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CATALYTIC TEST FOR EVALUATION OF THE DEACTIVATION OF CATALYSTS EMPLOYED AT THE FCC

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ABSTRACT

The time-scale deactivation of the catalysts used in heterogeneous catalytic processes is profoundly significant in the industry's expenditure. Fluid Catalytic Cracking (FCC) is highly impacted by this phenomenon, requiring the constant regeneration of these materials. Given this problem, this work intended to provide - to the students of the Chemical Engineering and Oil and Gas Engineering courses at the Salvador University (UNIFACS), and the students of the Graduate Program in Chemical Engineering (PPEQ) at the Polytechnic School of the Federal University of Bahia (UFBA) – one active learning, in the application of the theoretical concepts of some specific disciplines. This methodology was made possible by developing a bench-scale unit on the deactivation and regeneration of catalysts and additives used at the FCC. The unit reaction system features a stainless-steel reactor with a fixed bed, heated by an electric resistance furnace, with borosilicate saturator and upstream heater.

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INTRODUCTION

The industry has a significant economic and social role worldwide and is increasingly demanding its professionals' training. Consequently, the need to train engineers with technical skills involved in the production chain and prepare to operate in a competitive and globalized market has increased (Santos and Simon, 2018). A new teaching strategy in chemical engineering and oil and gas courses is the development of bench-scale test units. This approach promotes students to improve various skills and competences in the engineering area, such as team problem solving, multidisciplinarity, dimensioning, and maintenance of equipment. In this learning process, the contents theoretically addressed in the disciplines of chemical processes, heterogeneous catalysis, among others presented in Table 1, are worked on in practice.

Conducting studies on the catalytic processes and performance of the catalysts used in the refining of oil are essential for the context of learning of the production processes since the scenario of world expansion requires a high energy demand, attached mainly to the fuel production. Fluid Catalytic Cracking (FCC) process is responsible for the transformation of high molecular weight hydrocarbons into lighter compounds, with high added value, such as diesel, gasoline, and LPG. The formation of coke is one of the several ways of deactivating the catalysts, so it is an undesirable product in most of the processes and can cause losses for industrial units (Figueiredo, Pinto and Órfa, 1993; Persson *et al*., 2019). Deactivation by coke formation occurs on a time scale of seconds. This rapid deactivation implies the constant movement of the catalysts between two zones: a reaction zone, where the products of interest are formed, and a regenerative one.

Table 1. Examples of disciplines and content applied in the development of the bench-scale unit

Subjects	Content
Risk Analysis in the Industry	Risk analysis, security systems, and plant maintenance.
Heterogeneous Catalysis	Study of fundamental properties, preparation, characterization, and types of deactivation of catalysts.
Materials Science	Study of catalysts and selection of materials for the construction of the plant.
Process Control	Control strategies, selection of process controllers, and performance simulation.
Chemical Processes	Study of the mass and energy balance and elaboration of process flowcharts.
Inorganic Chemistry	Study of properties in the characterization of catalysts.
Organic Chemistry	Study of the characterization of coke and its interaction with catalysts.

The regenerative zone is responsible for the recovery of the catalytic activity of the catalysts, through the oxidation of coke in the regenerator (Vogt and Weckhuysen, 2015). At the reactor inlet, water vapor is used to dilute and increase the feed load. However, it also leads to the deactivation of catalysts. Unlike deactivation due to coke formation, the loss of catalytic activity by water vapor is not reversible in the FCC process, causing catalyst degradation at each regenerative cycle (Sadeghbeigi, 2020). The industrial consolidation of new catalysts usually goes through three stages. One of them is the study through catalytic tests in the laboratory. FCC catalysts, in industrial conditions, have a distribution of activity, due to the mixture of catalysts with a high degree of deactivation and low activity and a low degree of deactivation and high activity, called equilibrium catalyst (E-Cat). Due to the complexity of E-Cat catalysts, it is not easy to reproduce them on a laboratory scale. One of the ways to simulate an E-Cat is to perform the hydrothermal treatment (Moorehead, Mclean and Cronkright, 1993; BAI *et al*., 2019; American Society for Testing and Materials, 2019). In laboratories, investigations of regeneration by decomposition of coke and deactivation through hydrothermal treatments are usually carried out with little control of the process. Therefore, this work aimed to bring undergraduate and graduate students from Salvador University (UNIFACS) and Federal University of Bahia (UFBA) - Campus Salvador to industrial consolidation of catalytic processes. Thus, a catalyst deactivation/regeneration bench-scale unit was developed for the FCC, assisting the catalytic reactions in an academic and laboratory approach. This bench-scale unit allowed the development of scholarship holders for scientific initiation and undergraduate and graduate research projects, along with the practical approach to the theories seen in specific disciplines during its elaboration, assembly, and application.

MATERIALS AND METHODS

The concept of the unit was developed on the CAD (Computer-Aided Design) platform, using the SolidWorks® program. The bench unit design data were obtained from the definition of the structural profile, the process controllers, piping, and accessories. The unit concept was designed with an aluminum profile of the corner type, with dimensions of 25x25 mm and thickness of 2 mm. The pipes used were 1/8" in polyamide (nylon) and 1/4", 1/8" and 1/16" in stainless-steel. The union of the pipes and accessories were made with double ring connections in stainless steel from Swagelok® and Girolok®. The unit process control was developed using three pressure gauges (11 bar limit), two 1/8" Hoke® three-way valves, two 1/8" Hoke® micrometric needle valves and three temperature PID type controllers (two from Therma®, model TH91DP203-002 and one from Coel®, model HW1000). The structure of the plant was assembled using a 10" Black & Decker® miter saw (model Bt1400), Vonder® 1/2" bench drill (model PBV013), Black & Decker® 3/8" hand drill (model TM500B2), steel hand saw quick rigid with 24 Redstripe® teeth, 4 mm screws, standard nuts and nuts with nylon lock, and slotted flat head, Phillips head and 6" adjustable screwdrivers. The control panel was made with a 5 mm acrylic plate, in which the valves, temperature controllers, and switches were placed. The electrical components were connected with 2 mm cables, for the furnaces 4 mm cables were used. In the plant's supply, 4 mm multipolar cables were used, with single-phase voltage regulator coupling, adjusted to 24 V, for the heating system. The process flowchart used to model the bench unit on the CAD platform is shown in Figure 1. The process occurs with the injection of synthetic air or steam in the stainless-steel reactor, positioned vertically, with a downward flow. A saturator containing liquid water was used to generate steam by bubbling heated N_2. The flow rates of N_2 and synthetic air are controlled through micrometric needle valves.

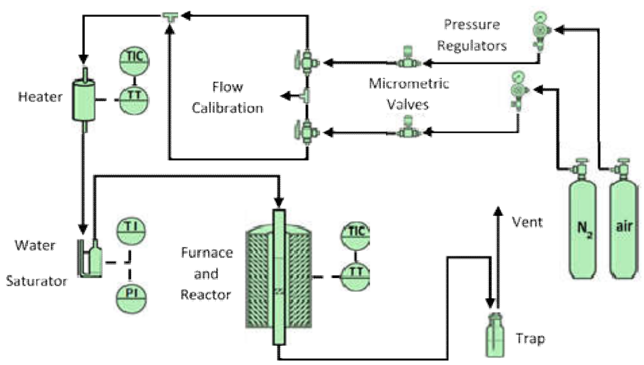

Figure 1. Process flowchart of the bench-scale unit. PI is pressure indicator, TI is temperature indicator, TT is temperature transmission, and TIC is temperature indicator and controller

RESULTS AND DISCUSSION

Bench-scale unit modeling: Deactivation by hydrothermal treatment or regeneration by depositing coke is done at elevated temperatures, using gas or steam flow. The unit was designed to supply synthetic air and N_2. The latter is used as a heated carrier gas to generate steam in a previously calculated amount when bubbled through a saturator. Synthetic air is used for combustion of coke in regeneration studies. Considering the possibility of using O_2 in these studies, the gas feed was modeled so that it is possible to vary its concentration, mixing the reaction and carrier gases (Figure 2). This measure makes it possible to reach different levels of the oxidizing atmosphere. The unit's structure was designed in an aluminum corner profile due to the variety of connections that the material enables. This type of material presents a more favorable cost/benefit ratio than the other profiles available on the market, such as V-slot or convex. The unit concept was based on the work of Santos *et al.,* (2019) and Da Silva *et al.,* (2019). The design of the unit facilitates maintenance, modifications, and periodic checks. In addition to inhibiting the overheating of electronic components, due to the ease of heat dissipation, Figure 3. The controllers and process indicators were arranged in a 5 mm acrylic plate, together with the electronic components.

furnace, the resistance can be allocated in zigzag, allowing a higher number of turns. The internal part of the furnace was filled with a ceramic fiber blanket (T_{max} = 1260 °C) to reduce

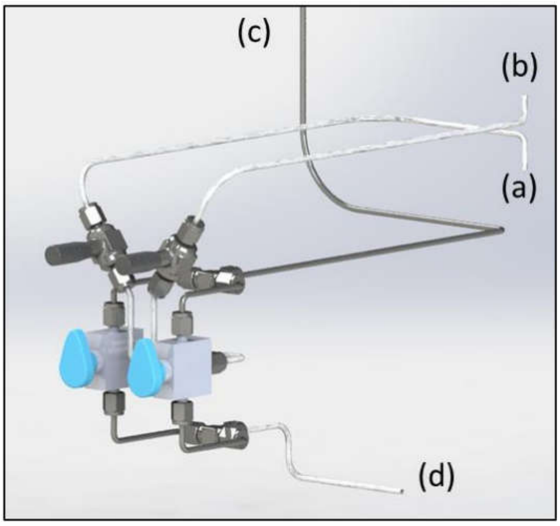

Figure 2. Gas mixture modeling: synthetic air supply lines (a), N_2 (b), reaction (c), and calibration (d). Lines (a), (b), and (d) are made of nylon, and line (c) is made of stainless-steel

Figure 3. Modeling of the catalytic bench-scale unit test using the SolidWorks® software

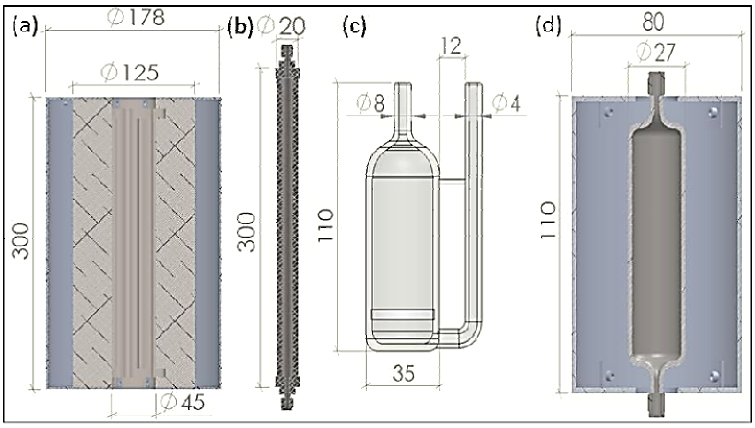

Figure 4. Modeling of the furnace (a), reactor (b), saturator (c), and heater (d) (unit of measurements in mm)

The unit has four main components: heater, saturator, furnace, and reactor. The reaction system heating was provided by a concentric cylindrical furnace type, where the reactor is allocated in the core region. This core region was built in refractory material, due to the high temperatures of the regeneration and deactivation processes. Inside this type of the energy transfer to the external environment, promoting higher thermal stability in the core region (Figure 4a). The reactor was designed as a fixed bed type, as it allows the use of powder or granular catalysts, with direct coupling by stainless steel nipples. The catalytic bed has a porosity of 2 µm, with a maximum capacity of 6 g of catalyst (Figure 4b). The saturator was made of borosilicate glass (maximum process temperature of 510 °C), considering the water's boiling point. This component features an inlet for carrier gas and a gas outlet, containing the reagent of interest in the vapor phase, (Figure 4c) (Perez-Lopez and Marcílio, 2003). The heater also has a cylindrical configuration, with the central part filled by an expansion vessel (Figure 4d). The material used for thermal insulation was also a ceramic fiber blanket and direct coupling by stainless-steel nipples.

Electronic components: The control and stability of process variables, such as temperature and heating rate, are important factors in bench studies. Thermal instability makes it difficult to repeat experiments, as well as having a negative influence on the reaction process. In order to minimize such effects, temperature controllers PID (proportional, integral, and derivative) type was selected. The combination of these three parameters gives excellent stability to the process. In Figure 5, the electrical diagram of the bench-scale unit is presented, showing the electronic components used and the electric mesh used in the system. The PID controllers act to maintain or raise the temperature, from the partial or total release of power (0-100%) to the equipment's electric resistance. Its operation requires switching components, such as electromechanical relays (EMR) or solid-state relays (SSR). In heating systems, these components are frequently activated, requiring high durability. The EMR relays act to open and close the resistive load from the actuation of a coil, which forces the contact between two plates. SSR relays act to open or close the system based on the light emission and reception by a photosensitive device. They present a higher switching speed, useful life, and are more compact. Based on the above considerations, Therma® SSR relays (model SS2425DZ) were used. Also, to guarantee the relay's integrity, a safety thermostat was added in series, with the maximum opening temperature of the system at 100 °C. The unit test has two electrical supply lines: one to energize the temperature controllers (control line) and another to power the furnace and heater (heating line). This concept was developed so that it was possible to couple the heating grid in series with a single-phase voltage regulator, aiming to use low voltages to provide safety to operators.

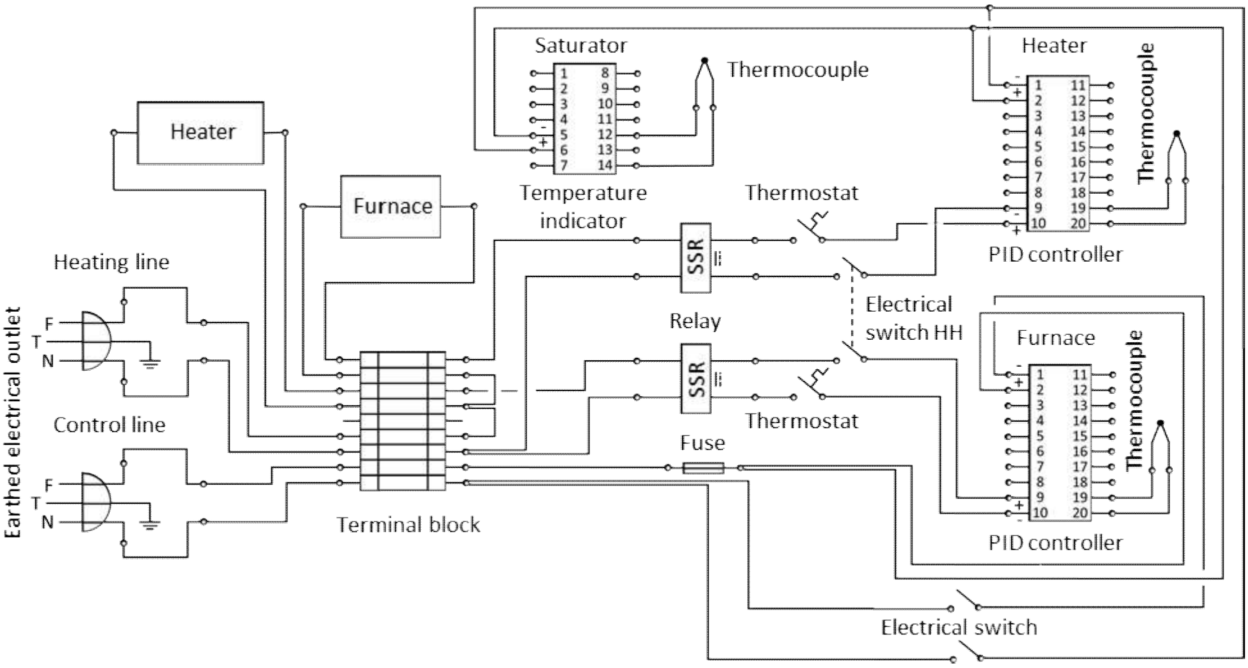

Figure 5. Wiring diagram of the bench-scale test unit

Figure 6. Assembled bench-scale test unity (450 mm wide, 550 mm long and 600 mm high)

The controllers have a fuse and two manual override switches in series, arranged on the control panel. One switch allows the controllers to be energized, while the other allows the signal to be sent to activate the relays. This measure sought to insert security into the heating process system.

Assembly of the bench-scale unit and description of the process: The bench-scale unit was manufactured according to the model developed in the SolidWorks® software (Figure 3). Initially, the unit's structure was set up, then the furnace, heater, and saturator were positioned. Then, the flow control system was assembled, together with the positioning of the valves on the panel and their connection with the process lines. Finally, the electronic components, temperature controllers, and switching devices were allocated (Figure 6). Lastly, process and electrical system tests were carried out to verify the unit's assembly and operation. The gas was supplied from the right side of the unit, with 1/4"stainless-steel pipes and the pressure adjusted to 1 bar (gauge) by the diaphragm valves. This process pressure is justified by the presence of borosilicate material from the saturator. The gases went to the micrometric valves through 1/8" nylon pipes, to carry out the flow adjustment. They pass through the three-way valves, where they are directed to the flow calibration or the process. With the three-way valves facing downwards, it is possible to calibrate the gas flow, coupling a bubble meter and using the soap bubble methodology (Associação Brasileira de Normas Técnicas, 1998). The three-way valves facing upwards allow the gases to continue to the process through 1/8 "stainless-steel tubing. The lines from this section are made of stainless-steel due to the elevation of the fluid temperature. Initially, the gases pass through the heater (200 W) coupled with 1/16" connections. The downstream and upstream lines have a short pipe section of 1/16", coupled with expansion and reduction nipples from 1/8" to 1/16", respectively. The gases are heated and go to the saturator through 1/8" tubing, passing through a crosshead before entering the saturator. A pressure gauge and thermocouple of type K (T_{max} = 1260 °C) were also attached to this connection, and they are in direct contact with the liquid. The saturator's pressure and temperature data make it possible to calculate the flow of water vapor, using Antoine's equation and Raoult's law. This process variable can be adjusted by changing the temperature of the carrier gas N_2, which enters the saturator.

In the downstream of the saturator, the reagents go to the reactor through a 1/8" pipe. The reactor used in the system is a differential type in stainless-steel with a fixed bed in quartz wool, coupled to the system by 1/8" nipples upstream and 1/4" downstream and placed concentrically in the furnace (5500 W and T_{max} = 1000 °C). The exhaust gases from the reactor are channeled through 1/8" piping to a bubbling vessel (trap) with liquid water. The trap indicates the gas flow and retains condensable compounds so that they are not released into the external environment through the vent system.

Final Considerations

The bench-scale unit test has the capacity for the development of studies on deactivation (using steam) and regeneration (by deposition of coke) in catalysts aimed at the FCC. It is possible to configure and adjust the temperature, flow, and feed composition variables of the catalytic tests, making it possible to carry out experiments in controlled conditions. The unit was successfully assembled without any significant changes. Its elaboration on the CAD platform was essential for the manufacturing stage since the 3D model allowed compacting the structural and arrangement of the system components. These designs were developed to allow the use of industrial data from FCC regenerators. The unit proved to be versatile, allowing the performance of several other studies, such as catalytic cracking, Temperature-Programmed Desorption (TPD), and reduction and calcination of catalysts. Based on the above considerations, it was possible to apply active learning to the participating students, resulting in better learning and an equipment that will allow the development of research and practical approaches for the other students of the engineering courses.

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