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Statistical techniques for the treatment and analysis of experimental data from laboratory reactors were considered, as applied to a CREC Riser Simulator reactor for the example of fluid catalytic cracking catalyst evaluation. Deviations in mass balances were reconciliated considering the variance in each product mass. After reconciliations, simple optimum performance envelope curves were used to fit the data due to their simplicity and proper representation of the yield curves. In the data fitting step, errors in both dependent and independent variables were considered by using information obtained in the reconciliation procedure. The impact of different levels of confidence bands in the models on the discrimination of experimental results was discussed. Significant improvements in catalyst evaluation could be achieved either in the CREC Riser Simulator or other types of laboratory reactors with the help of the statistical procedures described here without increasing substantially the number of experiments.

Introduction

One of the most important issues for researchers on catalysis is to be certain about the ability to discriminate among the results obtained in the evaluation of different commercial or prototype catalysts (that is, to distinguish if two or more catalyst performances or the result of changes in operative conditions show statistically significant differences in the products yields). This is absolutely necessary to support selection judgments or decisions. The first choice to evaluate or select catalysts is the execution of standardized or particular procedures in laboratory reactors, due to the fact that reproducibility, simplicity, low cost, and many other issues need to be fulfilled properly (Moorehead et al., 1993; Young, 1993). Overall, it is well known that important experimental efforts need to be done to ensure accuracy and reliability of the data generated with the laboratory reactors.

Fluid catalytic cracking (FCC) is one of the most important processes in the oil refining industry. This is due not only to the huge volumes of heavy hydrocarbon cuts processed, but also to its versatility and efficiency in converting those low value, high molecular weight feedstocks into high value fuels (particularly gasoline) and petrochemical raw materials (Jiménez-García et al., 2011; O'Connor, 2007). Thus, small differences in conversions or product yields have a high impact on refinery profits and, in light of a large commercial offer, reliable estimations of the potential behavior of proposed catalysts are necessary. Even though different laboratory reactors are used to evaluate FCC catalysts (Moorehead et al., 1993; Corma and Sauvanaud, 2013), most of the selection procedures have been based on the microactivity test (MAT, ASTM D-3907) technique, which requires a fixed bed reactor. However, due to some inconveniences (Sedran, 1994), a large number of configurations and operative approaches for MAT units has been developed (Corma and Sauvanaud, 2013; Rawet et al., 2001). Flow reactors with a confined fluidized bed (FFB) are used similarly, that is, with a time averaging approach, and have become very familiar in FCC laboratories (Biswas and Maxwell, 1990; Passamonti et al., 2012).

An alternative methodology for FCC catalyst and feedstock evaluation and process development was developed based on the CREC Riser Simulator laboratory reactor, which has clear advantages in reproducing contact between reactants and catalyst particles in riser units (de Lasa, 1992). The unit was designed specifically to address FCC studies and ideally mimics the riser reactor in commercial units, following the analogy between position in the riser and reaction or residence time in the laboratory unit. The reactor was previously used in the study of various subjects related to FCC, such as catalyst evaluation (Gilbert, et al., 2011), kinetic and diffusive modeling (Bidabehere and Sedran, 2001; de la Puente and Sedran, 2000), new operative modes (de la Puente et al., 1999; Spretz and Sedran, 2001; Tiscornia et al., 2002), and recycling of waste plastic (Passamonti et al., 2012). Nevertheless, the statistical analysis of its performance is necessary in order to confirm its capacities.

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Concerning the evaluation of FCC catalysts, the comparison between different samples can be established, for example, on the yield of a given cut (usually gasoline) at given conversion or coke yield. This procedure is also common to many other catalyst evaluation approaches. Coke yield is very important in FCC in terms of the key heat balance of commercial units. In practice, the various group yields at iso-conversion or iso-coke yield can be obtained by means of interpolation in functions that represent the particular yield curves (yield versus conversion), based on the experimental information. These model functions, which are assumed to represent properly the system under study, could take boundary conditions into account (Ko and Wojciechowski, 1983), could be the result of kinetic models based on lump schemes (Wallenstein et al., 1999; Weekman and Nace, 1970), or could just be functions that fit the experimental data based on the expertise of the laboratory (Cerqueira et al., 1999). Whatever the approach used, one of the problems is the low number of experimental data in routine catalyst screening (typically, about five experiments for each catalyst sample). This factor makes the use of sophisticated models difficult, due to the large number of parameters needed (Wallenstein and Alkemade, 1996).

In general, the observations in laboratory reactors are affected by errors from different sources. Sometimes these error sources cannot be eliminated, thus being always present in the measurement process. Other kind of errors may be caused by equipment malfunction or unexpected events during measurement. In the first case, those errors are typically small in magnitude and are considered random errors; while in the second case they may generate suspicious data, and are considered non-random or gross errors (Narasimhan and Jordache, 2000). As part of good laboratory practices, repeatability procedures are used to determine the correct operation of the reactors. They demand the execution of periodical tests, but allow assessing experimental errors and detecting problems related to the experimental equipment (Vergel-Hernandez, 2001).

It is absolutely necessary that all the experimental information gathered in laboratory reactors be backed by as accurate as possible mass balances, and the way in which deviations in the mass balances are adjusted must be considered. There are two simple ways to adjust mass balances: (i) to impose the deviation to the product with the highest proportion (it could be gasoline or residue in the case of FCC) or (ii) to distribute the deviation among all the products, in a way proportional to the magnitude of each of the yields. The main disadvantage of these procedures is that they ignore both the variability of each measurement (which is not necessarily proportional to its magnitude) and the variation in the feedstock volumes or masses injected to the reactor. Statistical techniques for data reconciliation can take into account the variability of each measurement (including the mass injected to the reactor), formulating the problem as the minimization of the sum of the square differences between reconciliated and experimental values, using the variance of the observations as a weighting factor (Narasimhan and Jordache, 2000). This method was used to reconciliate mass balances in fixed-bed reactors, showing how the reliability of the data analysis can be improved (Vergel-Hernandez, 2001).

With the aim of defining a tool to improve the discrimination capacity, the application of a statistical methodology in the analysis of the data from the evaluation of two equilibrium commercial FCC catalysts, using a commercial VGO feedstock and two reaction temperatures in a CREC Riser Simulator reactor, is reported. The approach included the reconciliation of the mass balances, the use of optimum performance envelope (OPE) equations (Wallenstein and Alkemade, 1996) to fit the various yield curves considering errors in both variables (yield and conversion), which are compared with other common fitting functions, and finally the use of different confidence bands for the models proposed.

Materials and Methods

Reactor Setup and Operation Mode

The CREC Riser Simulator is a batch reactor with a volume of 45 mL, which has a turbine on top of a chamber that holds the catalyst bed between porous metal plates. The turbine rotates at 7500 rpm, thus inducing a low-pressure area in the upper central zone in the reactor that makes gases to recirculate in the upward direction through the chamber, thus fluidizing the catalyst bed. When the reactor is at the desired experimental conditions the reactant is fed with a syringe through an injection port and vaporizes instantly, thus setting the initial time. After the desired reaction time is reached, the gaseous mixture is evacuated immediately and the products can be sent to analysis (de Lasa, 1992). Additional descriptive details can be found in Bidabehere and Sedran (2006), Al-Khattaf (2007), and Passamonti et al. (2009).

Reaction products were analyzed in a HP6890 + gas chromatograph with a HP-1 column (30 m length, 0.25 mm i.d., 0.25 µm phase thickness) connected to an FID detector. Figure 1 shows an overall view of the experimental setup. Experiments were performed at 510°C and 540°C and reaction times from 9 to 21 s. The catalyst to oil ratio (C/O, average 7.3) was initially chosen to be similar to those in the commercial operation; however, due to small variations on the mass of VGO injected to the reactor, the resulting C/O ranged from 7.2 to 7.5. The amount of coke on the catalysts was determined by means of a temperature programmed oxidation method and the further conversion of the carbon oxides into methane, which was assessed with an FID detector. Reaction products were grouped into dry gas, LPG, gasoline, middle distillates (light cycle oil, LCO), residue, and coke. Percentage conversion was calculated as the addition of the yields of dry gas, LPG, gasoline, LCO, and coke.

Materials

Two commercial equilibrium catalysts provided by refineries were used, their main properties being shown in Table I. In this table the specific surface areas of the catalysts were
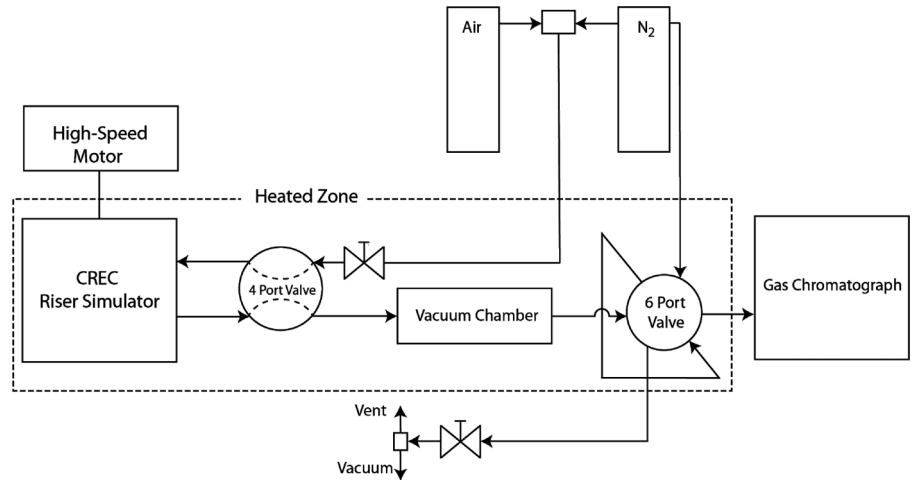
Fig. 1. Schematics of the reaction setup.

Table I. Properties of the catalysts used

Property	EcatL	EcatR
BET Specific surface area ($m^2\ g^{-1}$)	153	178
Zeolite content (wt.%)	18.9	18.1
Unit cell size (nm)	2.424	2.426
Rare earth oxides (wt.%)	0.64	2.50
Ni (ppm)	3250	1100
V (ppm)	175	920

determined by means of the BET method, the zeolite content was assessed by the method reported by Johnson (1978), the UCS determined by the ASTM D-3942 method, and the content of metals measured by X-ray fluorescence. The characteristics of the VGO feedstock, which was paraffinic in nature, were provided by a refinery and are shown in Table II.

Table II. Properties of the feedstock used

Density 20/4°C (g cm^{-3})	0.916
API Gravity (°)	22.3
Distillation ASTM 1160,°C	
IBP	226
5%v	322
10%v	361
30%v	408
50%v	432
70%v	456
90%v	494
95%v	513
FBP	539
Conradson carbon (wt.%)	0.11
Aniline point (°C)	80.1
V (ppm)	0.73
Ni (ppm)	0.1
Sulfur (wt.%)	2.03
Basic nitrogen (ppm)	400
Total nitrogen (ppm)	1441

Mathematical Data Treatment

Assessment of Experimental Errors

The repeatability procedures allow a precise determination of the experimental errors and possible information about outliers. Outlier points are data deviated from a general tendency, and may be caused by the presence of gross errors. Some authors have shown that experimental errors may depend on different aspects, like temperature, severity, or conversion (Cerqueira et al., 1999; Rawet et al., 2001; Vergel-Hernandez, 2001; Wallenstein and Alkemade, 1996). Taking into account that the experimental reaction time in this work changes in a relatively narrow range, it was assumed that the experimental errors did not depend on conversion, temperature or catalyst.

In this work the experimental errors in the mass balances were determined from the reiteration of experiments with catalyst EcatR under the same conditions (temperature 510°C, catalyst to oil ratio (C/O) 7.3, reaction time of 20 s) in a so-called repeatability analysis. This analysis is regularly performed in this laboratory unit with the aim of ensuring that the setup is working properly, and then the information gathered can be used to obtain statistic information. The conditions of the repeatability analysis were chosen so as to obtain a conversion level in the range of the conversions expected in the experiments with catalysts EcatR and EcatL. Since the reconciliation of mass balances was the first objective in this work, the values of the different product masses in the repeatability analysis were assessed in mg units, results being shown in Table III. Note that the largest standard deviation (square root of the variance) corresponded to the mass of gasoline, which did not translate into the percentage deviation due to the fact that it is one of the hydrocarbon groups with largest yields. On the other hand, the smallest deviation corresponded to the mass of dry gas, but due to the small amount produced, it reflected into the largest percentage deviation. In general, the percentage deviations of all the products are small, and similar to those

Table III. Experimental errors obtained in the repeatability analysis.

	Mean value (mg)	Standard dev.	% Deviation
Feed	106.2	3.2	3.0
Gas products	90.5	3.8	4.2
Coke	8.6	0.4	4.7
Dry gas	1.6	0.1	6.3
LPG	15.6	0.8	5.1
Gasoline	35.6	1.8	5.0
LCO	14.6	0.7	4.8
Residue	23.1	1.0	4.3

reported for MAT reactors (Vergel-Hernandez, 2001). From data in Table III it is possible to estimate that the mean mass balance recovery is 93.7%, which can be considered as an appropriate value, particularly considering the magnitude of the mass of reactant. In general, the lighter the feed, the higher the mass balance recovery. In this case of a heavy feed, mass balances recoveries lower than 90% were rejected and the experiments were repeated.

Statistical Reconciliation of Mass Balances

Equation (1) shows the mass balance in each experiment in the CREC Riser Simulator reactor.

$$m_{Feed} = m_{Gasproducts} + m_{Coke}$$
$$m_{Gasproducts} = m_{Drygas} + m_{LPG} + m_{Gasoline} + m_{LCO} + m_{Residue}$$
(1)

In this equation m_{Feed} corresponds to the mass of VGO injected to the reactor, which is quantified by weight difference of the syringe. The mass of gas products, $m_{Gasproducts}$, is quantified from the chromatographic data with the use of an internal standard, and the mass of coke as already mentioned.

Without experimental errors, that is, ideally, the mass balance in matrix form should obey the condition:

$$E_R F_R^* = 0$$
(2)

where E_R is the index matrix in the mass balance equations (see Equation (3)), and F_R^* is the vector of variables (see Equation (4)).

$$E_R = \begin{bmatrix} -1 & 1 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 1 & 1 & 1 & 1 & 1 \end{bmatrix}$$
(3)

$$F_R^* = \begin{bmatrix} m_{Feed} \\ m_{Gasproducts} \\ m_{Coke} \\ m_{Drygas} \\ m_{LPG} \\ m_{Gasoline} \\ m_{LCO} \\ m_{VGO} \end{bmatrix}$$
(4)

As a consequence of the experimental errors, the values observed for the variables hardly obey the condition described in Equation (2). Then, it is necessary to adjust data to satisfy the mass balance equation. The reconciliation of the mass balances can be achieved by minimizing the sum of the squares of the differences between reconciliated estimated values (F_R') and experimental values (F_R^+), using the variance of the observations as a weighting factor (Narasimhan and Jordache, 2000). Following the notation by Vergel-Hernandez (2001), the problem is

$$\min [F_R' - F_R^+]^T S_R^{-1} [F_R' - F_R^+]$$
(5)

and the solution is

$$F_R' = [I - S_R E_R^T (E_R S_R E_R^T)^{-1} E_R] F_R^+$$
(6)

where S_R is the covariance matrix, which in this case has only diagonal elements, and I is the identity matrix. A new set of variances S of the reconciliated variables can be calculated from:

$$S = [I - S_R E_R^T (E_R S_R E_R^T)^{-1} E_R] S_R [I - S_R E_R^T (E_R S_R E_R^T)^{-1} E_R]^T$$
(7)

This new set of variances of the masses was used to calculate the standard deviation in each product yield. As it can be observed in Equation (8), the yield of each hydrocarbon group was calculated as the relationship between the mass of product i and the total mass of hydrocarbons. It is clear that the functional relationship between variables in Equation (8) is not linear, so a linearization procedure was followed in order to obtain the value of the variance of each product yield (Himmelblau, 1970), as shown in Equation (9).

$$Y_i = 100 \frac{m_i}{m_{Feed}}$$
(8)

$$Variance[Y_i] \cong \left(\frac{\partial Y_i}{\partial m_i}\right)^2 S_i + \left(\frac{\partial Y_i}{\partial m_{Feed}}\right)^2 S_{Feed}$$
(9)

Y_i and m_i are, respectively, the yield and the mass of the product i, m_{Feed} is the total mass of products, and S_i is the variance of the mass of the group i obtained from Equation (7). The variances obtained with Equation (9) were used to calculate the standard deviation of each product yield.

Fitting of Experimental Data

The use of functions that describe the relationship between product yields and conversion is common in laboratory catalyst evaluation. These functions are used to interpolate data in order to compare results, to verify the correct trend of experimental data, to detect outliers and, finally, to discriminate between sets of results (Vergel-Hernandez, 2001). In this work the focus was on the discrimination between two catalysts, so the yield curves for the various products were built by using OPE curves (Wallenstein and Alkemade, 1996) and second degree polynomials so as to compare

differences between these two approximations. The OPE functions used were

$$Y_{Gasoline,LCO} = a \cdot X + b \cdot X^2 \qquad (10)$$

$$Y_{Coke} = a \cdot X + \exp(b \cdot X) \qquad (11)$$

$$X = a(1 - \exp(b \cdot t)) \qquad (12)$$

where Y represents yields, a and b are constants in each of the cases, X is the conversion for Equations (10)–(12), and t is time for Equation (12). The values of a and b in the previous equations are unique for each catalyst and temperature.

Erroneous conclusions could be achieved if the error in the dependent variable is neglected, even considering that a decrease in the discrimination capacity was shown when it was taken into account (Cerqueira et al., 1999). Then, in order to avoid misinterpretations, the standard deviations obtained for each product yield after the reconciliation of the mass balances were used as weighting factor in fitting data, considering the errors in both the dependent and the independent variables. It is necessary at this point to consider that previous related works followed simpler approaches. For example, Vergel-Hernandez (2001) used the covariance matrix following only a reconciliation purpose, while in this work the use of that matrix was included in the fitting step after mass balance reconciliations. On the other hand, Cerqueira et al. (1999) took into account the error in both variables, but no reconciliation procedure was performed before fitting. Covariances were not taken into account in this work, although they could be used not only in fitting, but also in reconciliating experimental data (Narasimhan and Jordache, 2000). It has been also reported that covariances in data fitting in laboratory evaluation of FCC catalysts could affect the discrimination capacity; however, to take covariances into account the number of experiments for each catalyst and temperature should be increased significantly so as to obtain reliable information (Rawet et al., 2001).

Finally, the 68.3% and 95% confidence intervals for the models fitted were assessed to define differences between the two catalysts in relation to product yields under the same conditions, or for a given catalyst under different conditions.

Results and Discussion

Reconciliation of Mass Balances

An example of data before and after the reconciliation of the mass balances is shown in Table IV. These results show that although there are changes in the masses of the products after reconciliation, variations in yields are small. In general, slight increases in gasoline and coke yields were observed, while the largest decrease was found in the Feed stream. However, the most important result was the change on the standard deviations, which decreased in all the yields. These values of standard deviations are similar to those reported for MAT (Cerqueira et al., 1999, Vergel-Hernandez, 2001) and FFB reactors (Vieira et al., 2004).

Comparison of Ecatr at 510°C and 540°C

Previous to the comparison of the performances of the two catalysts, it is necessary to recognize the magnitude of the expected differences. In order to acquire knowledge about the magnitude in differences and their significance, experiments were performed with EcatR at 510°C and 540°C. An increase in the reaction temperature should cause changes in the product distribution (Jiménez-García et al., 2011; Sadeghbeigi, 2000); then, the comparison of the catalyst performances at these two temperatures should show statistical differences. The data obtained were fitted using two kinds of models: OPE functions and second grade polynomials.

Regardless of the model used to fit data, the statistical confidence bands help to recognize whether differences in the models exist or not. Cerqueira et al. (1999) used 95% confidence bands in order to discriminate between catalysts; however, some issues need to be considered before selecting a reasonable confidence interval. First, due to the limited number of runs made in routine catalyst screenings (typically five experiments per catalyst [Wallenstein and Alkemade, 1996; Wallenstein et al., 1999]), a model with the lowest number of parameters should be chosen in order to obtain better estimates. Second, from a statistical point of view,

Table IV. Example of mass balance before (raw data) and after reconciliation (EcatR, 510°C, 18 s).

	Raw			Reconciliated		
	Data (mg)	Yield (wt.%)	Yield Std. dev. (wt.%)	Data (mg)	Yield (wt.%)	Yield Std. dev. (wt.%)
Feed	104.3			101.6		
Gas products	93.8			94.8		
Coke	6.5	6.5	0.5	6.8	6.7	0.4
Dry gas	1.2	1.2	0.1	1.2	1.2	0.1
LPG	14.1	14.1	1.0	14.3	14.0	0.8
Gasoline	34.8	34.7	2.2	35.4	34.8	1.6
LCO	15.1	15.1	0.9	15.2	15.0	0.8
Residue	28.5	28.5	1.5	28.7	28.3	1.0
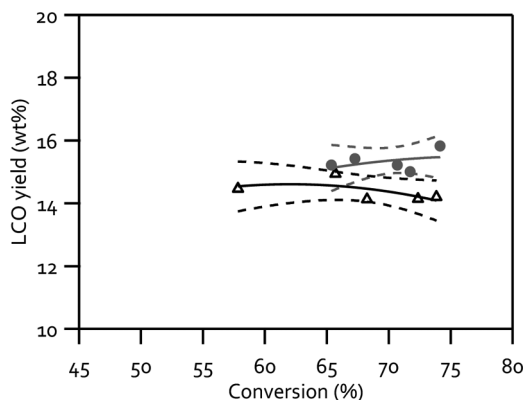
Fig. 2. LCO yield curves, catalyst EcatR. Symbols: (●) 510°C, (△) 540°C. Lines: solid, OPE curves; dashed, 68.3% confidence bands.
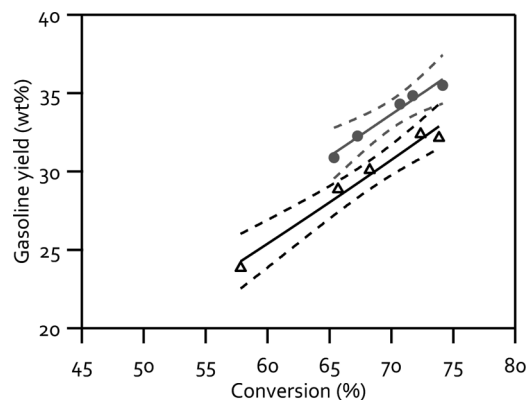
Fig. 4. Gasoline yield curves, catalyst EcatR. Symbols as in Figure 2. Lines: solid, OPE curves; dashed, 68.3% confidence bands.

the higher the number of experimental data, the narrower the confidence bands. Figures 2 and 3 show the yields of LCO obtained with EcatR at both temperatures, represented with OPE curves with different confidence bands.

It is known that if the confidence bands of the responses of the model at the diverse conditions (reaction temperatures in this case) do not overlap, they are statistically different. On the contrary, if the bands overlap, the test cannot discriminate between responses (Himmelblau, 1970). It is expected that an increase in reaction temperature causes lower LCO yields (Sadeghbeigi, 2000), a fact which is shown by the OPE functions. However, in order to discriminate the behavior of the catalyst at both temperatures, it is apparent that statistical differences can be seen at conversions higher than 70% in the case of 68.3% of confidence band. That is not the case with the 95% confidence band at any conversion level.

A similar analysis can be performed with gasoline, lower yields being expected at higher reaction temperatures (Sadeghbeigi, 2000). It is shown again in Figures 4 and 5 that choosing a high confidence level produces lack of discrimination between gasoline yields at different reaction temperatures. These two examples (LCO and gasoline yields) show

that the selection of a high value for the confidence interval in the responses of the model with a limited number of experiments could increase the risk of adopting erroneous conclusions. Besides that, even though the 68.3% confidence band could be considered as the one with lower significance, it has statistical meaning. For sounder comparisons, it is obvious that more experiments should be performed but, in the case of routine catalyst screening, the 68.3% confidence band option could be a good starting point and the basis for more detailed studies.

Since the number of parameters in the fitting function is another important issue, two different approaches with different number of parameters were selected: OPE functions (two parameters) and second-degree polynomials (three parameters). The corresponding results are shown for the case of coke yields in Figures 6 and 7, respectively, the 95% confidence band being plotted in both cases. Both models show that an increase in reaction temperature produces an increase in coke yield, as expected (King, 1992). In the case of OPE functions, it is clear that even the 95% confidence bands do not overlap in the whole range of conversions, in contrast with the same confidence level for the
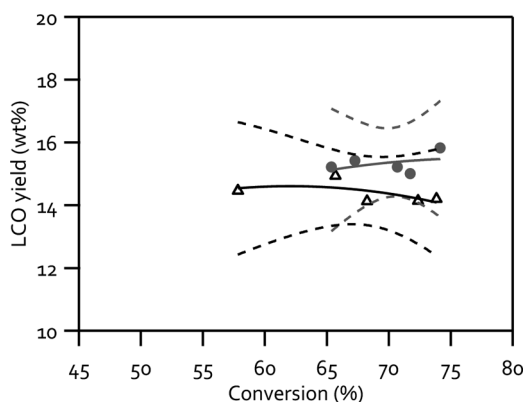
Fig. 3. LCO yield curves, catalyst EcatR. Symbols as in Figure 2. Lines: solid, OPE curves; dashed, 95% confidence bands.
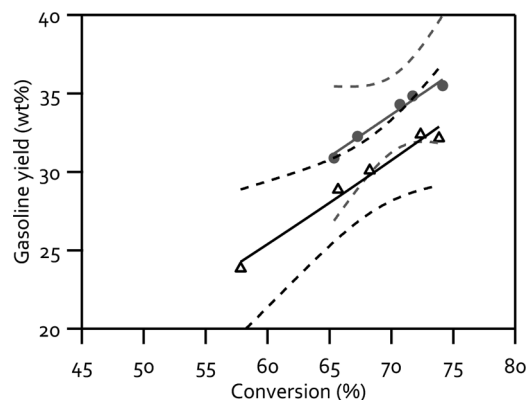
Fig. 5. Gasoline yield curves, catalyst EcatR. Symbols as in Figure 2. Lines: solid, OPE curves; dashed, 95% confidence bands.
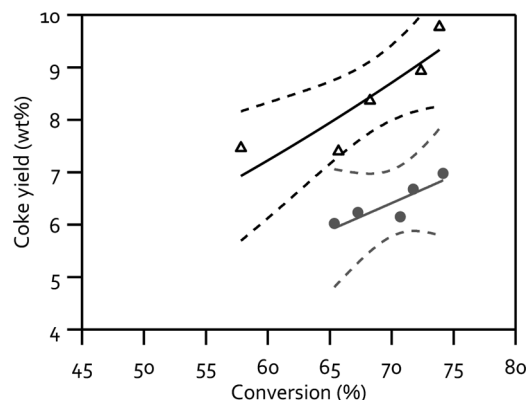
Fig. 6. Coke yield curves, catalyst EcatR. Symbols as in Figure 2. Lines: solid, OPE curves; dashed, 95% confidence bands.

second degree polynomials. Other drawback of polynomials is that, in occasions, the resulting curve shape does not represent the phenomena properly (Wallenstein and Alkemade, 1996); for example, the tendency shown by polynomials does not agree with theoretical or realistic knowledge. Examples of this feature can be seen in Figure 7, where the coke yield curves are flat at low conversion. Even though the previous analysis could be considered rather obvious, it was performed in light of polynomials being one of the most common tools for fitting and interpolating experimental product yield data, and drawbacks from their use could not be noticeable.

Comparison of Ecatl and Ecatr at 510°C

The comparison of the catalytic performance of the two catalysts was made at 510°C, a reaction temperature which can be considered representative of most of the commercial units (King, 1992). Figure 8 shows the conversion profiles of both catalysts. In this case, only the error in the dependent variable (conversion) was taken into account, due to the fact that errors in time measurements were not available. It can be seen that the confidence bands (68.3%) overlap at shorter times of reaction, while at longer times the difference
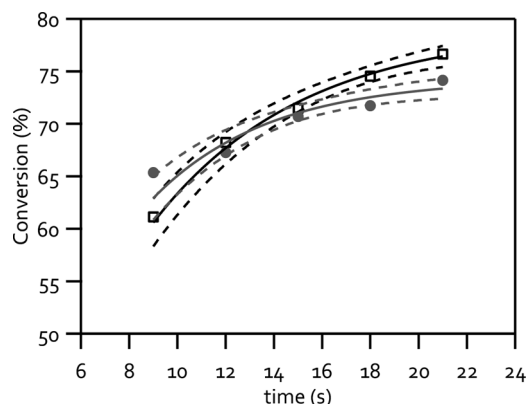

Fig. 8. Conversion as a function of reaction time. Reaction temperature 510°C. Symbols: (□) EcatL, (●) EcatR. Lines: solid, OPE curves; dashed, 68.3% confidence bands.

between both catalysts becomes statistically significant because the confidence intervals do not overlap. If higher confidence values are chosen, then the confidence bands turn wider, and no statistical difference would be found between catalysts.

The yield curves of gasoline, LCO, and coke for the two catalysts are shown in Figures 9–11. It is clear that there is no statistical difference in the production of gasoline at any conversion level. Nevertheless, catalyst EcatL has a higher production of coke and a lower production of LCO than catalyst EcatR, backed by statistical significance. The higher coke production of catalyst EcatL could be related to its higher content of nickel and vanadium, which are known as strong dehydrogenating agents (Tangstad et al., 2008). It is also apparent that catalyst EcatR shows a higher production of LCO than catalyst EcatL, which could be related to its lower activity, in turn one of the conventional ways used to maximize middle distillates cuts (Gilbert et al., 2007).

Similarities observed in the responses of the catalysts in relation to various issues are not surprising, since they are commercial, equilibrium catalysts, which were formulated to show as high as possible performances. Their different
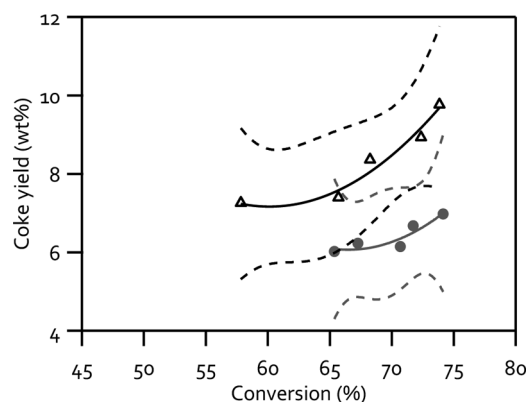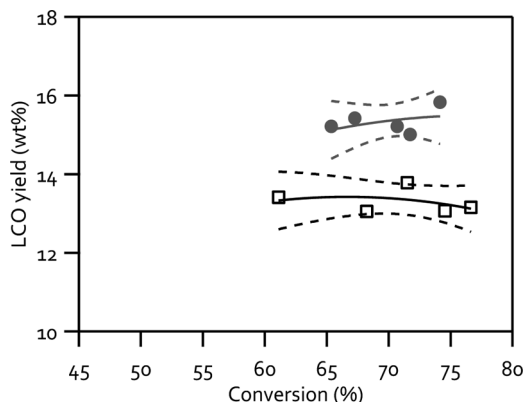

Fig. 7. Coke yield curves, catalyst EcatR. Symbols as in Figure 2. Lines: solid, second grade polynomials; dashed, 95% confidence bands.
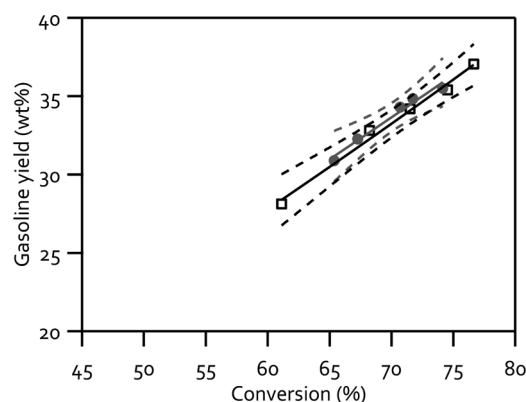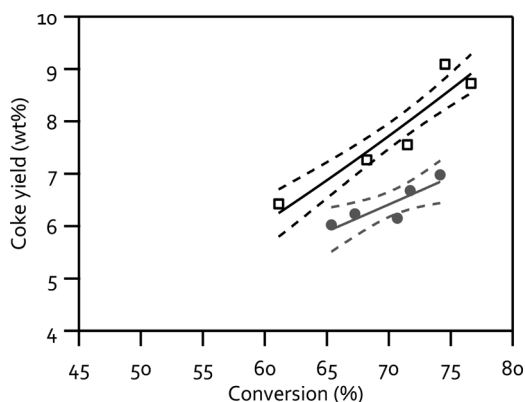

Fig. 9. Gasoline yield curves at 510°C. Symbols as in Figure 8. Lines: solid, OPE curves; dashed, 68.5% confidence bands.

Fig. 10. LCO yield curves at 510°C. Symbols as in Figure 8. Lines: solid, OPE curves; dashed, 68.5% confidence bands.

Fig. 11. Coke yield curves conversion at 510°C. Symbols as in Figure 8. Lines: solid, OPE curves; dashed, 68.5% confidence bands.

formulations, however, can be perceived in the lower coke yield in catalyst EcatR, which is a resid catalyst. This fact adds certainty to the method developed and differs from previous works that were performed using very different catalysts (Cerqueira et al., 1999).

Conclusions

The use of statistical techniques in the reconciliation of the mass balances improved the precision of the experimental data and showed to be a powerful tool applicable to routine catalyst screening, as exemplified with commercial FCC catalysts. The covariance matrix was successfully used to perform two actions: the reconciliation of mass balances and the fitting of the experimental data. This poses the repeatability analysis as an effective instrument to improve the reliability of the experimental data.

The deviations in the mass balances and products yields observed in the conversion of VGO over commercial equilibrium catalysts in a CREC Riser Simulator laboratory reactor under process conditions resulted similar to those reported in MAT and FFB reactors.

It was shown that a simple but powerful statistical analysis can improve catalyst evaluation or routine catalyst screening procedures, without the need for a considerable increase in the number of experiments. The use of high level confidence bands for the models describing the performance of FCC catalysts could cause a loss of discrimination capacity due to the small number of experiments executed. In that sense, addressing lower, but still statistically significant confidence bands, could be the starting point for sounder analysis, where usually the number of experimental points is larger.

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