–80 °C; and feed gas composed of methane, acetylene, ethylene, ethane, propadiene, methylacetylene, propylene, propane, hydrogen, and carbon monoxide, Godinez et al. (1995) proposed reaction rate equations, depending only on hydrogen partial pressure, for hydrogenation of acetylene, ethylene, methylacetylene, propadiene, and propylene. They assumed the first-order reaction for hydrogenation of acetylene and diolefins and the third-order for hydrogenation of olefins. Using pressures ranging from 0.1 to 3.2 MPa; a temperature range of 15–120 °C; and feed gas composed of methane, acetylene, ethylene, ethane, hydrogen, and carbon monoxide, Schbib et al. (1996) proposed first-order reaction rate equations for hydrogenation of acetylene and ethylene for all reactants.

One of the most serious problems in the acetylene hydrogenation reaction system is catalyst deactivation. Yajun et al. (1982) concluded that approximately 40% of the oligomer generated in the reactor (called green oil) is deposited on the catalyst, thereby deactivating it; the H_2/C_2H_2 ratio is the main parameter that affects oligomerization; and the elevation in the reaction temperature also contributes to the oligomer formation. They found that the oligomer structure in liquid phase is composed of long aliphatic chains with the formula $C_nH_{(1.8-1.9)n}$, with n varying from 14 to 17. According to Sarkany et al. (1984) the molecular formula of the green oil is $(C_2H_3)_n$, with n varying from 4 to 22.

Brown et al. (1991) developed a function that describes the catalytic activity based on the formation of green oil. The model assumes that the deposition of green oil is uniform throughout the reactor and therefore the activity is the same for all the points in the bed at the same time. The function describes the catalytic activity in terms of the amount of carbon deposited on the catalyst. Kalid (1999) optimized a tail-end reaction system for acetylene hydrogenation, using a parameter referred to as catalytic effectiveness to represent catalyst deactivation.

There are several articles in the literature that discuss the modeling of an acetylene hydrogenation reactor. Godinez et al. (1995), Schbib et al. (1996), and Szukiewicz et al. (1998) discussed the need for a heterogeneous modeling for this process. They concluded that a pseudohomogeneous model describes the system adequately.

Huang (1979) studied optimization of the tail-end system with only one reactor without presenting the objective function and its constraints and using a steady-state model. Brown et al. (1991) and Kalid (1999) also studied the tail-end system with a low acetylene concentration in the feed and only one reactor. Kalid (1999) designed an objective function for a tail-end system, taking into account some operating costs and using a catalyst deactivation function depending only on run time and not including the effects of green-oil concentration and temperature. Optimization of the front-end system was not found in the literature.

In this work, a pseudohomogeneous, one-dimensional, and adiabatic dynamic model for an industrial acetylene hydrogenation front-end system was developed. The reactor scheme is composed of three fixed-bed reactors in series with intermediary coolers. An equation for activity loss with time, due to hydrocarbon deposition resulting from acetylene oligomerization (green oils), was also developed. The acetylene conversion and ethylene selectivity profiles for the three reactors were optimized, taking into account the process constraints. This was done by controlling the inlet temperature of each reactor by means of heater and cooler for the first reactor and intermediary coolers for the second and third reactors. Optimal temperature profiles were then obtained in order to maximize ethylene production without violating of the product specification. Data from an industrial acetylene hydrogenation system were used to adjust the kinetic and transport parameters and to validate the model.

PROBLEM DESCRIPTION

In the tail-end configuration, the hydrogenation reactor is located after the de-ethanizer column, which means that only ethylene, ethane, and acetylene are found in the reactor feed. Hydrogen and carbon monoxide (the latter used to increase catalyst selectivity) are fed in separately (Brown et al., 1991). Consequently, the reaction control system is much simpler, since the main variables of the reaction, such as the hydrogen/acetylene ratio, spatial velocity, inlet temperature, and CO concentration, can be modified according to variations in the process and the reactor runs. In the front-end configuration, the reactor is placed after the depropanizer. Therefore, all C_4^- cut is found in the reactor feed stream, except for CO_2 and H_2S, which are removed in the washing columns (Schbib et al., 1994; Kalid, 1999). Composition of the reactants and CO concentration are determined by the pyrolysis reaction in the furnaces, with only inlet temperature and spatial velocity remaining for control of the hydrogenation unit (Schbib et al., 1994).

To compensate for catalyst deactivation, it is necessary to gradually increase the reactor inlet temperature. However, the gradual increase in temperature decreases selectivity for ethylene in favor of formation of ethane, which is a product with a commercial value about five times lower than that of ethylene. During the reactor runs, the ethylene selectivity decreases until reaching a limiting value when the catalyst bed is replaced or regenerated.

The proposed solution was formulating a dynamic optimization problem, using a first-principles mathematical model, to maximize the acetylene conversion, ethylene selectivity, and unit run time, subject to process constraints and catalyst deactivation, by controlling the inlet temperature of each reactor.

MATHEMATICAL MODELING

Fixed-bed reactors are usually modeled as either pseudohomogeneous or a heterogeneous system. According to Mears (1971), in order to verify which model is more appropriate to represent a catalytic reactor, it is necessary to determine the relative importance of intraparticle resistance, interparticle resistance, axial dispersion, and radial dispersion. The criteria used with respect to each effect were Weisz and Prater (1954), Mears (1971), Young and Finlayson (1973), and Mears (1971). Applying the Weisz and Prater (1954) criterion to plant data, the result was not conclusive, because its condition depends on an inequality (of the type $x < 1$) that was only poorly satisfied ($x = 0.479$, which is too close to 1). Using the Mears (1971) criterion it was possible to conclude that the interfacial mass transfer resistance is negligible because Mears' inequality was satisfied with a value about 10^5 times lower than its upper bound.

Godinez et al. (1995) conducted tests to verify the influence of particle size of the catalyst G83-C on conversion rate, concluding that it is insensitive to this parameter and that the intraparticle mass transfer resistance is insignificant. Using the Weisz and Prater (1954) criterion, Schbib et al. (1996) also concluded that the intraparticle resistance to the acetylene hydrogenation reaction is not important. Szukiewicz et al. (1998) compared the pseudohomogeneous and heterogeneous models, concluding that both can satisfactorily represent the acetylene hydrogenation reactor, even though the pseudohomogeneous model requires the use of an effectiveness factor to compare it to the heterogeneous model. Petrus et al. (1998) also showed that pseudohomogeneous models are able to satisfactorily represent an acetylene hydrogenation reactor. Based on the above criteria and on the work found in the literature, a pseudohomogeneous model was considered in this work.

In order to verify the deviations from a plug flow condition, Hill (1977) considered that, if the ratio between reactor length and catalyst particle diameter is larger than 100, then axial dispersion can be disregarded. Froment and Bischoff (1990) mention that, for the flow velocities used in industrial applications, axial dispersion is negligible when the reactor length exceeds by 50 times the value of the catalyst particles diameter. For the case under study, the ratio (reactor length)/(particle diameter) is 347, therefore indicating that the axial dispersion is negligible. Besides the above-mentioned criteria, the criterion of Young and Finlayson (1973) for axial dispersion and the criterion of Mears (1971) for radial dispersion were also tested, reaching the same conclusion.

As the length/diameter ratio of the reactors studied is small (= 0.53) and the reaction is highly exothermic, the temperature gradient in the radial coordinate could be significant. To assure the choice of the model, the Mears (1971) criterion was tried. However, this criterion takes into account the effective thermal conductivity in the radial direction, which includes the heat transfers (by conduction, convection, and radiation) in the radial direction in the solid and fluid phases. Some work (Kunii and Smith, 1960; Yagi and Kunii, 1957) presents correlations for radial effective thermal conductivity, which are not valid for high Reynolds numbers such as the one obtained in this work of about 10^6. Besides, in the available correlations for calculation of effective thermal conductivity, there are many parameters such as solid emissivity and others that depend on particle shape, which were not found for the case under study.

However, the temperature inside the reactors under study is appropriately monitored, allowing a detailed analysis of the data on the runs. It was observed that in the most extreme case, i.e., at the exit of the first reactor, the largest difference between the temperatures at the central point (r = 0) and the peripheral point (r = R) is of 4.9 ºC. Based on these small temperature differences in the radial direction, radial dispersion was not considered in the model.

The reactors under study are thermally isolated with ceramic fiber. Based on the largest internal reactor temperature and using the ASTM C680 standard, the heat losses were estimated at 60 W/m^2, corresponding to 0.02% of the generated heat. Based on this value, the heat loss was considered negligible and the reactors were modeled as adiabatic reactors.

At end of a reactor run, which is the worst condition, the pressure drop across the reactor's bed length is about 20 kPa, which is less than 1% of its operating pressure (about 3.5 MPa). Therefore, reactor pressure was considered constant and momentum balance was not included in the model.

Based on these criteria and on the operating conditions of the reactors, similar dynamic models with the following characteristics were built for the three reactors:

- pseudohomogeneous;
- without radial and axial dispersion;
- negligible pressure drop;
- adiabatic reactors;
- no overall mass accumulation.

Based on the above hypothesis, the mass balance can be written as

$$\varepsilon \frac{\partial C_i}{\partial t} = -\frac{\partial(\varepsilon \; u_z \; C_i)}{\partial z} + \sum_{j=1}^{4} \nu_{i,j} \; r_j \tag{1}$$

where t represents time, u_z the interstitial gas velocity, ε the bed porosity, $\nu_{i,j}$ the stoichiometric coefficient of the i-th component in the j-th reaction, and C_i the molar concentration for i = 1, ..., 6, corresponding to acetylene, ethylene, ethane, hydrogen, methyl-acetylene, and propadiene, respectively, and j = 1, ..., 4, corresponding to the rates of the hydrogenation reactions of acetylene, ethylene, methylacetylene, and propadiene, respectively. Due to the small amounts of 1,3 butadiene and propylene in the feed stream and especially to the fact that these components were not measured to estimate the kinetic constants, their hydrogenation reactions were not considered in the kinetic model.

The energy balance for each stage can be written as

$$[\varepsilon \rho c_p + (1-\varepsilon)\rho_s c_{ps}] \frac{\partial T}{\partial t} = -\varepsilon \; u_z \rho \; c_p \frac{\partial T}{\partial z} + \sum_{j=1}^{4} r_j (-\Delta H_{rj}) \tag{2}$$

where c_p and c_{ps} are the gas and solid specific heat, respectively; ρ and ρ_s are the gas and solid specific mass; T is the temperature; and $(-\Delta H_{rj})$ is the heat of the j-th reaction.

As the operating conditions used in the work of Schbib et al. (1996) are very similar to those used in the industrial reactor that is the subject of the present study, their kinetic model was chosen for use in this work. However, the hydrogenation reactions of methylacetylene and propadiene were not considered in those articles. The kinetic equations are presented below:

$$\left(-r_j\right) = \frac{k_j C_i C_H \;\; \rho_s (1-\varepsilon)}{\left[1 + \left(K_H C_H\right)^{\frac{1}{2}} + K_{CO} C_{CO}\right]^3} \tag{3}$$

$$k_j = k_{0,j} \exp\left(-\frac{E_j}{R\,T}\right) \tag{4}$$

where C_H and C_{CO} are the hydrogen and oxygen monoxide molar concentrations and K_H and K_{CO} are the adsorption constants for these compounds, respectively. The values of the pre-exponential factor, $k_{0,j}$, and activation energy, E_j, are given in Table 1. The pre-exponential factors for the reactions of acetylene and ethylene hydrogenation obtained by Schbib et al. (1996) were adapted to the data from the industrial plant under study. The kinetic constants for the reactions of methylacetylene and propadiene hydrogenations were estimated using transient data on reactor operation during a period of 400 days. The gas composition was measured by chromatographic analyses of the outlet mixture of the first reactor. It must be pointed out that no kinetic study was developed in this work; only the functional form of the reaction rates found in the literature were used to fit the plant data, and thus the estimated parameter may have no physical meaning.

Table 1: Kinetic and adsorption constants.

Component	log $k_{0,i}$	E_i (kJ/mol)
Acetylene (m^6/kmol kgcat s)	27.4	190.50
Ethylene (m^6/kmol kgcat s)	23.3	179.78
Methyl-acetylene (m^6/kmol kgcats)	-0.494	4.40
Propadiene (m^6/kmol kgcat s)	-0.130	8.96
Hydrogen (m^3/kmol)	17.2	88.84
CO (m^3/kmol)	10.2	41.66

DEACTIVATION

Catalyst deactivation in acetylene hydrogenation reactors is mainly caused by the oligomerization of light hydrocarbons, producing green oil (Yajun et al., 1982). In the deactivation model, it is assumed that there is uniform fouling over the length of the reactor bed such that there is an average catalyst deactivation term for the entire bed (Brown et al., 1991). Considering that the formation of green oil is proportional to the acetylene concentration and taking into account the main deactivation equations in the literature (Brown et al., 1991; Dixit and Grant, 1996), the following empirical equation was proposed in the present work:

$$\frac{\partial a}{\partial t} = -a^n C_{1,0}^{\theta} k_0 \exp\left(\frac{-E_A}{R T}\right) \quad (5)$$

where a is the catalyst activity and $C_{1,0}$ is the inlet acetylene concentration in the reactor, n and θ are their corresponding orders of apparent deactivation, k_0 is the pre-exponential factor, and E_A is the apparent activation energy for the catalyst deactivation reaction. These four parameters of the deactivation equation were estimated using transient data on reactor operation during a period of 400 days. The orders of reaction were limited to integer values. Table 2 shows the parameters obtained by the maximum likelihood method. The high apparent deactivation order θ related to acetylene concentration is in agreement with the observations of Brown et al. (1991), and the first order for catalytic activity is in accordance with Dixit and Grant (1996). However, it must be emphasized that the parameters of the empirical model given by Equation 5 are just a fit of the plant data, having no physical meaning.

Table 2: Deactivation parameters.

Parameter	Average	Standard deviation
n	1	-
θ	6	-
k_0 (m^{18}/kmol^6 s) $\times 10^4$	1.16	0.26
E_A (kJ/mol)	0.4374	0.002

RESULTS AND DISCUSSION

Using industrial plant data from the first reactor feed as input into the model, several dynamic simulations were carried out in order to verify whether the model reproduces plant behavior appropriately. Figures 1 and 2 illustrate the results obtained with the software gPROMS (Pantelides, 1996), where it can be observed that the model is capable of reproducing the process behavior during a long period of time. The partial differential equations, given by Equations 1 and 2, were discretized by the method of lines using the first-order backward finite-difference formula with a mesh size of 50 points in each reactor, which was small enough for the required accuracy (relative tolerance of 10^{-6} and absolute tolerance of 10^{-8}). The resulting system of differential-algebraic equations was solved by the multi-step code DASOLV, with variable order and variable step size, implemented inside the software gPROMS.

It can also be observed in Figure 1 that the predicted reactor temperature has some peaks with a relative deviation of about 1.6 %. These relatively higher deviations are caused by larger variations in the feed composition at those times, which can also be observed in the outlet acetylene concentration of the first reactor (Figure 2). These deviations could be reduced by improving estimation of the kinetic parameters using data from bench-scale reactors, thereby avoiding the effects of noise in industrial plant data. The average relative deviations of the measured variables used to estimate the model parameters are presented in Table 3. Considering that industrial plant data were used to estimate the model parameters, the relative deviations obtained are acceptable in order to have confidence in the simulation results.

Figure 3 shows the simulation results for a situation where the inlet temperatures of the three reactors were maintained constant at 55 °C. Under that condition, deactivation of the catalyst beds can be observed during their lifetimes. Clearly, some corrective action should be taken early in the first year of operation because the outlet acetylene concentration of the last reactor is above its specified value (5 ppm or less, Schbib et al., 1996), as illustrated in Figure 4.

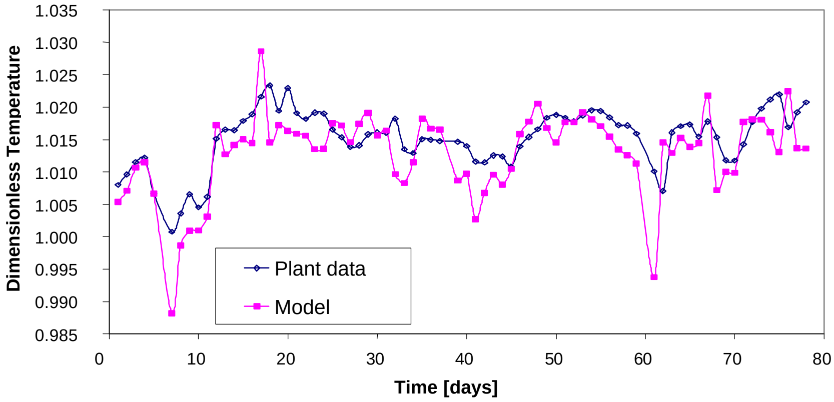

Figure 1: Dimensionless outlet temperature for the first reactor.

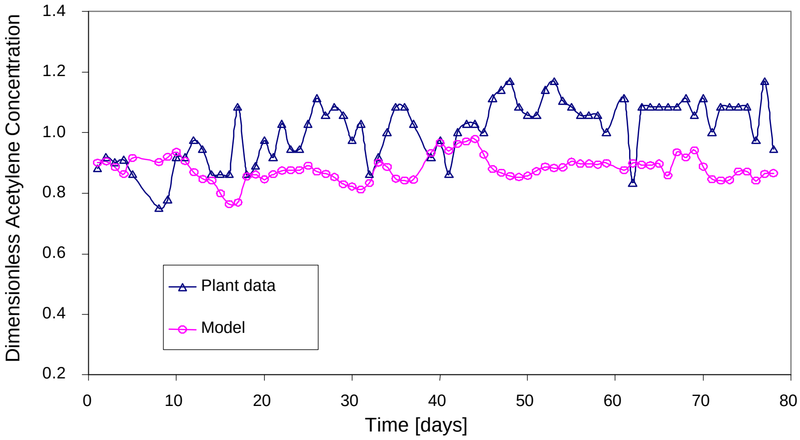

Figure 2: Dimensionless outlet acetylene concentration for the first reactor.

Table 3: Relative deviations of the measured variables used to estimate model parameters.

Measured variable	Average relative deviation, %	Maximum relative deviation, %
Outlet temperature of Reactor A	1.26	1.61
Outlet temperature of Reactor B	2.19	2.90
Outlet temperature of Reactor C	1.30	1.88
Outlet ethane concentration of Reactor A	2.83	9.57
Outlet ethane concentration of Reactor B	2.95	9.62
Outlet ethane concentration of Reactor C	3.00	10.16
Outlet acetylene concentration of Reactor A	7.48	29.14
Outlet acetylene concentration of Reactor B	13.34	39.82
Outlet methylacetylene concentration of Reactor A	6.93	19.30
Outlet propadiene concentration of Reactor A	11.22	24.20

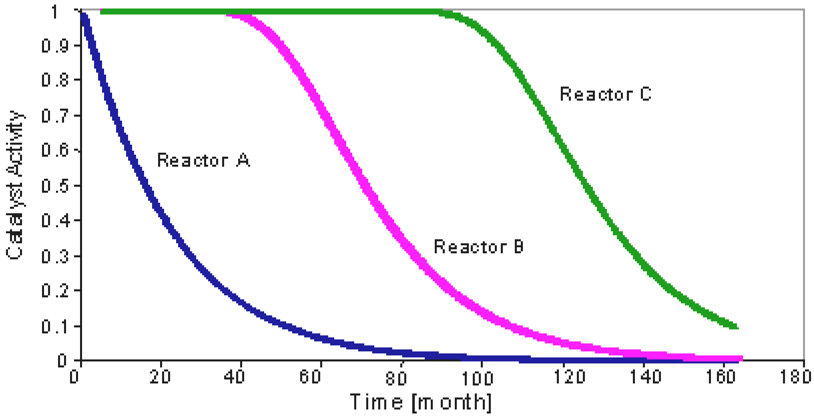

Figure 3: Catalyst activity in the reactors versus time with constant inlet temperature.

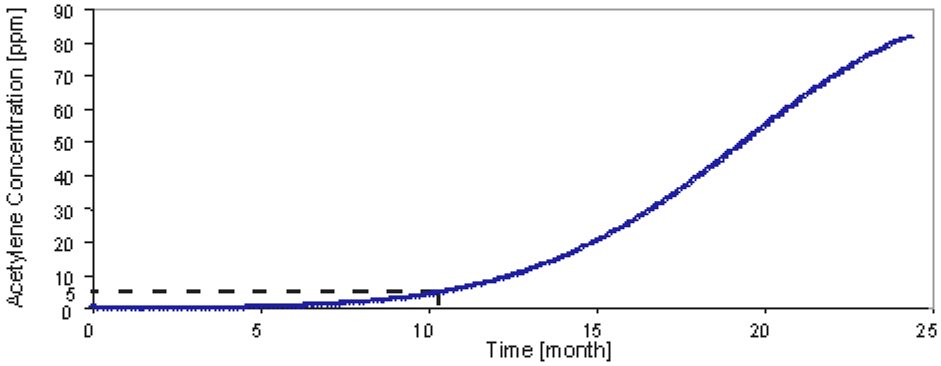

Figure 4: Outlet acetylene concentration for Reactor C.

To deal with the catalyst deactivation problem, it is necessary to develop an optimization tool to allow answering questions such as what is the run cycle time that minimizes the catalyst replacement and what is the optimal operating condition that maximizes ethylene formation, guaranteeing that the outlet acetylene concentration is within specifications.

The optimal operating condition would be that under which the largest possible portion of the acetylene fed in were converted into ethyleneat the lowest possible temperature to prevent formation of green oil and at the lowest deactivation rate to guarantee that the outlet acetylene concentration is within the specifications. The product specification must be for an acetylene concentration of5 ppm or less (Schbib et al., 1996).

The critical variable that should be carefully controlled during unit operation is ethylene selectivity, defined as

$$S = \frac{F_{C_2H_{4inlet}} - F_{C_2H_{4outlet}}}{F_{C_2H_{2inlet}} - F_{C_2H_{2autlet}}} \tag{6}$$

where F_i are the inlet and outlet molar flow rates of acetylene and ethylene in the unit.

Control of ethylene selectivity is important because the unit price of ethylene is about five times higher than that of ethane. For this reason, other operational costs, such as those of heating the reactor feed stream with vapor and cooling the outlet streams of reactors A and B with water, were not considered in the objective function. Another factor that could make a significant contribution to the objective function is the cost of a new catalytic bed. However, as the final time, t_f, was not fixed in the optimization, the cost of replacing a spent bed with a new one is constant, thus not affecting the objective function. The catalyst regeneration cost of a spent bed was not considered in this work, since that cost had not as yet been totally defined.

The constraints imposed on the objective function are fundamental to guaranteeing a feasible operating condition. The main constraint is the outlet acetylene concentration of the third reactor, as this limitation is the very reason for having a hydrogenation unit. If this concentration is above that specified, then the product has to be burned in the flare, resulting in a large loss to the plant. Besides, selectivity should at least be limited to positive values, so that all the acetylene contained in the load could be hydrogenated to ethane, specifying the product, but the fed ethylene should not be hydrogenated to ethane, reducing the conversion obtained in the pyrolysis furnaces.

Another important constraint imposed on the objective function is the acetylene conversion in the last reactor. In the case of front-end systems, where changes in operating conditions cannot be compensated for by adjustments to the hydrogen and CO feed flow rates, the third reactor should have an additional capacity to absorb possible process disturbances. Thus, the maximum conversion in reactor C was limited to 10 % of the overall conversion in the unit.

Catalyst type defines the lower limit of inlet temperature in the reactors. Moreover, as hydrogenation reactions are highly exothermic, the temperature and heat generation inside the reactors should be limited to prevent runaways. As heat generation is proportional to the temperature difference between the outlet and inlet streams of each reactor, this difference must be limited.

To achieve the above conditions, the following objective function was designed:

$$\begin{aligned} &\Phi(T_{0,1}, T_{0,2}, T_{0,3}, t_f) = \\ &= \frac{1}{t_f}\int_0^{t_f} \left(P_2 \quad \Delta w_2 + P_3 \quad \Delta w_3\right) \; d\xi \end{aligned} \tag{7}$$

subject to the following path constraints:

$$\begin{aligned} &C_{1,3}(t, L_3) \le 5 \ \text{ ppm} \\ &X_{1,3}(t, L_3) \le 10\% \\ &S(t) \ge 0\% \\ &T_{0,k}(t) > 52°C \\ &\Delta T_k(t) \le 55°C \\ &T_k\left(t, L_k\right) < 130°C \end{aligned} \tag{8}$$

for k = 1, 2 and 3, corresponding to reactors A, B and C, respectively. $T_{0,k}(t)$ is the inlet temperature of the k-th reactor; P_2 and P_3 are the ethylene and ethane specific prices, respectively; $\Delta w_2(t)$ and $\Delta w_3(t)$ are the ethylene and ethane net mass rates produced in the unit, respectively; L_k is the length of the k-th reactor; $C_{1,3}(t,L_3)$ is the outlet acetylene concentration of the third reactor (product specification); $X_{1,3}(t,L_3)$ is the acetylene conversion in the third reactor; S(t) is the ethylene selectivity of the unit; $T_k(t,L_k)$ is the outlet temperature of the k-th reactor; $\Delta T_k(t)$ is the temperature difference between the outlet and inlet of the k-th reactor; and t_f is the unit run time. As the objective function seeks the highest ethylene selectivity, because $P_2 > P_3$, the optimization has to maximize it. The maximum conversion constraint in the third reactor provides a greater flexibility to the unit to absorb load disturbances, guaranteeing that product specifications will be met. The last two constraints given by Equation 8 are defined to prevent runaways.

To solve the optimization problem, the Dynamic Optimisation Code (DAEOPT) which implements the single shooting technique in the software gPROMS, was used. With the software gPROMS it is possible to use piecewise constant (steps) and piecewise linear (ramps) functions for the control variables. Although it is also possible to use a continuous smooth function (polynomial, exponential, etc.) with time invariant parameters to be determined, this form was not explored in this work, because the solution is not practical for implementation in the industrial plant. The first two forms of temperature variation were adopted in this work, and the final decision was made based on a comparison of the optimization results.

Figure 5 shows a comparison of the optimal objective function with the situation wherein the inlet temperatures of the three reactors were maintained constant and with the situation wherein these temperatures varied linearly with run time (a typical operation of an industrial unit to compensate for the effects of deactivation). For the case of constant temperatures, the lowest value observed in the industrial practice was used. The linear profiles were used as initial estimates for the optimal profiles.

It can be observed in Figure 5 that the highest value for the objective function was obtained when the inlet temperatures were maintained constant at the lowest possible value. However, looking at Figure 6 it can be observed that the outlet acetylene concentration of the third reactor seriously violates the product specification constraint (5 ppm) for this situation.

The simulation results using a linear increase in the inlet temperatures approximately reproduces the profile usually established by the operators based on observation of unit behavior. This profile satisfies the constraints although, as can be observed in Figure 5, it is not optimal. The optimal profile has an increase in the objective function of about 20% relative to this linear profile, which is directly related to the improvement in selectivity and plant profitability.

As the outlet acetylene concentration of the third reactor is the most stringent constraint, the optimal profile will always reach this constraint at least once on the path (see Figure 6). Thus, for a more conservative solution, it is sufficient to lower the product specification constraint.

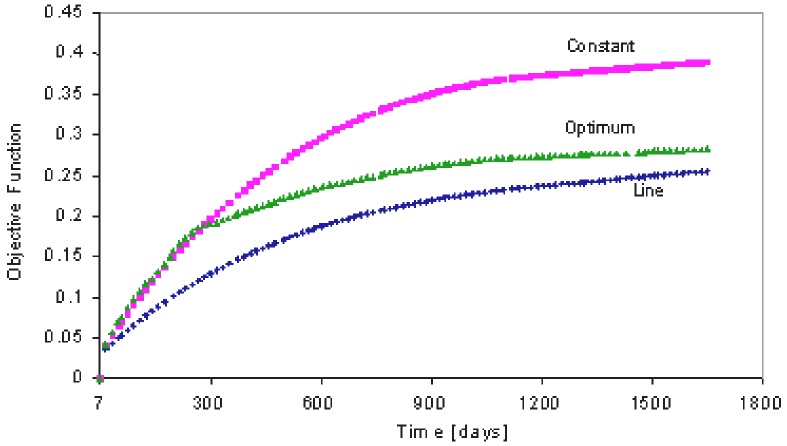

Figure 5: Objective function for the three inlet temperature profiles for the reactors.

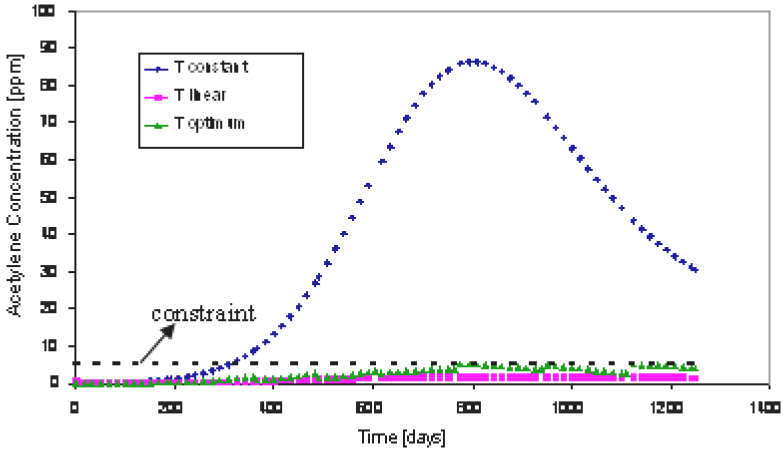

Figure 6: Outlet acetylene concentration for the last reactor for the three inlet temperature profiles.

Figures 7 to 9 illustrate the dimensionless inlet temperatures for the three profiles in each reactor. It can be observed that in the first reactor the optimal profile represents an intermediary situation between maintaining the temperature constant and to increasing it linearly. For this reactor, the industrial unit operates at high temperatures, resulting in additional costs that could be avoided. It can also be observed in Figures 7 to 9 that the time period of each interval of the optimal inlet temperature profile is about 150 days. In other words, during almost half the year the inlet temperature of each reactor remains constant, which is an easier operation than the linear profile.

The behavior observed in the second reactor is a consequence of the profile adopted for the first one because a compensation tendency exists between them, i.e., due to the constraint in the conversion of the third reactor, at least 90% of the acetylene conversion must occur in the first two reactors. Therefore, instead of a large increase in temperature in the first reactor during the time period of 300 to 800 days to compensate for catalyst deactivation, the optimal solution is an increase in conversion in the second reactor to maintain selectivity as high as possible (see Figure 5). After 800 days that situation was reversed to meet the product specification that reached its constraint, i.e., the temperature in the first reactor was increased while in the second reactor the temperature was decreased (see Figure 6). The behavior observed in the third reactor results from the constraint imposed by the product specification and unit flexibility (a conversion constraint of 10%).

With the optimal solution it was possible to vary the inlet temperature of the reactors in order to maximize ethylene selectivity and to keep the catalyst activities of the beds at proper levels to guarantee that product specification were met. Although the catalytic bed of the first reactor tends to deactivate faster than those of the other two, it was possible to prolong the process runs by decreasing the temperature in the first bed and increasing the temperature in the second and third reactors.

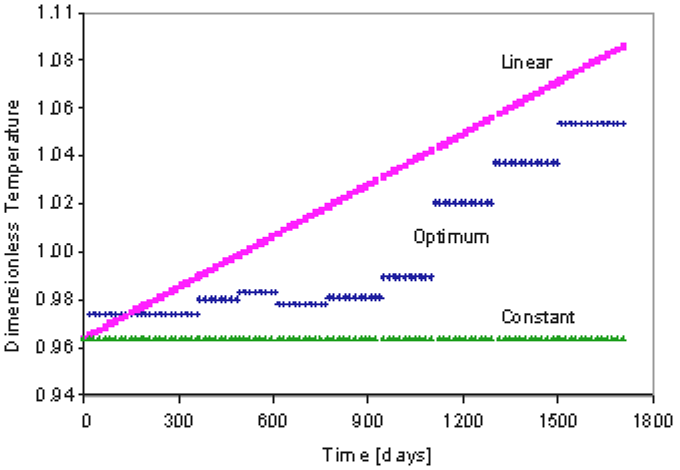

Figure 7: Dimensionless inlet temperatures for the three simulated situations for the first reactor.

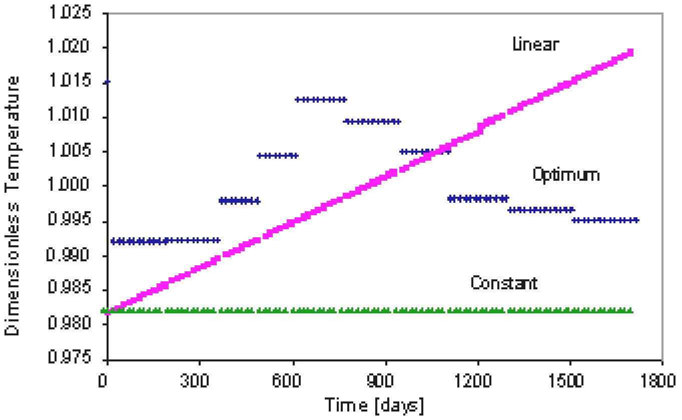

Figure 8: Dimensionless inlet temperatures for the three simulated situations for the second reactor.

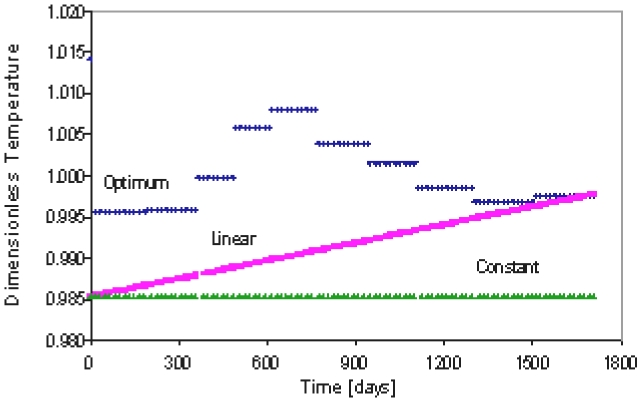

Figure 9: Dimensionless inlet temperatures for the three simulated situations for the third reactor.

CONCLUSIONS

The modeling, simulation, and dynamic optimization of an industrial reaction system for acetylene hydrogenation were carried out in this work. The model is able to satisfactorily predict the outlet temperature and concentrations of ethane, acetylene, methylacetylene, and propadiene in each reactor (the available measured variables). The model developed also describes the catalyst deactivation process as a function of acetylene concentration and reactor temperature. The results were able to represent the conditions in an industrial plant with a front-end configuration.

The acetylene conversion and ethylene selectivity profiles were optimized for the reactors, taking into account catalyst deactivation and process constraints. A dynamic temperature profile that maximizes ethylene production and satisfies product specifications, varying the inlet temperatures of the reactors, was obtained. The optimal profile represents an intermediary solution in between maintaining the temperature constant and in increasing it linearly. When the inlet temperatures are kept at constant low values, the product specification constraint is violated, but the best selectivity is achieved. On the other hand, a linear increase in the inlet temperatures maintains the outlet acetylene concentration in the last reactor well below the constraint, but selectivity is lost. The optimal profile is a compromise between product quality and selectivity. In practice, the optimal profile could be adjusted periodically and automatically, based on plant feedback, thus avoiding violation of constraints. Although similar results were obtained with the use of piecewise linear profiles, the use of piecewise constant profiles is more adequate for practical implementation.

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NOMENCLATURE

a	catalyst activity	(-)
C	molar concentration	(kmol m^{-3})
c_p	specific heat	(kJ kg^{-1} K^{1})
E	activation energy of the hydrogenation reactions	(kJ mol^{-1})
E_A	activation energy of the deactivation reaction	(kJ mol^{-1})
F	molar flow rate	(kmol s^{-1})
ΔH	reaction heat	(kJ $kmol^{-1}$)
k	kinetic constant	(-)
K	adsorption constant	(-)
k_0	pre-exponential factor	(-)
L	reactor length	(m)
n	deactivation order for the activity	(-)
P	price per unit of mass	(\$ kg^{-1})
r	specific hydrogenation reaction rates	(kmol m^{-3} s^{1})
R	universal constant	(kJ mol^{-1} K^{-1})
S	ethylene selectivity	(-)
T	temperature	(K)
T_0	inlet temperature	(K)
t	time	(s)
t_f	unit run time	(s)
u_z	interstitial velocity	(m s^{-1})

Δw	net production rate in the unit	(kg s^{-1})
X	acetylene conversion	(-)
z	axial coordinate	(m)

Greek Letters

ε	bed porosity	(-)
ν	stoichiometric coefficient	(-)
ρ	specific mass	(kg m^{-3})
θ	deactivation order for the acetylene	(-)

Subscripts

i	components of the reactional mixture: 1 - acetylene, 2 - ethylene, 3 - ethane, 4 - hydrogen, 5- methylacetylene, 6 - propadiene, CO - carbon monoxide
j	hydrogenation reaction: 1 - acetylene, 2 - ethylene, 3 - methylacetylene, 4 - propadiene
k	hydrogenation reactor: 1 - Reactor A, 2 - Reactor B, 3 - Reactor C
s	catalyst

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