

Diffusion and Reactivity of Gas Oil in FCC Catalysts

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Abstract

This study considers the effects of diffusion and intrinsic catalytic reactivity for the cracking of gas oil on FCC catalysts. A four-lump kinetic model, initially developed in a novel CREC Simulator, is employed to estimate the unconverted gas oil, the gasoline, the light gases and the coke fractions. The model incorporates a modified Thiele modulus, based on zeolite crystal properties, and an effectiveness factor. The calculated effectiveness factor is found to increase with the gas oil conversion and to decrease with the intrinsic rate constant and the zeolite crystal size. The proposed model predicts that crystal size changes in the 0.13 to 1.3- μm range affect both primary and secondary cracking reactions and the yields of gasoline, coke and light gas yields.

Key words: FCC, cracking catalysts, diffusion, reaction, zeolite size

Introduction

Even if the FCC process can be considered as a mature technology there is still need for technical improvements. In fact, modifications, either in the process or in the catalyst, can lead to yield gains of significant economic importance.

Y zeolites are the major components of the commercial FCC catalysts. The 60- μm commercial FCC catalyst pellets are manufactured with 1-1.5- μm Y-zeolite crystals dispersed in an amorphous silica-alumina matrix (Venuto and Habib,1979). These zeolites have openings of 7.4 Å allowing penetration inside the 12 Å super-cages of molecules smaller than 10.2 Å (Karger and Ruthven,1992).

Gas oil molecules evolve in the catalyst matrix, reaching the external surface of the zeolite crystals. These molecules diffuse through the zeolite pore structure until they reach an active site and the cracking event takes place. Products diffuse first towards the outer crystal zeolite surface, subsequently throughout the matrix and finally they are transported in the gas stream (Maselli and Peters,1984). Thus, in addition to the reaction event, catalytic cracking involves diffusion of hydrocarbons throughout the matrix and the crystal zeolite structure. However, and given that diffusivities in the 20-250 Å pore matrix are much greater than in the zeolite, gas oil cracking appears to be strongly influenced by mass transport processes inside the zeolite crystals (Maselli and Peters,1984).

Although Y-zeolites show better activity, selectivity and stability than the previous used amorphous silica alumina catalysts, these catalysts can be affected by diffusional limitations. In fact, diffusion through the zeolite crystals can control the overall rate of reaction. Even more this problem may become particularly acute with very active zeolites, with these zeolites displaying severe diffusional limitations at high reaction rates (Shichi et al,1998).

Over the last decade, processing heavy oil in FCC units has become more prevalent due to the declining availability and as a result higher prices of lighter crudes. These trends have made residue upgrading with FCC economically more attractive. However, cracking heavier feedstocks, containing bulky molecules, offers additional challenges in terms of molecule transport limitations inside the zeolite structure (Nace,1970).

Diffusion in catalysts belongs in many cases to the Knudsen regime. However, diffusion in zeolites falls more in a so-called "configurational regime" since the size of the hydrocarbon molecule is nearly the size of the zeolite inner channels (Karger and Ruthven,1992; Gates et al,1979). As a result, diffusion of the hydrocarbon molecules is governed by an almost continuous interaction between the zeolite crystal and the diffusing molecules (Karger and Ruthven,1992; Gates et al,1979) with molecules experiencing a restricted accessibility to the catalyst active sites. In addition, there may be compounded effects with larger hydrocarbon molecules hindering the diffusion of

smaller molecules. As a result, lighter product molecules may be trapped or delayed in a zeolite pore network already filled with sorbed heavier molecules (Gates et al, 1979).

Diffusional transport limitations of gas oil molecules and its effects on catalytic cracking were reported by Nace (1970). When a REHX catalyst was used for cracking, the rate constants increased with molecule size up to a maximum value. Then, the rate constants decreased, for three and four ring reactant molecules, quite drastically. This fact was a confirmation that there are diffusional constraints in the intra-crystalline zeolite pore structure with the diffusivity becoming more limiting with increasing molecular size. On the other hand, Maselli and Peters (1984) reported that small size Y-zeolite crystals were both more active and produced more liquid products than the larger crystals. Rajagopalan et al (1986) cracked gas oil using small and large Y-zeolite crystals. These authors concluded that small size zeolites produce more liquid products, less coke and light gases than the larger zeolites. Gianetto et al (1994) observed that the small Y-zeolite crystals yield, while compared to the larger zeolite crystals, more olefins and iso-paraffins and less aromatics and coke.

Haag et al (1982) estimated the effectiveness factor (η) for the cracking of different model compounds using different ZSM-5 crystal sizes. For the small ZSM-5 crystals, it was found that these model compounds display consistently an effectiveness factor close to 1. However, the effectiveness factor was reduced to 0.03-0.5 while cracking large (branched) molecules and using larger size ZSM-5 crystals. Moreover, Kennedy et al (1991) studied the effect of different ZSM-5 crystal sizes and concluded

that the lost in activity with the larger crystals was due to diffusivity constrains. On the other hand, deactivation was also invoked as a main reason for loses of catalytic activity while employing small size zeolite crystals. Bonetto et al (1992) used β -zeolite with different crystal sizes for the cracking of gas oil. These authors reported that an average crystal size of 0.4 μm provides altogether a good compromise between stability, activity and selectivity.

Al-Khattaf and de Lasa (1999) have recently estimated the effective gas oil diffusivity in Y-zeolites. The effectiveness factor for gas oil cracking was calculated for 1 μm and 0.1 μm zeolite crystal sizes. It was demonstrated that while diffusional constrains have a major impact on primary cracking reactions, secondary reactions (e.g. hydrogen transfer, gasoline overcracking) involving smaller molecules remain essentially unaffected by changes in the zeolite crystal size. Consideration of these competing effects shows that diffusional constrains have an impact on gasoline composition.

While one of our previous studies (Al-Khattaf and de Lasa, 1999) has focused on diffusional effects and their impact on gasoline composition, additional modeling is needed to elucidate the influence of diffusional transport on various FCC product lumps: unconverted gas oil, gasoline, coke and light gases.

With this end, in the present study, both a model accounting for diffusional effects and data from the CREC Riser Simulator. The CREC Riser Simulator is a novel unit invented by de Lasa (1992) which overcomes the technical problems of the standard

micro-activity test (MAT), are considered. Additional details about the CREC Riser Simulator components and sequence of injection and sampling can be found in Kraemer and de Lasa (1988a).

Modeling Catalytic Cracking in FCC Catalysts

The effectiveness factor is a dimensionless quantity expressing the extent of diffusional constrains inside a catalyst. The effectiveness factor for a zeolite crystal (η_i) is defined as the ratio of the actual reaction rate to the reaction rate in the absence of the internal diffusional resistance:

$$\eta_i \cong \frac{\tanh(h_i')}{h_i'} \quad (1)$$

The effectiveness factor, η_i , requires the definition of a modified Thiele modulus, h_i' . This modified Thiele modulus, h_i' , depends on the zeolite size, the zeolite crystal geometry, the zeolite crystal apparent density, the reactant diffusivity, the reaction order and the intrinsic rate constant as follows (Smith,1981;Aris,1969):

$$h_i' = \frac{1}{a_{\text{ext}}} \sqrt{\frac{(n+1) k_{i0} \rho_c \varphi_{\text{int}} C_{i,0}^{n-1}}{2 D_{e,i}}} \quad (2)$$

with a_{ext} being the zeolite crystal external surface area ($a_{\text{ext}} = 6/L$), L the zeolite crystal average characteristic dimension, $C_{i,0}$ the bulk concentration, n the reaction order, $D_{e,i}$ the

effective diffusivity of the "i" species, ϕ_{int} the intrinsic catalyst decay function and k'_{i0} the intrinsic kinetic constant for "i" hydrocarbon species at time $t=0$.

Regarding eq(2) there is a number of parameters that have to be carefully selected:

- a) The effective gas oil diffusivity ($D_{e,go}$) at 525°C for steamed Y-zeolite estimated at 6.10^{-14} m²/sec (Karger and Ruthven,1992).
- b) The intrinsic catalyst decay function modeled as a function of the coke yield ($\phi_{int} = e^{-2\alpha X_c}$).
- c) The order of the reaction for catalytic cracking assumed as second order. Thus, the n-1 power in eq(2) can be set at 1.

Consequently given these various hypothesis the following modified Thiele modulus, h_{go}' can be considered for gas oil:

$$h_{go}' = \frac{1}{a_{ext}} \sqrt{\frac{3 k_o \rho_c e^{-2\alpha X_c} C_{go}}{2 D_{e,go}}} \quad (3)$$

An important result from eq(3) is that for catalytic cracking h_{go}' is not a constant parameter given it decreases with both the gas oil concentration or the equivalent with the progress of the catalytic reaction (gas oil conversion) and with coke concentration. Thus, h_{go}' displays a maximum value at the feeding conditions with a minimum value at riser reactor outlet.

Kinetic Modeling of Catalytic Cracking in the Riser Simulator

Catalytic cracking of gas oil involves the cracking of a wide range of hydrocarbon molecules into gasoline, coke and light gases lumps. Thus, a model can be advanced based on four lumps (Fig. 1) (Yen et al,1987). It is frequent to assign to the cracking of gas oil a second reaction order (Weekman,1968) while a first order is retained for the cracking of gasoline (over-cracking), and this given gasoline contains molecules with a narrower distribution of molecular weights than gas oil.

Regarding modeling of FCC in the CREC Riser Simulator the following assumptions can be adopted: a) mixing in this batch reactor is such that hydrocarbon concentration at any given reaction time is uniform, b) thermal cracking reactions for the gas oil conversions are considered negligible, c) isothermal operation can be assumed and this given typical temperature changes in the unit are 2°C (Kraemer,1991).

Thus, mass balances in the Riser Simulator for gas oil, gasoline and light gases (based on gas phase concentrations) and for coke (based on mass fractions) yield the following set of equations:

- For gas oil cracking:

$$-\frac{V}{W} \frac{dC_{go}}{dt} = \eta_1 k_0 \phi_{int} C_{go}^2 = \eta_1 (k_1 + k_{31} + k_{32}) \phi_{int} C_{go}^2 \quad (4)$$

- For gasoline formation:

$$\frac{V}{W} \frac{dC_g}{dt} = v_1 \eta_1 \phi_{int} k_1 C_{go}^2 - \eta_2 \phi_{int} C_g (k_{21} + k_{22}) \quad (5)$$

- For light gases formation:

$$\frac{V}{W} \frac{dC_{lg}}{dt} = v_2 \eta_1 k_{31} \phi_{int} C_{go}^2 + v_3 \eta_2 k_{21} \phi_{int} C_g \quad (6)$$

- For coke formation:

$$\frac{dX_c}{dt} = (v_4 \eta_1 k_{32} \phi_{int} C_{go}^2 + v_5 \eta_2 k_{22} \phi_{int} C_g) MW_c \frac{W}{m_{go}} \quad (7)$$

with $\eta_1 = \tanh(h_{go}')/h_{go}'$, $\phi_{int} = \exp(-2\alpha X_c)$ and

$$h_{go}' = \frac{1}{a_{ext}} \sqrt{\frac{3 k_0 \rho_c \phi_{int} C_{go}}{2 D_{e,go}}}$$

Note that two effectiveness factors are considered in eqs(4-7) as follows:

- η_1 for the primary reactions, case of gas oil cracking with η_1 assuming, for 1.3 μm crystals at 65% gas oil conversion, values smaller than 1 (e.g. $\eta_1=0.081$ and 0.153 for CAT-AG and CAT-AO respectively).
- η_2 for secondary reactions (over-cracking of gasoline) with η_2 remaining close to 1 (13).

Modeling catalytic cracking reactions involves given a set of kinetic constants ($k_0, k_1, k_{22}, k_{21}, k_{31}$ and k_{32}) and stoichiometric coefficients (v_1, v_2, v_3, v_4, v_5) the simultaneous numerical solution of eqs (4-7). These stoichiometric coefficients, as reported in the Notation list, can be calculated using the average molecular weight for various lumps (Table 1).

Results

THE THIELE MODULUS AND THE EFFECTIVENESS FACTOR

Numerical solution of the set of eqs (4-7) with the constants and under the conditions reported in Table 2 allows to establish the evolution of various lumps and to study the effect of zeolite crystal size.

Kinetic constants involved in the numerical solution of this set of equations were estimated by regression and using a number of experiments developed in the Riser Simulator (Kraemer,1991) as follows: a) using commercial CAT-AO and CAT-AG catalysts with average zeolite crystal size (L) of $1.3\mu\text{m}$ (Table 3), b) employing a commercial feedstock as reported in Table 4. This allowed to estimate $k_o = 316.5 \text{ m}^6/(\text{kmole.kgcrystal.s})$ and $\alpha = 68 \text{ Kg gas oil}/(\text{kg coke})$ for CAT-AO and $k_o = 552.1 \text{ m}^6/(\text{kmole.kgcrystal.s})$ and $\alpha = 40 \text{ kg gas oil}/(\text{kg coke})$ for CAT-AG. The observed difference on the intrinsic kinetic constants for CAT-AG and CAT-AO was assigned to the different unit cell sizes with CAT-AG displaying the larger unit cell size and correspondingly the larger intrinsic rate constant (Ino and Al-Khattaf,1996). As well,

differences in the α decay constant were assigned to the different coking tendency of the catalysts tested with catalyst CAT-AG showing faster activity decay than CAT-AO.

Fig. 2 reports the calculated effectiveness factor, η_1 , for gas oil cracking as function of the modified Thiele modulus (h_{go}'). Results reported correspond to CAT-AO catalyst, two zeolite sizes and several gas oil conversions. Two extreme cases in terms of zeolite crystal sizes are considered and the following can be concluded:

- a) The 0.13- μm zeolites gives a modified Thiele modulus below 1 and consequently an effectiveness factors close to 1,
- b) The 1.3- μm zeolite gives a Thiele modulus well above 1 and as a result effectiveness factors smaller than 1.
- c) For both, the 0.13 and 1.3- μm zeolites increases in the gas oil conversions led to a reduction of the Thiele modulus and consequently to higher η_1 values. Thus, one can view an FCC catalyst as one changing both the h_{go}' and η_1 parameters while the gas oil catalytic cracking reaction is progressing.

Figs. 3 and 4 report η_1 as a function of the catalyst contact time and the gas oil conversion for both CAT-AO and CAT-AG catalysts. As it can be appreciated, the effectiveness factor increases considerably with the extent of catalytic cracking. This finding is consistent with a second order reaction being affected by coke concentration through a catalyst decay function. As a result, both the Thiele modulus (eq(3)) and the η_1 , become functions of the gas oil concentration and of the coke concentration and are expected to considerably augment with hydrocarbon species contact time.

Moreover, Fig. 5 reports the changes of the η_1 effectiveness factor with L , the characteristic zeolite crystal dimension, for a typical gas oil conversion of 65%. It can be noticed that, for both catalysts, in one hand η_1 approaches the value of one for $L < 0.1\text{-}\mu\text{m}$ while becoming smaller than one for larger crystals. Moreover, given commercial FCC catalysts usually contain Y-zeolites with typically $1.3\text{-}\mu\text{m}$ average crystal size, $\eta_1 = 0.15$ and 0.081 values can be anticipated for both CAT-AO and CAT-AG respectively. As expected, the catalyst with the highest intrinsic constant $k_{go} = 552.1 \text{ m}^6/(\text{kmole.kgcrystal.s})$ for CAT-AG versus $k_{go} = 316.5 \text{ m}^6/(\text{kgmole.kgcrystal.s})$ for CAT-AO, yields the higher h' value (eq(3)) and leads to the lower η_A and all this points towards higher levels of diffusional constrains for the CAT-AG catalyst.

EFFECT OF THE CRYSTAL SIZE ON LUMP YIELDS

Fig. 6 reports the changes of gas oil conversion with reaction time and this for several zeolite crystal sizes. Manufacturing of FCC catalysts using zeolite of different sizes has been demonstrated (Al-Khattaf, 2001). It can be noticed that for reaction times of 3 seconds (CAT-AO) there is a significant effect of crystal size on gas oil conversion as follows:

a) For an L of $1.3 \mu\text{m}$ there is a 38.5% gas oil conversion, b) for an L of $0.4 \mu\text{m}$ there is a 60.8% conversion, c) for an L of $0.13\mu\text{m}$ there is a 74.0% conversion. Further reduction of crystal size barely improves gas oil conversion with the effectiveness factor being

already very close to unity. This effect of crystal size on gas oil conversion was found consistently for both CAT-AO and CAT-AG catalysts studied.

Fig 7 displays the changes of gasoline lump, an intermediate species in the cracking of gas oil. For example for CAT-AO, at 65% gas oil conversion a reduction of L from 1.3 to 0.13- μm gives a gasoline mass fraction increase from 31.8% to 38.7%. Similar results (35.3% to 40.8%) were found for the CAT-AG catalyst.

These differences in gasoline yields can be traced to the changes on the importance of the over-cracking reaction. In fact, it can be speculated that these differences in gasoline selectivity with changing zeolite crystal size, is the result of the net effect of competing reactions:

- a) gasoline formation reactions, primary reactions involving the cracking of large gas oil molecules. These reactions are severely affected by intra-crystalline diffusion and zeolite crystal size (e.g. $\eta_1 \ll 1$ for 1.3- μm crystals),
- b) gasoline over-cracking reactions which secondary involving smaller molecules hence not too affected by crystal size (η_2 about 1 for both smaller and larger zeolite crystals).

Thus, with sub-micron zeolites the gasoline formation reactions are increased while over-cracking reactions remain essentially unchanged. This leads overall, while reducing zeolite crystal size, to higher gasoline yields. Finally, it is important to mention that the results of the present study, showing that gasoline yield increases with the

reduction of L, agree well with data reported in the technical literature (Maselli and Peters,1984;Rajagopalan et al,1986;Cambolor et al,1989).

It is important to mention that these findings are in agreement with a recent experimental study (Al-Khattaf and de Lasa, 2000, 2001) where 1,3,5-tri-iso-propylbenzene (1,3,5-TIPB) was cracked using Y zeolite crystals of different sizes. It is shown that the fraction of formed cumene, an intermediate product of 1,3,5,-TIPB cracking, is increased with the smaller zeolite crystals while the fraction of benzene a final product of this reaction sequence is augmented with the larger crystals.

However, given that there are reports suggesting reduced thermal stability for small zeolite crystals (Maselli and Peters,1984; Rajagopalan et al,1986; Cambolor et al,1989) a compromise could be proposed between reduced diffusional constrains and adequate crystal stability. This can be achieved using zeolite crystals having a size close to 0.4- μm (Bonetto et al, 1992; Al-Khattaf and de Lasa, 2000, 2001). For 0.4- μm , gasoline yield gains at 65% gas oil conversion are, as predicted by eqs (4-7), for CAT-AO close to 6%. While these gains are lower than the ones achieved with 0.13- μm zeolites they are still valuable and could justify the use of zeolites of a closely selected size crystal.

There are also other interesting effects resulting of the reduced diffusional constrains. It can be expected that a decreased zeolite size reduces the relative importance of hydrogen transfer while compared to catalytic cracking (Al-Khattaf and de

Lasa, 1999; Cambor et al ,1989) and consequently diminishes the aromatic content in the gasoline product. This is particularly relevant if one wishes to produce a more environmentally friendly gasoline with a lower content of total aromatics and benzene.

Regarding light gases, it can be observed that the proposed model predicts a decrease of light gases with a reduction of zeolite crystal size (refer to Fig.8). Overall this result is again the net effect of a reduced relative importance of over-cracking reactions (secondary reactions) versus an increased influence of gas oil cracking. In this respect for CAT-AO light gases differences as high as 7.1% are obtained at 65% gas oil conversion while comparing the performance of submicron (0.13 - μm) and micron (1.3- μm) zeolites.

Finally, modeling calculations for CAT-AO predict, at 65% gas oil conversion, 2.19 wt% coke for 0.13- μm zeolites versus 2.42 wt% coke for 1.3- μm zeolites (Fig.9). These results, in agreement with previous literature data (Maselli and Peters,1984;Rajagopalan et al,1986), can be explained given coke is formed as a result secondary reactions mainly hydrogen transfer and condensation involving molecules (cracked products) of a size smaller than gas oil molecules. Thus, decreasing crystal size augments significantly η_1 leaving η_2 essentially unchanged. On this basis, it is expected that sub-micron zeolites can help to control coke yields and this can be of significance for cracking heavier feedstocks normally leading to the formation of increased amounts of coke and introducing, as a result, important constrains for the operation of the FCC regenerators.

In summary, it is demonstrated, in the present study, that reducing the zeolite crystal size decreases the diffusional path, increases the rate of gas oil cracking and reduces the tendency of the gasoline to over-crack. This phenomenon leads to higher gasoline yields and lower amounts of light gases and coke.

Conclusions

- a) A four-lump model is considered to describe the effects of diffusion on both activity and selectivity. This kinetic model allows to calculate the time needed to achieve a given gas oil conversion and the effects of changes of zeolite crystal sizes.
- b) A modified Thiele Modulus, which includes an intrinsic catalyst deactivation function, is used to describe the effectiveness factor for gas oil cracking in FCC catalysts. It is shown that decreasing crystal sizes reduces in one hand the modified Thiele Modulus and increases, on the other, the effectiveness factor η_1 . At $L < 0.1\text{-}\mu\text{m}$, η_1 approaches unity and hence it can be predicted that FCC catalysts formed with these small crystals do not show appreciable differences in terms of measured and intrinsic catalyst activity. Furthermore, for L being varied in the 0.13 to $1.3\text{-}\mu\text{m}$ range, η_1 augments with gas oil conversion, decreasing with the crystal size and with the intrinsic rate constant.
- c) The model proposed shows that a reduction in the crystal size (L) has an effect on gasoline, coke and light gas lumps with an appreciable increase in the gasoline fraction. Consistent with this there is a reduction in coke and light gases.

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Nomenclature

- a_{ext} specific external surface area of the zeolite crystal = $6/L$ (1/m).
- A refers to the gas oil lump (Fig. 2)
- B refers to the gasoline lump (Fig. 2)
- C refers to coke lump (Fig. 2)
- C_i gas phase concentration of the lump "I" (kmole/m^3).
- C_i^* dimensionless gas phase concentration (-).
- $C_{i,0}$ gas phase concentration in the bulk phase (kmole/m^3).
- D refers to light gases (Fig. 2)
- $D_{e,i}$ effective diffusivity for the "i" lump (m^2/s).
- h_i' modified Thiele modulus (-)
- k_0 intrinsic kinetic constant for gas oil cracking ($\text{m}^6/\text{kmole.kgcrystal.s}$).
- k_1 intrinsic kinetic constant for gasoline formation from gas oil ($\text{m}^6/\text{kmole.kcrystal.s}$).

- k_{21} intrinsic kinetic constant for gasoline over-cracking into light gases ($\text{m}^3/\text{kgcrystal.s}$).
- k_{22} intrinsic kinetic constant for gasoline overcracking into coke ($\text{m}^3/\text{kgcrystal.s}$).
- k_{31} intrinsic kinetic constant for light gases formation from gas oil ($\text{m}^6/\text{kmole.kgcrystal.s}$).
- k_{32} intrinsic kinetic constant for coke formation ($\text{m}^6/\text{kmole.kgcrystal.s}$).
- K_i adsorption constant for the “i” species ($\text{m}^3/\text{kgcrystal}$)
- L characteristic dimension of the crystal, average value from several measurements taken with random orientations (m).
- m_{go} mass of gas oil injected (g).
- MW_c molecular weight of coke (kg/kmole).
- n reaction order (-)
- r equivalent radius of the crystal (m).
- r_i rate of formation/consumption of the “i” species (kmole /kgcrystal. s)
- r^* dimensionless equivalent radius of the crystal(-).
- R equivalent radius of the crystal (m)
- V volume of the Riser Simulator (cm^3)
- W weight of zeolite crystals in the catalyst (kg.)
- X_c weight fraction (kg of coke /kg of gas oil)

Greek Symbols

- α catalyst activity decay parameter (kg gas oil/Kg coke).
- β $D_{e,go}/D_{e,g}$ (-)

- ε void fraction in a zeolite crystal (m^3 void/ m^3 crystal)
- v_1 Average molecular weight of gasoil/average molecular weight of gasoline=2.8 (-).
- v_2 Average molecular weight of gasoil/Average molecular weight of light gases=6.88 (-).
- v_3 Average molecular weight of gasoline/Average molecular weight of light gases=2.4 (-)
- v_4 Average molecular weight of gas oil/Average molecular weight of coke=0.415 (-).
- v_5 Average molecular weight of gasoline/Average Molecular weight of coke=0.143 (-).
- η_i effectiveness factor (-).
- η_1 effectiveness factor for gas oil cracking (-).
- η_2 effectiveness factor for gasoline over-cracking (-).
- φ_{int} intrinsic deactivation function (-).
- ρ_c zeolite apparent density = 825 ($\text{kgcrystal}/\text{m}^3$)

Subscripts

- c coke lump
- lg light gases lump
- g gasoline lump
- go gas oil lump

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Appendix

A balance of “i” chemical species in a differential thickness of crystal leads to the following partial differential equation:

$$\frac{D_{e,i}}{r^2} \frac{\delta}{\delta r} \left[r^2 \frac{\delta C_i}{\delta r} \right] = \rho_c [r_i] - [K_i \rho_c + \epsilon] \frac{\delta C_i}{\delta t} \quad (\text{A.1})$$

with r_i (kmol/kgcrystal.s) being the rate of consumption/formation of any of the species in the reacting system and ρ_c (kgcrystal/m³) the bulk density of the zeolite crystals in the catalyst .

Solving eq(A.1) numerically for gas oil species (“i”=gas oil) and 1.3micron crystals, it can be shown that after 2 seconds the $\delta C_i/\delta t$ term can be neglected and consequently the “cuasi-steady state” approximation for the crystal can be adopted (Al-Khattaf et al.,2001).

Consistent with this, for gasoline (i=g) the following is obtained:

$$\frac{D_{e,g}}{r^2} \frac{d}{dr} \left[r^2 \frac{dC_g}{dr} \right] = \rho_c [k_1 \phi_{int} C_{go}^2 - (k_{21} + k_{22}) \phi_{int} C_g] \quad (\text{A.2})$$

This equation can be expressed in a dimensional form using $r^* = r/R$, $C_{go}^* = C_{go}/C_{go,o}$ and $C_g^* = C_g/C_{go,o}$ with $C_{go,o}$ representing the gas oil concentration in the bulk gas phase:

$$\frac{1}{r^{*2}} \frac{d}{dr^*} \left[r^{*2} \frac{dC_g^*}{dr^*} \right] = \left[\frac{D_{e,go}}{D_{e,g}} \right] \left[\frac{R^2 \rho_c k_1 \phi_{int} C_{go,o}}{D_{e,go}} \right] C_{go}^{*2} - \left[\frac{R^2 \rho_c (k_{21} + k_{22}) \phi_{int}}{D_{e,g}} \right] C_g^* \quad (\text{A.3})$$

or

$$\frac{1}{r^{*2}} \frac{d}{dr^*} \left[r^{*2} \frac{dC_g^*}{dr^*} \right] = 6\beta h_{go}^2 C_{go}^{*2} - 9h_g^2 C_g^* \quad (\text{A.4})$$

with $\beta = D_{e,go}/D_{e,g}; a_{ext} = 6/L$

$$h'_{go} = \frac{1}{a_{ext}} \sqrt{\frac{3 k_1 \rho_c \phi_{int} C_{go,o}}{2 D_{e,go}}}; h'_g = \frac{1}{a_{ext}} \sqrt{\frac{(k_{21} + k_{22}) \phi_{int} \rho_c}{D_{e,g}}}$$

As a result, using h'_i , the modified Thiele modulus based on L (average characteristic dimension of the crystals) the dimensionless concentrations of gas oil and gasoline can be defined with the following set of equations:

- Gas oil Balance

$$\frac{1}{r^{*2}} \frac{d}{dr^*} \left[r^{*2} \frac{dC_{go}^*}{dr^*} \right] = 6 h'_{go}{}^2 C_{go}^{*2} \quad (A.5)$$

- Gasoline (intermediate species) Balance

$$\frac{1}{r^{*2}} \frac{d}{dr^*} \left[r^{*2} \frac{dC_g^*}{dr^*} \right] = 6 \beta h'_{go}{}^2 C_{go}^{*2} - 9 h'_g{}^2 C_g^* \quad (A.6)$$

This set of equations is affected by the following parameters and these parameters can be defined in a worst scenario case:

- $\beta = D_{e,go}/D_{e,g} = 6 \times 10^{-3}$
- $h'_{go} < 70, h'_{go}{}^2 < 4900, \text{ at } \phi_{int} = 1$
- $h'_g < 0.44, h'_g{}^2 < 0.1 \text{ at } \phi_{int} = 1$

Integration of the resulting concentration profile with the boundary conditions, at $r^* = 0, dC_{go}^*/dr^* = 0, dC_g^*/dr^* = 0$; at $r^* = 1, C_{go} = C_{go,o}, C_g = C_{g,o}$ leads to the definition of the effectiveness factors for both gas oil and gasoline conversions:

$$\eta_1 = \frac{1}{0} \frac{3 \int k_1 \rho_c C_{go}^2 r^{*2} dr^*}{k_1 \rho_c C_{go,o}^2} \quad (A.7)$$

$$\eta_2 = \frac{1}{3} \frac{\int_0^1 (k_{21} + k_{22}) \rho_c C_g r^{*2} dr^*}{(k_{21} + k_{22}) \rho_c C_{g,0}} \quad (\text{A.8})$$

Thus, the effectiveness factors are $\eta_1 < 0.015$ and $\eta_2 < 0.977$ respectively. As a result of these calculations it can be demonstrated that it is correct to hypothesize that η_2 is one, given that the lowest expected value for η_2 is 0.977.

Figures Captions

Fig.1. Schematic representation of the four lump model showing the different reaction steps included in the kinetic model. A= gas oil, B= gasoline, C= coke, D= light gases.

Fig.2. Change of the effectiveness factor with Thiele modulus for CAT-AO FCC catalyst. Gas oil conversion as follows: (a) 55%, (b) 65%, (c) 75%. (Δ) 1.3 μm zeolite crystal size. (\blacklozenge) 0.13 μm zeolite crystal catalyst.

Fig.3. Change of the effectiveness factor with contact time for two types of FCC catalysts. (CAT-AO and CAT-AG). Crystal size =1.3 μm .

Fig.4. Change of the effectiveness factor with gas oil conversion for types of FCC catalysts (CAT-AO and CAT-AG). Crystal size =1.3 μm .

Fig.5. Change of the effectiveness factor with crystal size:

(a) Full line: CAT-AO catalyst.

(b) Broken line: CAT-AG catalyst.

Fig.6. Change of the gas oil conversion with reaction time for different zeolite crystal size: CAT-AO catalyst.

- (a) 1.3- μm zeolite crystal.
- (b) 0.75- μm zeolite crystal.
- (c) 0.4- μm zeolite crystal.
- (d) 0.13- μm zeolite crystal.
- (e) 0.01- μm zeolite crystal.

Fig.7. Change of the gasoline yield with gas oil conversion for CAT-AO catalyst with two different zeolite crystal sizes.

Fig.8. Change of the light gases yield with gas oil conversion for CAT-AO catalyst with two different zeolite crystal sizes.

Fig.9. Change of the coke yield with gas oil conversion for CAT-AO catalyst with two different zeolite crystal sizes.

Table 1. Average molecular weight of the four lump model.

Lump	Average molecular weight , (kg/kmole)
Gas oil	330
Gasoline	115
Light Gases	48
Coke	800

Table 2. Intrinsic kinetic constants for the four lump model using a commercial feedstock

and CAT-AO and CAT-AG catalysts. Temperature=525°C, C/O=5

k_0, k_1, k_{31}, k_{32} with units in $m^6/(kmole.kgcrystal.s)$,

k_{21}, k_{22} with units in $m^3/(kgcrystal.s)$, k_0' with units in $m^3/(kmole.s)$,

α with units kg gas oil/(kgcoke)

Catalyst Code	k_0	k_1	k_{31}	k_{32}	$k_{21}.10^3$	$k_{22}.10^2$	α
CAT-AG	552 +/- 15%	356+/-15%	180+/-15%	17+/-10%	7+/-20%	3+/-20%	40+/-15%
CAT-AO	316 +/-20%	195+/-20%	111+/-20%	11+/-25%	1.7+/-20%	5+/-20%	68+/-20%

Table 3. Properties of FCC Equilibrated Catalysts-60 μ m average size

(Kraemer, 1991)

	CAT -AO	CAT – AG
Al ₂ O ₃ (wt%)	26	34
SiO ₂ (wt)	74	66
Na (wt%)	0.22	0.37
REO (wt%)	>2	4.5
Unit cell size of zeolite (A)	24.24	24.40
Surface area of 60- μ m pellets (m ² /g)	145	126

Table 4: Properties of the gas oil (Kraemer, 1991)

Property	Feedstock
Specific Gravity	0.9117
Aniline Point (°C)	79.4
Sulfur, wt%	1.19
Nitrogen, wt%	0.0012
Volumetric Average Boiling Point (°C)	377.2
Molecular Weight	344.8
Composition (220 to 345°C)	
Light Paraffins, wt%	17.35
Light Naphthenes, wt%	6.4
Light Aromatics, wt%	6.25
Heavy Paraffins,wt% (345°C ⁺)	43.03
Heavy Naphthenes, wt% (345°C ⁺)	20.08
Heavy Aromatics, wt% (345°C ⁺)	6.89