CONTRIBUTION TO REACTOR DESIGN IN A FLUID CATALYTIC CRACKING UNIT. COMPUTATION OF THE ACTIVITY DISTRIBUTION FUNCTION OF THE ZEOLITE ALONG THE RISER.

M. OLAZAR[a], J.M. ARANDES[a], J. BILBAO[a], J. CORELLA[b], R. BILBAO[b]
Department of Technical Chemistry, Universidad del Pais Vasco, Apdo 644, 48080 Bilbao, Spain (a)
Department of Technical Chemistry, Universidad de Zaragoza, Zaragoza, Spain (b)

ABSTRACT

A method based on the population balance model to design the riser in a FCCU is shown. From the deactivation kinetic equation, activity-time on stream, the activity distribution function is evaluated along the riser.

The use of the population balance model to evaluate the average activity, which gives the same results that from the residence time distribution function when the deactivation equation is of first order, avoids the error of this last method when the deactivation order is not the unity.

The design method has been used with experimentally obtained kinetic data in a riser of pilot plant with a MZ-7P zeolite as catalyst. The average activity, temperature, gas oil conversion and gasoline yield have been evaluated along the reactor.

INTRODUCTION

The population balance model is utilized to solve problems that can not be treated by means of models based on mass, momentum and energy balances. These models could range from microscopic models of transport phenomena to macroscopic models [1]. The population balance has been used to represent the age distribution in flow systems, crystal size distributions in steady state, age and size distribution of microbiological cultures, etc.

The population balance was applied before [2] to design fluidized bed catalytic reactors with deactivation and with continuous feed catalyst in order to calculate activity distribution and average activity of particles, in the simplest case in which the deactivation equation, $-da/dt= \psi a^{d}$, is first order with respect to activity (d=1). However, the traditional method to calculate the average activity is the use of residence time distribution, macrofluid analysis, for any order of deactivation and of the design equation for microfluids, microfluid analysis, when the deactivation equation is firs order [3]. These methods give an accurate value of the average activity when the catalyst is fed continuously with uniform activity. However, this is not so when the activities of the inlet catalysts are distributed [2].

In this work population balance has been applied to the design of a riser in a FCCU in which the activity of the inlet catalyst is distributed because it comes from a fluidized bed regenerator. In Fig 1 it is shown a scheme of the reaction and regeneration sections, where f_1 is the distribution function of catalyst activity at riser inlet and f_2 the distribution function in any point along the riser.

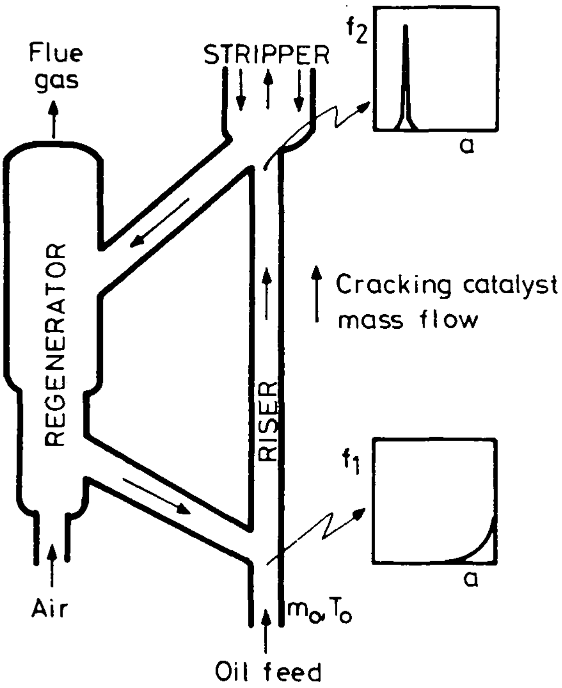


Fig. 1. Scheme of the reaction and regeneration sections in a FCCU.

DESIGN EQUATIONS

In the more advanced methods of riser design the following hypothesis are made [4]: Adiabatic reactor (heat losses below 5%, measured in a commercial unit [5]). Fluid and particles circulating at the same velocity [6,7]. There are not radial gradients of temperature and concentrations. Plug flow if the D/L ratio is small enough [8].

The general equation of macroscopic population balance with respect to activity is:

$$\frac{df}{dt} + \frac{1}{\tau}.\frac{df}{dz'} + \frac{d}{da}\left(f\frac{da}{dt}\right) = 0 \quad ; \quad dz' = dz/L \qquad (1)$$

where f is the activity distribution function and τ the average residence time of the catalyst in the riser.

As it is plug flow, the activity distribution function at outlet can be obtained from the distribution function at inlet. $f_1(a_o)da_o$ represents the fraction of particles that have its activity in the a_o and a_o+da_o range. Later, these particles will have an activity between a and a+da and as the number of particles is the same:

$$f_1(a_o)da_o = f_2(a)da \qquad (2)$$

As it is easier, the activity distribution function can be obtained from this equation instead of solving eqn(1).

For kinetic equations of deactivation independents of reactants and/or products concentration:

$$-\frac{da}{dt} = k_d.a^d \qquad (3)$$

for $d > 1$, activity distribution function is given by the equations:

$$f_2(a)=[(1-a^{d-1}(d-1)k_d t)^{-d/(d-1)}].f_1\left\{\frac{a}{[1-a^{d-1}(d-1)k_d t]^{1/(d-1)}}\right\} \qquad (4)$$

for $a<a_e=a_o[1+a_o^{d-1}(d-1)k_d t]^{-1/(d-1)}$

$$f_2(a)=0 \quad \text{for } a>a_e \qquad (5)$$

When d=1 the activity distribution function is given by:

$$f_2(a)= \frac{1}{\exp(-k_d t)}.f_1\left(\frac{1}{\exp(-k_d t)}\right) \quad \text{for } a<a_o\exp(-k_d t) \qquad (6)$$

$$f_2(a)=0 \quad \text{for } a>a_o\exp(-k_d t) \qquad (7)$$

In these equations a_e is the upper value in the range where activity distribution function exists.

After knowing activity distribution function the average activity is given by:

$$\bar{a}= \int_0^{a_e} a\ f(a)da \qquad (8)$$

The average activity value along the riser is introduced in the design equations, which will be:

-Mass balance $m_o dX = (-r_o)dW$; $W=0,\ X=0$ (9)

-Heat balance $(-\Delta H_r)(-r_o)dW = (F_s Cp_s+\Sigma m_i Cp_i)dT$; $W=0,\ T=T_o$ (10)

The average reaction heat is 70 Kcal/kg and the specific heats of gas oil and catalyst, supposing them to be constants in the studied temperature range, are 0.80 and 0.24 Kcal/kg K.

The solution of eqns(9) and (10) has been performed by a 4th order Runge-Kutta. The difficult lies in obtaining an average activity for each step. In order to compute it, the value of limit activity from which the distribution function does not exist is calculated in each step along the reactor. Next, the distribution function for lower values than the limit activity is obtained from the distribution function in the previous step. Knowing the distribution function, the average activity in each step can be computed by eqn(8).

THE STUDIED KINETIC SYSTEM

An experimental study of gas oil cracking on a MZ-7P zeolite catalyst supplied by Akzo-Chemie has been carried out in a pilot plant riser The characteristics of this catalyst are related in Table 1.

Table 1

Characteristics of the MZ-7P catalyst

Chemical composition	
Al_2O_3	33
Na_2O	0.2
Fe	0.3
SO_4^{2-}	0.3

Particle size distribution	
dp (μ)	cumulative weight,%
0 - 20	5
0 - 40	20
0 - 80	60
0 -105	85
0 -150	98

Physical properties	
Pore volume	0.28 cm^3/g
Surface area	140 m^2/g
Zeolite content	10%
Bulk density	0.82 g/cm^3

Zeolite: Faujasite Y rare earth exchanged.

The gas oil used comes from Puertollano refinery (ENPETROL) and it has the properties related in Table 2.

Table 2

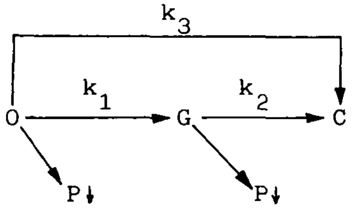
Properties of gas oil

Density at 15^{o}C, g/cm^{3}	0.896
Molecular weight.	315
Aniline point	73.5
Ramsbotton carbon residue, % weight . .	0.17
Conradson carbon residue, % weight. . .	0.14
Hydrogen, % weight	11.9
Sulfur, % weight.	2.14
Nitrogen, ppm	562
Melting point, ^{o}C	+24
ASTM colour	4.5
Viscosity at 40^{o}C (cs).	11.54

Reaction equipment, which setup and description can be found in a previous work [9], allows work with the following conditions: Temperature: 480-540^{o}C. Time on stream: 0.5-3 s. Catalyst/oil ratio: 2-7 (w/w). Gas oil flow rate: 0.8-120 g/min. Cracking catalyst mass flow: 14-174 g/min.

Vaporized feed is put in contact with the preheated catalyst. Both raise togheter along the reactor and the deactivated catalyst is removed from gas by two cyclones placed at the top. There the catalyst is stripped with steam. Finally, gases are cooled and the gaseous and liquid products are collected and also the catalyst for their posterior analysis.

The reaction model used has been the Weekman's of three lumps[10]



It consists of supposing that there are three characteristics groups of reactants and products: The gas oil, the gasoline and the gases and coke. The gas oil is cracked to give gasoline, coke and gases and the gasoline cracks to coke and gases.The kinetic equations at zero time are:

$$(-r_o)_o = (k_1+k_3)(1-X)^2 = k_o(1-X)^2 \quad (11)$$

$$(r_G)_o = k_1(1-X)^2 - k_2Y_G \quad (12)$$

$$(r_C)_o = k_3(1-X)^2 + k_2Y_G \quad (13)$$

where X is the gas oil conversion and Y_G the gasoline yield.

By kinetic experiments carried out in the before mentioned equipment, the following values have been found for the kinetic constants:

$$k_o(min^{-1}) = 3.5\ 10^4 exp(-12750/RT) \quad (14)$$

$$k_1(min^{-1}) = 1.1\ 10^9 exp(-29700/RT) \quad (15)$$

$$k_2(min^{-1}) = 4.2\ 10^5 exp(-32670/RT) \quad (16)$$

In the deactivation kinetic equation, eqn(3), it has been found that the order d changes throughout the time [11]. For that catalyst and gas oil, it has been found that for contact times shorter than 11 s the deactivation order is 3, for times between 11 and 42 s the order is 2 and for times longer than 42 s it is 1. In a riser the contact time is shorter than 11 s, then the deactivation order will be 3 and the deactivation rate constant is given by:

$$k_d(min^{-1}) = 2.5\ 10^9 exp(-27000/RT) \quad (17)$$

RESULTS

The activity distribution function at the riser inlet has been supposed given by $f_1(a) = 30.a^{29}$, to which corresponds 0.97 average activity. In Figure 2 activity distribution functions have been plotted for different times on stream at inlet temperature 530°C and C/O ratio 5. The area under the curve of all the functions is the unity because distribution function is normalized. It can be noticed the way the

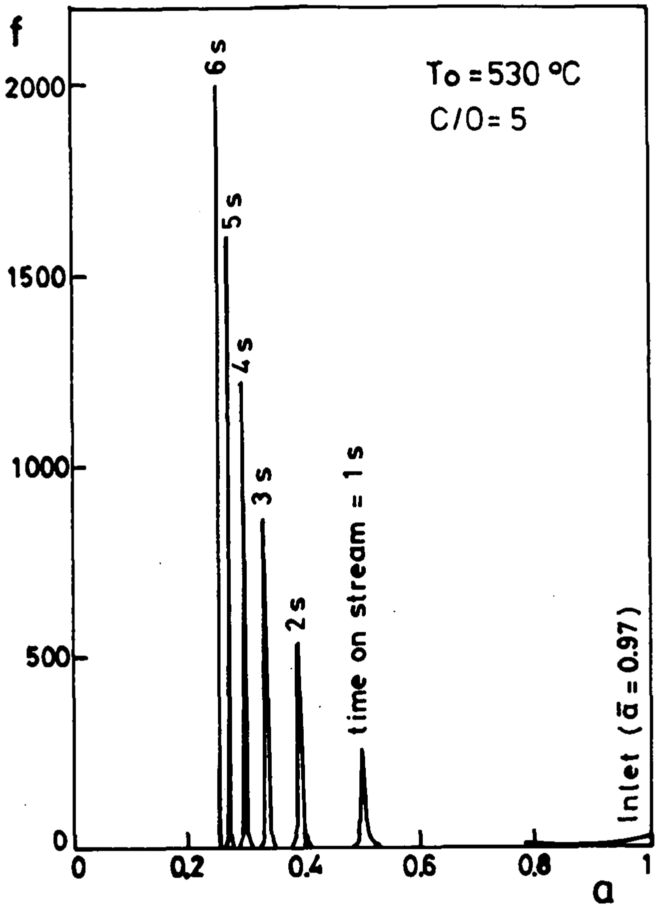


Fig. 2. Activity distribution function for different times on stream.

shape of the distribution function is changing getting more rough because there is plug flow.

The effect of operating variables in the following ranges has been studied:

-catalyst/gas oil ratio (w/w), C/O: 3.7

-temperature of riser inlet, T_o: 520-540^{o}C.

-time on stream: 0-6 s.

In Figure 3 gas oil conversion vs. time on stream has been plotted for different values of C/O: 3, 5 and 7, and temperatures 520, 530 and 540^{o}C. As most interesting result it can be noticed that in very short times, less than 1 s, more than half of the conversion is reached, that is to say, most of the conversion takes place along the initial length of the riser. As temperature increases for the same value of C/O, the conversion increases lightly.

In Figure 4 gasoline yield vs. time on stream has been plotted. Y_G has been evaluated solving the equation:

$$\frac{dY_G}{dX} = \frac{k_1}{k_o} - \frac{k_2 Y_G}{k_o(1-X)^2} \qquad (18)$$

which can be obtained dividing the equations (12) and (11).

In this Figure it can be seen the great impact that has the temperature, so that increasing this, the same gasoline yield as with C/O ratios a lot of higher, at the same temperature, can be obtained.

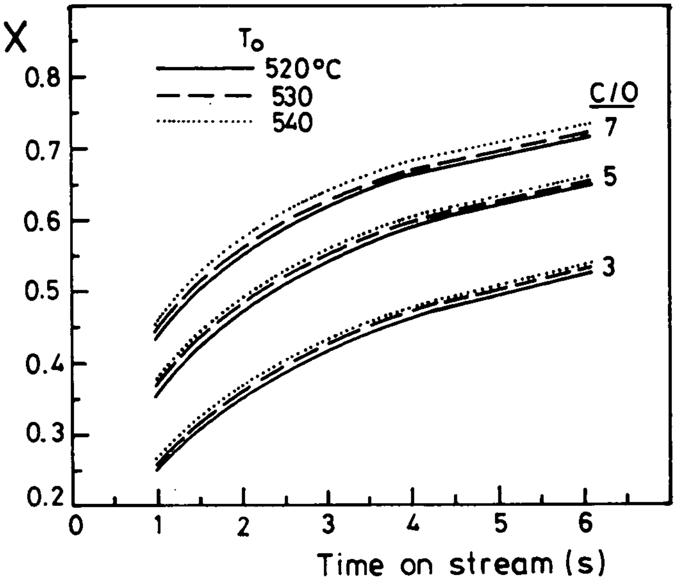


Fig. 3. Gas oil conversion vs time on stream at different temperatures and C/O ratios.

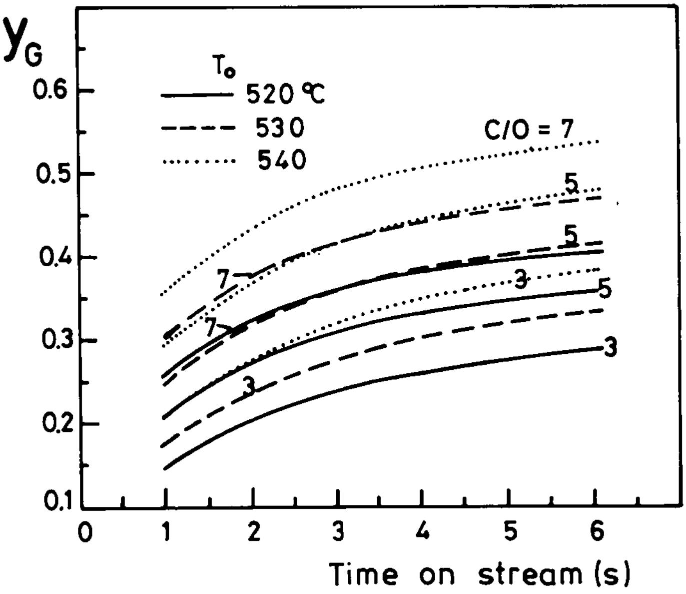


Fig. 4. Gasoline yield vs time on stream at different T_o and C/O.

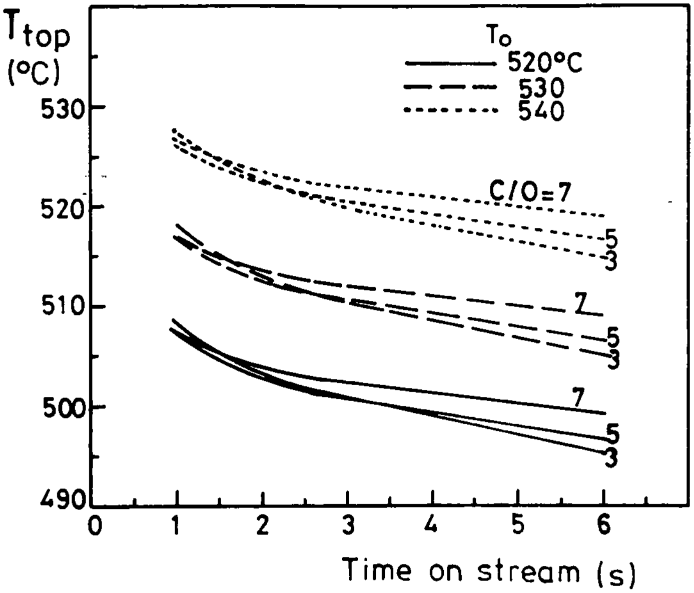


Fig. 5. Temperature vs time on stream at different T_o and C/O ratios.

In the Figure 5, temperature along the riser vs time on stream is drawn. Temperature drops practically in the early instants at the beginning of the riser, and the lower is the C/O ratio the bigger is the temperature drop, since there is less catalyst present.

DISCUSSION

Due to the narrow activity distribution, Figure 2, the results of average activity obtained by application of the population balance are not very different to that obtained using the residence time distribution.

The most interesting innovation in the design method is the use of the activity-time relationship instead of coke-time relationship, the more usual in bibliography. As the coke is not a well defined and stable compound, there is a lot confussion about the existing data.

At the present, in the Dpt. of Technical Chemistry of the Universidad de Zaragoza they are working in finding more accurate deactivation equations for each reaction of three lumps, since the active sites that takes place in each reaction do not have to be the same.

On other hand, in reaction-regeneration systems, it is interesting to know the distribution function of activity. This way, wide variance in the activity distribution in the reactor could be avoided, since a wide distribution means that there is a catalyst fraction with so low activity that its regeneration is not interesting.

Being clear that in the riser there are deviations from plug flo [12], we are working in designing a riser introducing real data of axial dispersion in the design equations. That will contribute to a more realistic design of the riser of a FCCU.

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