

## Influence of operational variables of the catalytic cracking unit on the circulation of the catalyst at constant mass conversion: Acting on the reduction of particulate emissions

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### Abstract

This article analyzes the operational variables of a catalytic cracking plant that affect the catalytic circulation and conversion results. It is considered that the analysis of the impact of these variables on the catalytic circulation is essential for the refiner to determine the best operational strategies, without loss of profitability and to minimize friction mechanisms, which reduce particulate emissions. The Analysis of Variance revealed how, statistically, the parameters are related, presenting equal, opposite directions and with different magnitudes. The results of  $R^2$ , F significances and analysis of residuals showed an excellent fit of the model, therefore, validating the design of the experiments carried out. The application model demonstrated a reduction capacity of 25% in the circulation of the catalyst, with no impact on the conversion of the unit. This result demonstrates the refiner's ability to act, improving its unit optimization techniques from an environmental and economic bias.

**keywords:** FCCU (Fluidized Catalytic Cracking Unit), catalyst circulation FCCU, conversion FCCU, particulate emissions, optimization FCCU.

## 1. Introduction

The refining industry plays a fundamental role in the development and promotion of a value chain focused on innovative and sustainable strategies that aim to ensure improved energy efficiency, reducing atmospheric emissions and generating a greater competitive advantage, thus allowing the achievement of the imminent goals they seek. improving air quality (OMS, 2021).

The refining industry finds in the Fluidized Catalytic Cracking Unit (FCCU), one of the most important stages of the refining process, capable of transforming heavy feeds coming from several processing units into liquid fuels with high added value. This important unit uses zeolitic catalysts as the main tool to direct the production of its products according to the general objectives of the refinery (Brasil, Araújo and Sousa 2014).

Given the importance of the cata-

lytic cracking process, even though delayed coking has gained importance in recent years, the FCCU is still the main focus of investments in conversion in world refining, looking to its optimization and adequacy for global pollution reduction policies (Carruthers, Solomon and Waddams 2018).

The catalytic cracking reaction takes place at an elevated temperature in a fluidized bed reactor, generating products with high added value and coke. At the heart of this unit is the fluidized bed used to burn the spent catalyst surface coke (E-cat). The coke is completely burned, regenerating the catalyst's activity, and providing the necessary energy for the thermal balance of the process. In addition, during the catalyst regeneration process, emissions of particulate matter into the atmosphere occur (Brasil, Araújo and Sousa 2014).

The catalytic cracking process, un-

like other units in the refining park, has a greater degree of freedom of action on the part of the refiner, as can be seen in Figure 1. In addition to the catalyst, the operational variables of the catalytic cracking unit directly impact the catalyst circulation and unit conversion results, as well as the selectivity of catalytic reactions. Operational variables are classified as independent and dependent (Sadeghbeigi, 2020).

The unit allows the refiner to operate at different points in the process, from the riser inlet, at the preheating temperature (TPC) and at the lifting steam (VLFT). At the end of the riser, the refiner can act on the reaction temperature, as well as on the reactor pressure and stripper steam. In addition to these variables that act directly in the conversion section, the refiner can also act on the specific replacement of the catalyst that enters directly into the regenerator (Sadeghbeigi 2020).

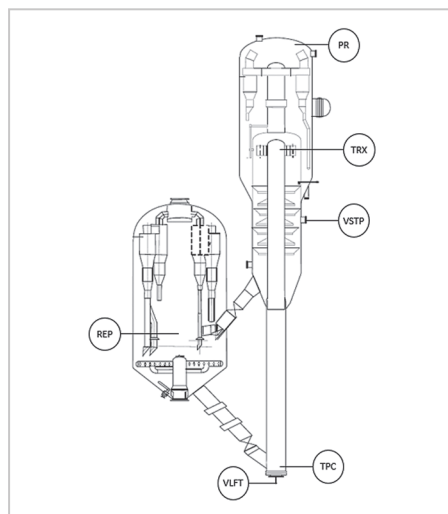


Figure 1 - Catalytic Cracking Unit.

(Source: Adapted from Sadeghbeigi, 2020.)

The main source of emissions are anthropogenic denominations, since they are related to human activities. In addition to causing local and regional impacts, particulate emissions on a global scale can significantly impact the quality of life on the planet. Therefore, the advancement of air quality management becomes essential to ensure the preservation or improvement of the air quality (IEMA 2021 – Maranhão State Institute of Education, Science and Technology).

According to Yateem, Nassehi and Hkan (2011), the catalytic cracking unit is the one responsible for the emission of particulates, causing adverse effects and

impacts on the immediate vicinity of the refinery. One of the main differentials of the Catalytic Cracking Unit to act in the reduction of particulate emissions is its high capacity for operational variability. It provides the process with a high degree of freedom that allows the refiner to adjust its operating conditions and catalyst, according to market variations, refinery strategies and environmental requirements (Szkalo, Uller and Bonfá 2012).

According to Fletcher & Evans (2010), within this variability of the catalytic cracking process, continuous attention is focused on optimizing the unit conversion section, aiming at maximum profitability. However, in

addition to profitability, the refiner also needs to focus on particulate emissions, which have become a critical point for the operational continuity of a unit, and which can be directly affected by the operational optimization of the unit.

Optimization studies of operational variables aimed at profitability have been widely developed over time, bringing significant contributions to the refiner to solve problems and optimize the FCCU. (Barreto & Chermat-costa 2015).

Within the operational variables, the circulation of the catalyst in the FCCU is a fundamental point of analysis, because it directly affects the mechanisms of catalyst breakdown, influencing

the total losses of particulate matter by the regenerator (Abadi 2002).

The results of this research contribute to studies developed in the academic field, expanding the analyzes already carried out in this field, bringing an op-

## 2. Materials and methods

For this research, data collection was chosen from thermodynamic simulation, which in simple terms, can be defined as a mathematical and thermodynamic model of a chemical process or unitary operation that aims to predict the thermodynamic and physical behavior of a process, without the need to carry out experiments and tests in pilot units. or in the industrial plant (Nunes 2014).

There are different performance models for UFCC mentioned in the literature. However, these patterns, involving multiple parameters, are mathematically complex and likely to be time-consuming. However, newer versions of commercial thermodynamic software include detailed information on the performance of catalytic cracking units, along with several options applicable to UFCC. By changing one of the input variables in the model, it is possible to verify the operational consequences based on the calculation results (Sutikno 2024).

For the implementation of the experimental design, the complete factorial design was chosen. This allows

operational perspective on catalytic cracking units. It also contributes to the UFCC operational knowledge, with the aim of boosting operational action to reduce particulate emissions. Finally, it brings social contributions, as it will expand efforts

evaluating, in general, the degree of influence of each factor on the response variable, obtaining a mathematical model that correlates the response variable to the independent variables and their interactions (Montgomery 2020).

For the experiments, the thermodynamic responses of the simulator, the changes in the main independent variables and their influence on the catalyst circulation and mass conversion were investigated. Based on available literature regarding the operation of catalytic cracking units, the independent variables were determined.

To determine the appropriate experimental conditions that portray the conditions of the commercial units, the operational limits of the main independent variables of different projects of commercial units were used. Table 1 presents the variables and the maximum and minimum levels.

To validate the results and verify the reliability of the generated models, a sensitivity analysis of the models was carried

to reduce particulate emissions, favoring the reduction of environmental impacts caused by catalytic cracking units.

All graphs and tables presented in the article were produced by the authors in 2023.

The residual graphs were checked, which made it possible to examine the existence of unwanted patterns, which could indicate biased results. After that, the quality of fit test statistics was also checked (Krishnamoorthy 2016).

In the goodness-of-fit test, the  $R^2$  (coefficient of determination) was checked, which estimates the proportion of the variability of the dependent variable (Y) that is explained by the set of k independent variables of the regression model (X). This allowed statistical verification of how close the data is to the fitted regression line (Krishnamoorthy 2016).

The F for global significance was also checked, using Fisher's method and the P values for each variable were validated. In this research, a significance level  $\alpha \leq 0.05$  was determined, which allowed us to reject or not the null hypothesis (the independent variables are not correlated with the dependent variables), thus validating the experimental design proposed for collecting research data (Krishnamoorthy 2016).

Table 1 - factors, levels and response variables of the experiments.

Factors		Levels		Response Variable	
		-1	1		
X1	TRX - Reaction temperature	495	540	CC - Circulation of Catalyst	C.U - Unit Conversion
X2	TPC - Preheating temperature	190	270		
X3	REP - Virgin Catalyst Replacement	-30%	30%		
X4	VLFT - Lift Steam	-30%	30%		
X5	VSTP - Stripper Steam	-30%	30%		
X6	PR - Reactor Pressure	1.9	2.1		

The operating point of each of the variables can be seen in Figure 1. The TRX is one of the variables most used by the refiner to adjust its yield profile, as well as the quality of its products. It has a direct influence on catalytic and thermal reactions, acting on the circulation of the catalyst and the mass conversion of the unit. TPC is a variable that is easy for the refiner to act on, but with a smaller effect compared to TRX, knowing the magnitude of its impacts on catalyst cir-

ulation and unit conversion is essential for optimizing the unit (Letzsch 2022; Sadeghbeigi 2020).

Replacement of the catalyst is always seen from its economic perspective, considering the cost of the virgin catalyst. Acting on this variable with an economic and environmental bias is a valuable competitive advantage for the refiner (Letzsch 2022; Sadeghbeigi 2020).

Converter vapors (VSTP and VLFT) are widely known by the refiner, but they

are variables that often act in a fixed or percentage way in relation to the load flow. Acting on these variables from the perspective of mitigating catalyst emissions will broaden the vision of the refiner over the unit's operational optimization window (Letzsch 2022; Sadeghbeigi 2020).

Reactor pressure is one of the refiner's least active variables, and is sometimes considered fixed, but it directly affects the unit's conversion, due to changes in the partial pressure of hydrocarbons as well

as in the residence time in the riser. Opportunities to optimize it will be fundamental for a strategy to mitigate particulate emissions with constant mass conversion

(Letzsch 2022; Sadeghbeigi 2020).

In this research, the thermodynamic simulator licensed by Fábrica Carioca de Catalisadores S.A. (FCC S.A.) was used.

The catalyst factor data (CDB) used in the experiments was provided by the Performance and Development Center of FCC S.A.

### 3. Results

From the measured responses in the experiments for catalyst circulation and unit conversion, statistical analysis was performed to obtain re-

gression models. Analysis of variance (ANOVA) was used to determine the parameters that significantly influence catalytic circulation and unit

conversion. The ANOVA results for the response variable and their corresponding F and P statistics are shown in Tables 2 and 3.

Table 2 - ANOVA from the design of experiments for the circulation of the catalyst.

	gl	SQ	MQ	F	F for meaning
Regression	6	1181.2	196.9	1792.2	5.328E-63
Residue	57	6.26	0.1098		
Total	63	1187.4			
Terms		Coefficients	standard error	Stat t	P-value
Intersection		-45.0070	1.30770	-34.417	7.88E-40
TRX		0.1640	0.00184	89.049	7.05E-63
TPC		-0.0515	0.00104	-49.712	1.23E-48
REP		-0.2432	0.01973	-12.329	1.02E-17
VLFT		0.2710	0.02302	11.773	6.8E-17
VSTP		0.1418	0.04315	3.286	0.001742
PR		-2.9584	0.41428	-7.141	1.85E-09

Standard error = 0.3314, R-Square = 99.47%, Adjusted R-Square = 99.41%.

The ANOVA, presented in tables, was used to define which parameters of the regression model significantly affect the experimental results. These tables provide the aliquot (%) of variance explained by the mathematical model in comparison with the variance contained in the experimental results. The probability for ANOVA (F significance) of the design of experiments for the circulation and for the conversion were 5.328 E-63 and 1.51E-54, respectively. The

two results were less than 0.05, confirming the validity of the suggested model, and therefore, allowing the development of mathematical models to be able to understand the effects of the studied variables and their interactions with the catalyst circulation and with the unit conversion.

Tables 2 and 3 also present the estimated regression coefficients and P-values for each independent variable. The degree of statistical reliability established for the

chosen model was 95%, where it is observed that for each independent variable chosen, whose P-value was less than or equal to 0.05, there is a significant correlation with the dependent variables.

The regression coefficients estimated in the catalyst circulation model show that all studied variables present a remarkable correlation with the dependent variable, where the P-values are below the accepted value of 0.05.

Table 3 - ANOVA from the design of experiments to unit conversion.

	gl	SQ	MQ	F	F for meaning
Regression	6	2939	489.9	900.4	1.51E-54
Residue	57	31.01	0.5440		
Total	63	2970			
Terms		Coefficients	standard error	Stat t	P-value
Intersection		-84.7772	2.910414	-29.128	6.41E-36
TRX		7.73755	0.922017	8.3919	1.54E-11
TPC		-0.05446	0.002305	-23.626	3.96E-31
REP		0.66186	0.043906	15.074	1.52E-21
VLFT		-0.23536	0.051223	-4.5947	2.44E-05
VSTP		0.17126	0.096043	1.7831	0.079883
PR		0.27557	0.004098	67.248	5.42E-56

Standard error = 0.767, R-Square = 98.95%, Adjusted R-Square = 98.84%.

Therefore, the six interactions are significant. However, in the unit conversion model, it is observed that the VSTP variable did not present a correlation that met the reliability value proposed in the study, with only five significant interactions valid.

Tables 2 and 3 also show the results for the  $R^2$  and adjusted  $R^2$  values for each regression model. The results obtained in both models showed high levels (above 95%) being, respectively, 99.47% and 99.41% for catalyst circulation and 98.95% and 98.84% for conversion. It

is observed by the adjusted  $R^2$  results that the models have an excellent predictability. The model equations obtained from the experiments are shown below. Residual analysis was performed to verify the ANOVA assumptions and validate the proposed regression models.

$$C.C = -45.01 + 0.1640 \cdot TRX - 0.0515 \cdot TPC - 0.2432 \cdot REP + 0.2710 \cdot VLFT + 0.1418 \cdot VSTP - 2.958 \cdot PR \pm 0.3314 \quad (1)$$

Where C.C: Catalyst circulation.

$$C.U = -84.77 + 7.7375 \cdot TRX - 0.0546 \cdot TPC + 0.6618 \cdot REP - 0.2353 \cdot VLFT + 0.27557 \cdot PR \pm 0.7376 \quad (2)$$

Where C.U: Unit Conversion.

The diagnosis of normality was examined through the construction of Normal Probability Charts (Figures 2 and 3). This diagnosis allows us to deter-

mine whether each set of data obtained in the experiments for each random variable is well modeled by a normal distribution or not (Krishnamoorthy 2016). As we

can see in the graphs, the standardized residuals revealed a normal distribution without outliers for both models.

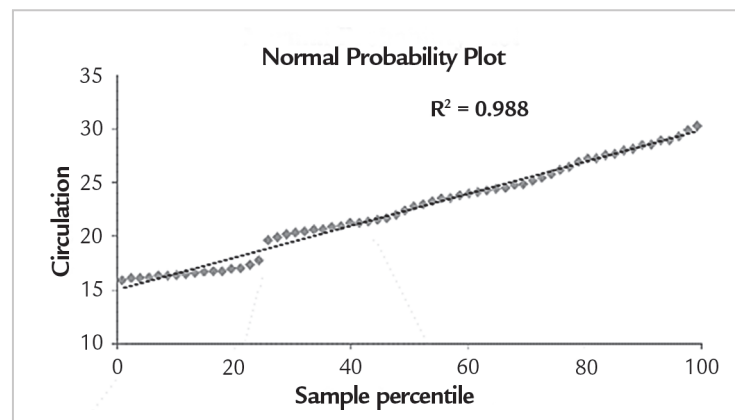


Figure 2 - Residue analysis: Diagnosis of Normality - Catalyst Circulation.

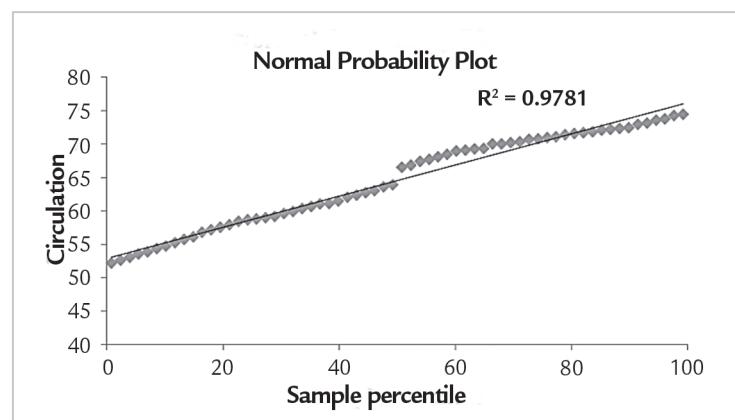


Figure 3 - Residual Analysis: Diagnosis of Normality - Unit Conversion.

Compliance with the assumptions of independence of residues was analyzed using graphs of residues in temporal sequence (Figures 4 and 5). This analysis allows us to

diagnose whether the residuals are uncorrelated, being independent and identically distributed, important factors for obtaining reliable models. (Krishnamoorthy 2016).

The residual independence diagnoses proved to be satisfactory, as no positive correlations were identified that would indicate non-compliance with this assumption.

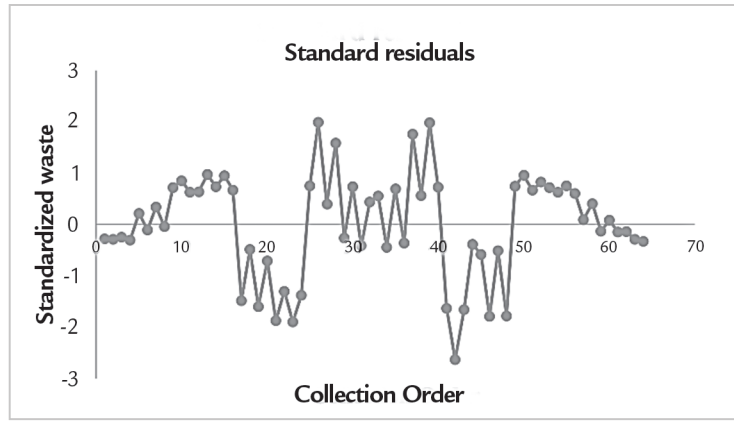


Figure 4 - Residual Analysis: Independence Diagnosis - Catalyst Circulation.

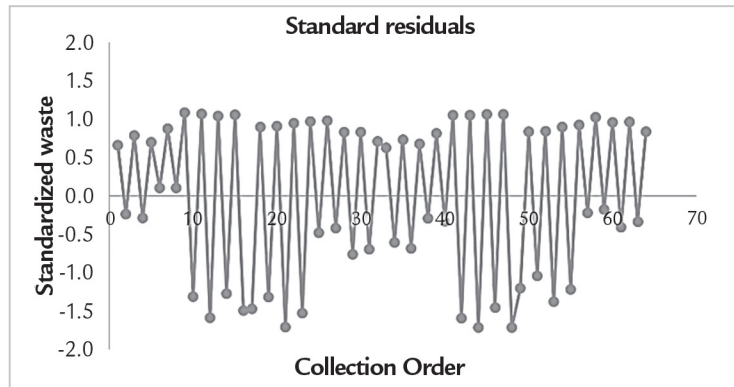


Figure 5 - Residual Analysis: Diagnosis of Independence - Unit Conversion.

Finally, the homoscedasticity diagnoses were evaluated using graphs that correlate the standardized residuals

with the response values predicted by the model (Figures 6 and 7). This analysis allows us to evaluate whether the proposed

linear regression models present constant estimation errors throughout the observations. A constant variance allows us to

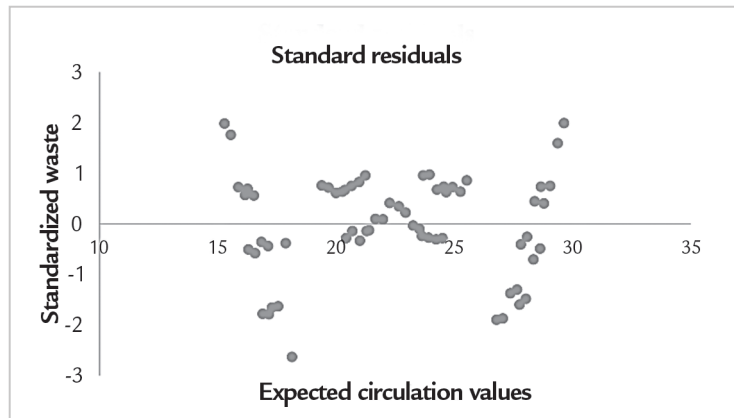


Figure 6 - Residue Analysis: Diagnosis of Homoscedasticity - Catalyst Circulation.

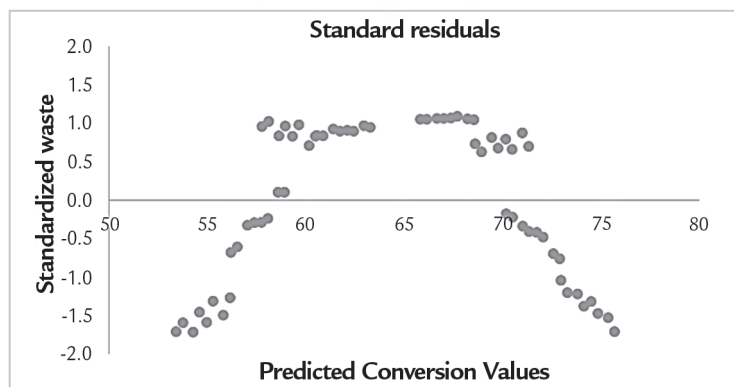


Figure 7 - Residual Analysis: Diagnosis of Homoscedasticity - Unit Conversion.



conclude that the models are reliable (Krishnamoorthy 2016).

As seen in the graphs, the points

#### 4. Discussion

In Equation 1, it can be seen that the model for catalytic circulation includes six linear terms with different directions and magnitudes of influence on the study variable. The model for unit conversion, Equation 2 presented five linear terms, also with different directions and magnitudes of influence.

When comparing the two models, it can be seen that some variables have opposite directions, while others do not. This can be explained due to the need for unit operation to maintain the coke and pressure thermal balances.

The reaction temperature (TRX) and load preheating temperature (TPC) show the same direction between the two models, even if they are opposite to each other. This is explained by the fact that the increase in reaction temperature requires an increase in catalyst circulation, for thermal adjustment of the unit. However, this results in increased unit conversion. The same occurs with the increase in the preheating temperature, which will lead to a reduction in the circulation of the catalyst for thermal

are distributed around 0, without showing a trend, with concentrated variances, thus assuming that there

adjustment of the unit, also converging in the reduction of conversion (Wear 1993; Sadeghbeigi 2020).

The factors of Catalyst replacement, escaping steam flow from the Lifty and reactor pressure have opposite directions. Increased catalyst replenishment causes increased activity in the unit's circulating catalyst inventory, which results in increased conversion. However, increased conversion shifts the coke balance, increasing the regenerator temperature, which in turn, causes a reduction in catalyst circulation (Wear 1993; Sadeghbeigi 2020).

The Lifty steam flow directly affects the thermal balance of the unit, causing an increase in catalyst circulation. However, the increase in steam also reduces the residence time in the riser, causing a reduction in conversion (Wear 1993; Sadeghbeigi 2020).

The reactor pressure directly affects the pressure balance of the unit and the pressure profile in the riser, causing an increase in conversion, but the increase in conversion generates a shift in the coke

is no autocorrelation of the residues, and therefore, that the variance of the residues is homoscedastic.

balance of the unit, causing an increase in the temperature of the regenerator, and consequently, the reduction in circulation (Wear 1993; Sadeghbeigi 2020).

The equations were applied in an application model, with the objective of evaluating the potential of reduction of catalytic circulation in a commercial unit. The data of the studied variables that were applied in the application model were provided by FCC S.A. and represent an overall average of the catalytic cracking units in the South American market.

Based on these data, the circulation and basic conversion of the unit were determined from the application of Equations 1 and 2 of the validated models. The results obtained were 22.3 ton/min and 64.9 %WT, respectively. Applying the Excel solver function to the two model equations, determining the limits of the variables, and the conversion objective set at 64.9 %Wt, according to the basic operation data, a reduction of 25.19% in the circulation of the unit catalyst was achieved according to the results in Table 4.

Table 4 - Application model optimization.

Code	Reactor Pressure	Basis	Limits		Optimization
			Minimum	Maximum	
TRX	Reaction temperature, °C	520	495	540	521
TPC	Preheating temperature, °C	250	190	320	320
REP	Virgin Catalyst Replacement, ton/dia	6	2	9	9
VLFT	Lift Steam, Kgh/h	6	4	7.8	4
<b>PR</b>	Reactor Pressure	2	1.9	2.2	2.2
VSTP	Stripper Steam, Kgh/h	3.2	2.2	4.2	2.2
Circulation, ton/min		<b>22.3</b>			<b>16.6</b>
Conversion, %wt		<b>64.9</b>			<b>64.9</b>

It can be observed in the results of the application model that when used together, the models allow the variables to be adjusted, according to

#### 5. Conclusion

In view of the analyses performed, it is concluded that the reduction of the catalyst circulation, without the loss of mass conversion of the unit, from the op-

the specific operational limits of each unit, in order to optimize the catalyst circulation, seeking to reduce the friction mechanisms, the particle load of

timization of the operational variables of the catalytic cracking unit, it is possible to use an operational technique that aims to mitigate the total emission of particulate

the cyclones, and consequently, the reduction of particulate emissions, without causing conversion losses in the unit (profitability).

matter by the catalytic cracking unit. The equations contribute to the operational knowledge of the refiners, allowing the elaboration of mitigating actions to reduce

the emission of particulates from their operational variables, expanding the vision beyond the reaction temperature and catalyst replacement.

Statistical analysis of the evaluated variables established a first-order linear model for catalytic circulation and unit conversion. The ANOVA revealed how, statistically, the parameters are related, showing the same direction, opposite direction and with different magnitudes. With the results of  $R^2$  adjusted above 95%, the low F significances and the analysis of residues, demonstrated an excellent adjustment of the regression model, validating

the design of the experiments carried out.

The evaluation of the application model, based on the average of the South American market, showed a reduction capacity of 25% in the circulation of the catalyst, with no impact on the conversion of the unit. This result demonstrates the refiner's ability to act, improving its unit optimization techniques from an economic and environmental bias.

The equations obtained are not only limited to the application by the bias of particulate emission reduction, but also, they can be applied in operational optimizations that need

to optimize the catalyst circulation for operational issues, such as: operating problems in the circulation valves; pressure problems in the pipe stands; mechanical problems in regenerator cyclones; operation problem in the cyclones of the separator vessel.

To expand the studies, it is considered opportune to carry out an analysis of the impacts of circulation on the friction mechanics of the catalyst in the catalytic cracking unit (particle-particle friction and grinding) and the impacts of increased replacement of virgin catalyst on the total emission of particulates.

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