

## INVERSE HEAT TRANSFER AND SPECIES PARAMETER ESTIMATION PROBLEM FOR MODELING FCC RISERS

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### ABSTRACT

The FCC (Fluidized Catalytic Cracking) is one of the most important processes in a petroleum refinery plant. It is responsible for the profitable conversion of the heavy gas oil into valuable products like LPG and gasoline. Due to the complexity of the chemical composition of the gas oil and the complex reaction mechanisms it is very difficult to describe the kinetics for each single compound of the mixture. Therefore, the modeling of such process can be simplified by lumping the chemical species with similar structure. This work proposes the utilization of the inverse parameter estimation method to fit a 6-lump kinetic model to a specific gas oil feedstock using experimental data obtained by direct measurements performed in a pilot FCC unit at Petrobrax Six [13]. The method consists of determining six fitting parameters of the mathematical model. The fitting parameters were obtained by solving a non-linear system of algebraic equations where the outputs of the mathematical model were compared to the experimental data. The procedure was repeated for 9 different experimental sets. The best fitting parameters were obtained by statistical means. The calculated constants were used to predict the output conditions of 18 data sets. The numerical results are in good qualitative agreement with the experimental data.

### NOMENCLATURE

$A_{gs}$  = specific surface area of the solid based on the unit reactor volume ( $m^2/m^3$ )

$C$  = lump concentration ( $kmol/m^3$ )  
 $C_p$  = specific heat ( $kJ/kg\ K$ )  
 $E$  = activation energy ( $kJ/kmol$ )  
 $h$  = gas-particle heat transfer coefficient ( $kJ/m^2\ s$ )  
 $H$  = riser height (m)  
 $K$  = reaction pre-exponential constant ( $m^3/kg_{cat}$  or  $m^6/kmol\ kg_{cat}\ s$ )  
 $M$  = molecular weight ( $kg/kmol$ )  
 $n$  = reaction order  
 $N$  = number of lumps  
 $p$  = pressure (Pa)  
 $r, z$  = cylindrical coordinates (m)  
 $R$  = universal gas constant ( $kJ/kmol\ K$ )  
 $t$  = tempo (s)  
 $T$  = temperature (K)  
 $v_r, v_z$  = fluid velocities (m/s)

### Greek symbols

$\Delta H$  = reaction enthalpy ( $kJ/kg$ )  
 $\Omega$  = reaction term ( $kmol/m^3$ )  
 $\epsilon$  = porosity  
 $\phi$  = catalyst deactivation function  
 $\mu$  = viscosity ( $N\ s/m^2$ )  
 $\rho$  = fluid density ( $kg/m^3$ )

### Subscripts

ad = adsorption  
c = coke  
cat = catalyst  
gas = gas-phase  
i = lump  
reac = reaction  
st = steam  
vgo = gas oil

## INTRODUCTION

The catalytic cracking of heavy gas oil has been the subject of study of a large number of researchers during the last three decades. It is responsible for the profitable conversion of the heavy gas oil, the bottom output of petroleum distillation, into much more profitable products like LPG and gasoline.

The cracking reactions responsible for the conversion of heavy petroleum fractions into lower molecular-weight products take place in a riser reactor, where liquid, gas and solid flow together. Many works in the literature treat the problem in complex details [1-3], however, other authors could successfully describe the riser reactor with a one-dimensional mass, energy and chemical species balances [4-7]. These simple models have the advantage that they are much easier to be solved.

The kinetic modeling of the catalytic cracking reactions is essential for the mathematical model. It is responsible for the determination of the gas oil conversion and products rates of formation along the riser reactor. Due to the complexity of the chemical composition of the gas oil and the complex reaction mechanisms involved, it is very difficult to describe the kinetics for each single compound within the mixture. Therefore, the modeling of such a complex system can be simplified by lumping the large number of chemical compounds into a small set of pseudo components. However, the weakness of lumping models is that the kinetic parameters rely on the feedstock properties [8].

There are many kinetic models available in the literature. The first model for the catalytic cracking was the 3-lumps model (gas oil, products and coke) [9]. Blasetti and Lasa [5], presented a 4-lump model, where the coke and the light gases are treated as separate lumps. A 5-lump model was introduced by Juaréz [8]. More detailed models, normally with more than 10 lumps are also available. They have the advantages that all the most important FCC products can be predicted separately and the kinetic constants could be used for various feedstocks. The disadvantage of these methods is the need of a large number of kinetic constants. Examples of such methods are the 10-lumps model of Jacob *et al* [10], the 12-lumps of Cerqueira *et al* [11] and the 19-lumps presented by Pitault *et al*. [12].

The purpose of the present work is to use the inverse parameter estimation method to fit a

general kinetic model for a specific gas oil feedstock. The experimental data were obtained in a pilot FCC unit [13]. The best set of parameters can be used to simulate other operational conditions of the FCC unit. Therefore, the number of experimental runs necessary to optimize the operational conditions can be reduced. The method consists of including, for each known output (mass concentrations and reaction temperature) 6 fitting constants multiplying selected kinetic and other physical parameters of the mathematical model. The fitting parameters were obtained by solving a non-linear system of algebraic equations where the outputs of the mathematical model were compared to the experimental data. The procedure was repeated for 9 different experimental conditions and the best fitting constants were obtained using a simple statistical approach. The mathematical model for the gas oil cracking process inside the riser is a bi-dimensional fluid flow field, combined with a 6 lumps kinetic model and two energy balance equations. The model with the fitted constants was validated with 18 sets experimental conditions.

## PROBLEM DESCRIPTION

A general sketch of the problem is shown in Fig. 1. The geometry and the input of the catalyst, steam and gas oil at the bottom of the riser and the output of the lumps mass concentrations at the top are schematically represented. In Fig. 1,  $H$  is the length of the riser in the flow direction and  $R$  the riser's radius.

The input variables for the model are the mass flow and temperatures of the catalyst, steam and gas oil. These variables determine the operational conditions of the unit. Table 1 shows the operating conditions and the physical properties of the input variables used for the 9 adjusting simulations.

In an industrial riser, the catalyst and the lift steam are injected at the bottom of the riser; while the gas oil and atomization steam enter the riser through injection nozzles in a higher radial section. Here, it is assumed that all the matter (particulate, gas oil and steam) is introduced at the bottom of the riser. This is a good approximation considering the geometry of the riser used, 0.05m of internal diameter and 18m high.

Table 1. Riser characteristics and operating conditions

<b>Geometry</b>	
Length (m)	10, 14 and 18
Diameter (m)	0.0508
<b>Feedstock</b>	
Gas oil mass flux (kg/h)	170
Water vapor mass flux (kg/h)	13
Catalyst oil ratio	6.9 – 9.4
<b>Physical parameters</b>	
Catalyst density (kg/m <sup>3</sup> )	1400
Catalyst specific heat (kJ/kg K)	1.09
Catalyst input temperature (°C)	680 – 720
Gas oil (vapor) density (kg/m <sup>3</sup> )	10
Gas oil specific heat (kJ/kg K)	2.5
Gas oil input temperature (°C)	220
Steam (vapor) density (kg/m <sup>3</sup> )	0.5
Steam specific heat (kJ/kg K)	2.0
Steam input temperature (°C)	220

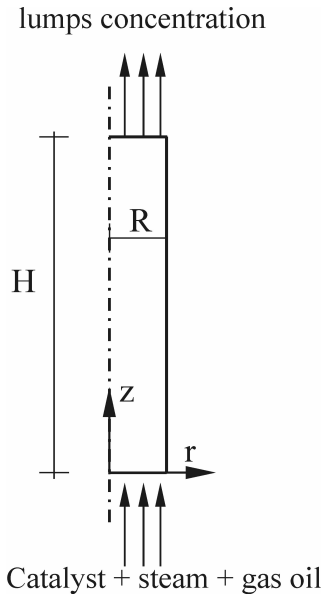


Fig. 1 – Problem sketch

## MATHEMATICAL MODEL

Although the system consists of a multiphase problem, it is modeled as a well-mixed single phase. The flow is assumed to be bi-dimensional, and incompressible, with constant physical properties. The mass and momentum conservation equations for a Newtonian fluid are given by

$$\frac{\partial v_r}{\partial r} + \frac{v_r}{r} + \frac{\partial v_z}{\partial z} = 0 \quad (1)$$

$$\rho \left( \frac{\partial v_r}{\partial t} + v_r \frac{\partial v_r}{\partial r} + v_z \frac{\partial v_r}{\partial z} \right) = -\frac{\partial p}{\partial r} + \mu \left( \frac{\partial^2 v_r}{\partial r^2} + \frac{1}{r} \frac{\partial v_r}{\partial r} - \frac{v_r}{r^2} + \frac{\partial^2 v_r}{\partial z^2} \right) \quad (2)$$

$$\rho \left( \frac{\partial v_z}{\partial t} + v_r \frac{\partial v_z}{\partial r} + v_z \frac{\partial v_z}{\partial z} \right) = -\frac{\partial p}{\partial z} + \mu \left( \frac{\partial^2 v_z}{\partial r^2} + \frac{1}{r} \frac{\partial v_z}{\partial r} + \frac{\partial^2 v_z}{\partial z^2} \right) \quad (3)$$

where,  $r$  and  $z$  are the cylindrical coordinates, m;  $p$  the pressure, Pa;  $\rho$  the fluid density, kg/m<sup>3</sup>;  $v_r$  and  $v_z$  the fluid velocities, m/s;  $t$  the time, s; and  $\mu$  the viscosity, N. s/m<sup>2</sup>.

For the catalytic cracking reaction simulation, a 6 lump kinetic model [13] was adopted (Fig. 2).

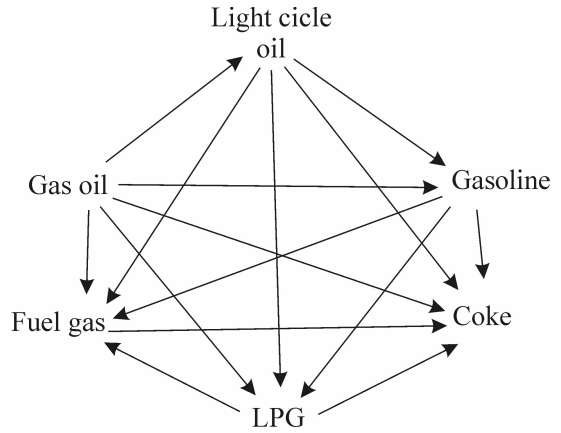


Fig. 2 – Lumped kinetic scheme

Even though the kinetic model is built of only 6 lumps, it is still possible to predict the key FCC products separately. Another important thing to be noticed is that adsorption is also included in the kinetic model.

The proposed set of species equations are as follows:

$$\frac{\partial C_i}{\partial t} + v_r \frac{\partial C_i}{\partial r} + v_z \frac{\partial C_i}{\partial z} = \Omega_i \quad (4)$$

$$\Omega_i = \left[ \sum_{j=1}^{i-1} M_j K'_{j,i} (C_j^*)^{n_{j,i}} - \sum_{j=i+1}^N M_i K'_{i,j} (C_i^*)^{n_{i,j}} \right] \times \phi (1 - \varepsilon) \frac{\rho_{cat}}{M_i} \quad (5)$$

$$C_i^* = \frac{1-\varepsilon}{\varepsilon} \rho_{cat} K'_{ad,i} C_i \quad (6)$$

$$K'_{i,j} = K_{i,j} e^{\left(\frac{-E_{i,j}}{RT_{cat}}\right)} \quad (7)$$

$$K'_{ad,i} = K_{ad,i} e^{\left(\frac{-E_{ad,i}}{RT_{cat}}\right)} \quad (8)$$

$$\phi = e^{(-406.4C_c)} \quad (9)$$

$$C_c = \frac{M_{coke} C_{coke}}{C_{cat}^{in}} \quad (10)$$

where,  $C_i$  – lump concentration, kmol/m<sup>3</sup>;  $\Omega_i$  – reaction term of lump  $i$ , kmol/m<sup>3</sup> s;  $C_c$  – coke concentration, kg<sub>coke</sub>/kg<sub>cat</sub>;  $E$  – activation energy, kJ/kmol;  $K$  – reaction pre-exponential constant, m<sup>3</sup>/kg<sub>cat</sub> s or m<sup>6</sup>/kmol kg<sub>cat</sub> s;  $M$  – molecular weight, kg/kmol;  $n$  – reaction order;  $N$  – number of lumps;  $R$  – universal gas constant kJ/kmol K;  $T$  – temperature, K;  $\varepsilon$  – porosity and  $\phi$  – catalyst deactivation function. The subscripts “ad” and “cat” represent adsorption and catalyst, respectively. The superscript “in” means input.

Finally, to complete the formulation, two additional equations are necessary, the catalyst and the gas energy balance equations. Even though a one-phase model was presented in the fluid flow formulation, two energy equations are necessary to characterize a temperature gradient between gas and solid. In the reaction term (Eq. (5)), the catalyst temperature is used to calculate the reaction kinetics constants, while for the heat exchange between the particulate and gaseous phases a second energy equation is necessary. The two energy equations are written as follows

$$M_{cat} C_{cat} Cp_{cat} \left( \frac{\partial T_{cat}}{\partial t} + v_r \frac{\partial T_{cat}}{\partial r} + v_z \frac{\partial T_{cat}}{\partial z} \right) = \left[ (-\Delta H) \Omega_{vgo} M_{vgo} + (\Delta H_{coke} \Omega_{coke} M_{coke}) \right] + hA_{gs} (T_{cat} - T_{gas}) \quad (11)$$

$$\left( \sum_{j=1}^N M_j C_j Cp_j + \rho_{st} Cp_{st} \right) \left( \frac{\partial T_{gas}}{\partial t} + v_r \frac{\partial T_{gas}}{\partial r} + v_z \frac{\partial T_{gas}}{\partial z} \right) = -hA_{gs} (T_{cat} - T_{gas}) \quad (12)$$

where, the not yet defined variables are:  $Cp$  – specific heat at constant pressure, kJ/kg K;  $\Delta H$  – reaction enthalpy, kJ/kg;  $h$  – gas-particulate heat transfer coefficient, kJ/m<sup>2</sup> s K;  $A_{gs}$  – specific surface area of the solid based on the unit reactor

volume, m<sup>2</sup>/m<sup>3</sup>. The subscripts “cat”, “gas”, “st” and “vgo” indicate catalyst-phase, gas-phase, steam and gas oil, respectively.

## INVERSE PROBLEM FORMULATION

The original 6-lump kinetic model shown in Fig. 1, can capture the major conversion characteristics of the gas oil inside the riser reactor. Therefore, if precise conversion profiles and operational conditions are sought, it is necessary to fit the kinetic model for each specific gas oil feedstock. This can be done with a number of experimental runs in a FCC pilot unit with low consumption of resources and time. For these reasons, a computational program, capable to estimate optimal operational conditions and products formation is a useful tool for the optimization of the large FCC industrial units.

The methodology used in this work to fit a generic kinetic model to a determinate type of gas oil feedstock is based on the inverse parameter estimation method. First, it is necessary to define some additional variables. Let  $f(\bar{q}, \bar{u})$  be a function that represents the mathematical model outputs,  $\bar{q}$  the vector of the unknown fitting constants and  $\bar{u}$  all the other variables of the mathematical model. With these two definitions it is possible to write a non-linear system of equations, implicitly as

$$\bar{f}(\bar{q}, \bar{u}) = \bar{b} \quad (13)$$

where  $\bar{b}$  is the vector with the known experimental output conditions at the top of the riser, and  $\bar{f}(\bar{q}, \bar{u})$  a vector of functions  $f(\bar{q}, \bar{u})$ , where  $\bar{q} = \{q_i\}$  are the unknowns.

The solution of Eq. (13) will be a vector whose components are the specific fitting constants ( $\bar{q}$ ) for a selected known experimental vector of output conditions ( $\bar{b}$ ). Solving Eq. (13) for  $n$  different experimental conditions it was possible to determine  $n$  different adjusting constants vectors ( $\bar{q}$ ), each one specific for an experimental operational condition. Next, the general vector of fitting constants  $\bar{q}_{ave}$  was obtained by taking the average of the  $n$  solutions, as follows:

$$\bar{q}_{ave} = \frac{1}{n} \sum_{i=1}^n \bar{q}_i \quad (14)$$

The number and location of the fitting constants inside the mathematical model will depend on: the number of known experimental output conditions, and the mathematical model itself.

The experimental data available were the 6 lumps mass fractions at the riser output and the reaction temperature. Thus, it would be possible to formulate the inverse problem solution with a 7 elements vector of fitting constants. In fact, only 5 lumps mass fractions are needed, since the sixth lump mass fraction results from mass conservation. Therefore, the system of equations was set for 6 fitting constants. Five of these constants were assigned to multiply the pre-exponential constants of the gas oil reactions (second order reactions) and a sixth constant was assigned to multiply the gas oil (vgo) enthalpy reaction term. Therefore, for the inverse problem solution Eqs. (7) and (11) were rewritten, respectively, as follows:

$$K'_{i,j} = q_j K_{i,j} e^{\left(\frac{-E_{i,j}}{RT_{cat}}\right)} \text{ for } i = 1 \quad (15)$$

and

$$M_{cat} C_{cat} C_p \left( \frac{\partial T_{cat}}{\partial t} + v_r \frac{\partial T_{cat}}{\partial r} + v_z \frac{\partial T_{cat}}{\partial z} \right) = \left[ (-q_6 \Delta H) \Omega_{vgo} M_{vgo} + (\Delta H_{coke} \Omega_{coke} M_{coke}) \right] + hA_{gs} (T_{cat} - T_{gas}) \quad (16)$$

## RESULTS

From the available experimental data set, with 27 different operating conditions, 9 were used to determine the adjusting constant vector ( $\bar{q}_{ave}$ ), by solving the system of equations defined by Eq. (13) nine times. The solution was obtained numerically by a quasi-Newton method, where the Jacobean was approximated with numerical derivatives and Eqs. (1)-(12) were solved with an upwind finite-differences scheme, in each Newton iteration. The other 18 known experimental operating conditions were used to validate the adjusted model.

The general operating conditions for the 9 fitting runs is summarized in Table 1. For all the adjusting runs, the reaction temperature was set to 550 °C.

The resulting average adjusting constants vector found in the process is

$$\bar{q}_{ave}^T = [7.98 \ 16.83 \ 42.42 \ 20.35 \ 16.19 \ 1.4] \quad (17)$$

Table 2 shows the sets of adjusting constants obtained by solving the inverse problem for each of the 9 selected experimental runs as described previously in the text. Equation (17) shows the average vector  $\bar{q}_{ave}$  computed with Eq. (14).

Running again the 9 cases presented in Table 2, and using the  $\bar{q}_{ave}$  vector as the generalized adjusting constants, it was possible to visualize the capability of the adjusted model to predict the behavior of the output variables (6-lumps mass concentration). The influence of the height of the riser on the products formation is shown in Fig. 3.

Table 2. Sets of calculated adjusting constants for the 9 selected experimental runs

run	CO*	T <sub>cat</sub>	$\bar{q}^T$
R1	9.1	680	[6.97 13.59 31.79 12.63 13.95 1.17]
R2	9.4	680	[6.01 13.24 36.29 14.16 13.75 1.28]
R3	8.6	680	[10.09 23.13 58.82 25.36 23.73 1.15]
R4	8.5	700	[8.42 16.47 39.12 16.83 16.04 1.38]
R5	8.7	700	[7.11 14.54 41.97 19.32 14.22 1.47]
R6	8.6	700	[8.44 19.97 48.78 25.01 18.28 1.48]
R7	7.9	720	[8.49 16.14 36.23 18.34 14.18 1.51]
R8	8.4	720	[7.48 15.08 43.00 22.17 14.77 1.72]
R9	8.6	720	[8.69 20.33 45.80 29.29 16.79 1.84]

\*catalyst to gas oil ratio

The influence of the input temperature of the catalyst in the product formation is shown in Fig. 4. Again the experimental and numerical results are in good agreement.

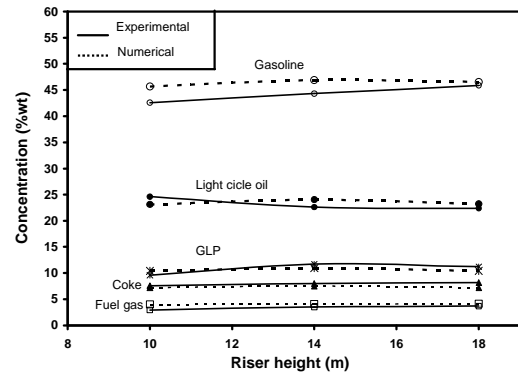


Fig. 3 – Lumps mass concentrations as functions of the riser's height ( $T_{reac} = 550$  °C and  $T_{cat} = 680$  °C)

After this initial procedure, the adjusted model was used to predict other 18 operating conditions (Table 3). Good agreement (Fig. 5 to Fig. 8) was obtained with the experimental data available, assuring the capability of the method to predict

the behavior of the unit for a large number of operational conditions, using for this, only a few numbers of runs to set the fitting constants of the model.

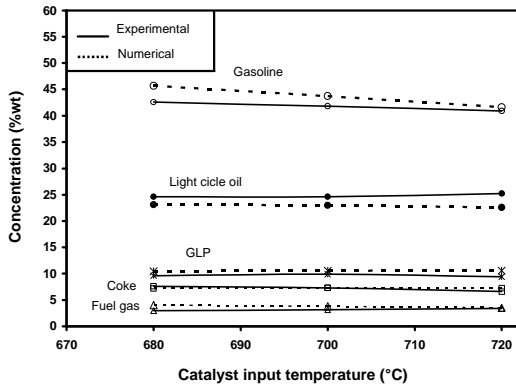


Fig. 4 – Lumps mass concentrations as functions of the catalyst input temperature ( $H = 10$  m and  $T_{\text{reac}} = 550^\circ\text{C}$ )

Table 3. Specific operational condition for the 18 validating runs

run	C/O*	$T_{\text{cat}}$ (°C)	$T_{\text{reac}}$ (°C)
R10	8.5	680	540
R11	8.9	680	540
R12	8.9	680	540
R13	8.2	700	540
R14	8.2	700	540
R15	8.1	700	540
R17	7.4	720	540
R18	7.6	720	540
R19	7.7	720	540
R20	8.0	680	530
R21	8.2	680	530
R22	8.5	680	530
R23	8.2	700	530
R24	7.7	700	530
R25	7.6	700	530
R26	7.2	720	530
R27	7.0	720	530
R28	6.9	720	530

\*catalyst to gas oil ratio

The mass concentration of each lump for the operating conditions of a reaction temperature of  $540^\circ\text{C}$  and input catalyst temperature of  $680^\circ\text{C}$ , as a function of the height of the riser is shown in Fig. 5. It can be seen in Fig. 5, a good agreement between the experimental and the numerical solutions was obtained.

The influence of the catalyst input temperature on concentrations for the runs with the reaction temperature of  $530^\circ\text{C}$  is shown, both for experimental and numerical solutions, in Fig. 6.

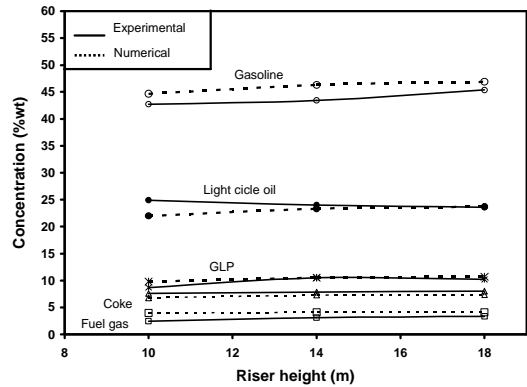


Fig. 5 – Lumps mass concentrations as functions of the riser's height ( $T_{\text{reac}} = 540^\circ\text{C}$  and  $T_{\text{cat}} = 680^\circ\text{C}$ )

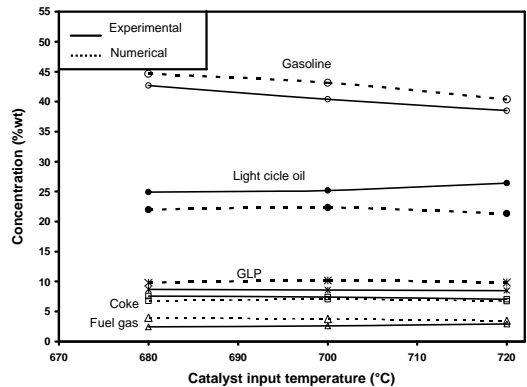


Fig. 6 – Lumps mass concentrations as functions of the catalyst input temperature ( $H = 10$  m and  $T_{\text{reac}} = 540^\circ\text{C}$ )

The same investigation that was performed in Fig. 5 and Fig. 6 was repeated in Fig. 7 and Fig. 8 for the cases where the reaction temperature was set to  $530^\circ\text{C}$ . Considering that all the fitting constants were obtained for the case where the reaction temperature was set to  $550^\circ\text{C}$ , it was shown that good agreement was obtained among all experimental data and the calculated results.

## CONCLUSIONS

The numerical results are in good quantitative and qualitative agreement with the experimental data. As a consequence, the mathematical model

is considered validated for future utilization in FCC riser design and optimization.

The methodology developed in this work is an alternative to fit a simple kinetic model to a specific feedstock with a small number of data sets. As a result, many other operating conditions can be simulated with the model with an important reduction of costs on the search for the optimal condition.

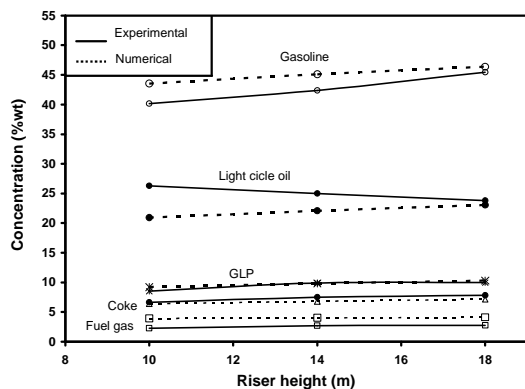


Fig. 7 – Lumps mass concentrations as functions of the riser's height ( $T_{\text{reac}} = 530\text{ }^{\circ}\text{C}$  and  $T_{\text{cat}} = 680\text{ }^{\circ}\text{C}$ )

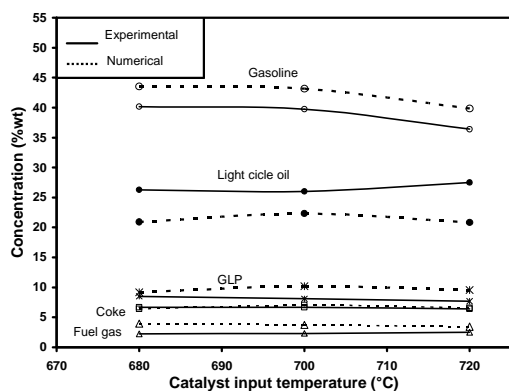


Fig. 8 – Lumps mass concentrations as functions of the catalyst input temperature ( $H = 10\text{ m}$  and  $T_{\text{reac}} = 530\text{ }^{\circ}\text{C}$ )

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