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Light paraffins dehydrogenation in a fluidized bed reactor

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Abstract

The FBD-4 (fluid bed dehydrogenation) technology for the dehydrogenation of isobutane to isobutene is described, including the scenario in which the development of this technology was decided and the scale-up procedure used. The paper is then particularly focused on the efforts to develop a reliable mathematical model for design and simulation of the fluid bed reactor. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Fluid bed reactor; Isobutane; Isobutene

1. Fundamentals of fluidization

Fluidization is a phenomenon in which a bed of solid particles is kept suspended by a gas flow passing upwards through it. Fluidization occurs when superficial gas velocity is in the range between the minimum fluidization velocity (U_{mf}) and the terminal velocity (U_{t}). When gas velocity is lower than U_{mf}, the bed behaves like a fixed bed of particles. When gas velocity is higher than U_{t} of the largest particles, the whole bed of particles is eventually transported upwards by the gas stream. Both U_{mf} and U_{t} are mainly function of the density and diameter of the solid particles. Beds of particles with average diameter in the range 50–150 microns have the smoothest fluidization features.

Some features of fluidization can be positively exploited in chemical processes. A fluid bed behaves like a liquid:

- Gas pressure drop through the bed is equal to the weight per unit area of the bed itself and independent on gas velocity.
- The upper surface of fluid beds in communicating vessels is positioned at the same height.
- Fluidized solids can be transferred in pipes like liquids.
- The high intensity of mixing of solid particles enhances heat and mass-transfer phenomena.

These features attracted an increasing interest of industrial and academic researchers in the last decades. The fundamentals of fluidization have been widely investigated and a number of industrial processes is now based on a fluid bed technology (pioneering application was the Fluid Catalytic Cracking in the 1940s), followed by acrylonitrile and vinyl chloride synthesis and more recently by ethylene and propylene polymerization. However, the complex hydrodynamic behavior of fluid beds results in a risky and expensive scale-up procedure from lab-scale to industrial process and is still limiting their application. The increasing availability of powerful and reliable

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calculation tools (computational fluid dynamics) will expand the field of application of fluid bed technologies in the near future.

A number of books have been dedicated in the last decades to the topic of fluidization and reference is made to some of these texts to deepen the theoretical aspects of fluidization [1–4].

2. Dehydrogenation of light paraffins

2.1. Industrial interest

The current chemical scenario shows an increased interest in light olefins considered as starting material for some of the most important chemical products as polymers, synthetic rubbers and oxygenated compounds for reformulated fuels. Unfortunately light olefins are not available as a natural resource. Ethylene and propylene are co-produced in steam cracking furnaces using natural gas or naphtha as feedstock. C_4 and C_5 olefins are also present in steam cracking effluent streams and are produced in FCC (fluid catalytic cracking) plants in refineries.

The introduction of oxygenated compounds as gasoline additives caused methyl *tert*-butyl ether (MTBE) production to boom in the last decade. This ether is produced by the liquid phase reaction of isobutylene and methanol on a strong acidic resin [5]. The traditional sources of isobutylene are already heavily exploited for MTBE production. Exploitation of field butanes has recently gained a remarkable interest as a valid answer to the growing market demand. The widely available normal-butane can be isomerized to isobutane and then dehydrogenated to isobutylene.

Additional considerations must be given to propylene. This olefin is a major co-product from Steam Crackers and the economics of the process are highly dependent on the supply/demand situation for both propylene and ethylene. In some geographic areas, propylene demand is increasing faster than ethylene demand. The dehydrogenation of propane with high selectivity to propylene gives the chance to de-couple the productions of ethylene and propylene and will be of great interest in next years if the trend in the market of polymers will persist. The need for flexibility in refinery and petrochemical olefin supply/demand has led in the last decade to the development and commercialization of processes for the catalytic dehydrogenation of C_3–C_5 paraffins to the respective mono-olefins with high yields.

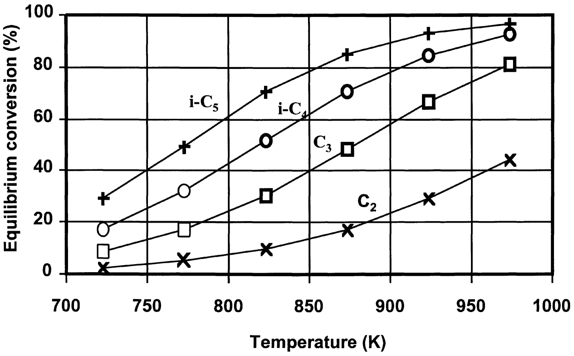

Fig. 1. Equilibrium conversion vs. temperature for C_2–C_5 paraffins.

Finally, dehydrogenation of light paraffins provides an interesting way to locally exploit natural gas liquids (NGL) sources by converting the relatively inert light paraffins into olefins, which in turn can be transformed into more valuable and easy-to-ship chemicals by means of well-known petrochemical routes.

The main features of current commercial dehydrogenation technologies were recently reviewed [6].

2.2. Features of the reaction

The reactions of dehydrogenation, schematized as

$$\text{Paraffin} \Leftrightarrow \text{Mono-olefin} + H_2$$

are strongly endothermic and the attainable conversion is limited by thermodynamics. As shown in Fig. 1, the temperature required to achieve an equilibrium yield around 50% ranges from 800 to 1000 K for C2–C5 paraffins and increases while decreasing molecular weight: ethane dehydrogenation needs the highest temperatures.

It is then clear from the stoichiometry of the reaction that high pressures adversely affect the reaction. High endothermicity results in a high adiabatic temperature decrease. In spite of operating at high temperatures, the dehydrogenation reactions are slow. Furthermore, side reactions like isomerization, thermal cracking and coking, which are thermodynamically and kinetically favored over the main one, can occur in the required operating conditions. Consequently the use of a catalyst is necessary in order to keep a suitable conversion while obtaining high selectivity towards the desired olefin.

The unavoidable formation of coke on the catalyst surface results in progressive reduction of catalytic activity, requiring a periodical regeneration of the catalyst.

Many materials have been proposed as catalysts for the dehydrogenation of paraffins, but in practice up to now only alkali promoted chromia/alumina and platinum/alumina have shown characteristics good enough to be brought to industrial development.

3. Industrial reactors for dehydrogenation

The main problem to be solved in the development of a suitable reactor for an industrial dehydrogenation process, is how to supply the huge quantity of heat needed by the reaction at temperatures well above 500°C, maintaining in the meantime a careful control of temperature to minimize the formation of by-products and maximize the yield to the desired product.

At the same time, since a small formation of coke on the surface of the catalyst cannot be avoided, the problem of its periodical regeneration must be solved, remembering that large-scale production plants should operate continuously and in a steady state. Every equipment working batchwise or in a non-stationary state complicates the operation of the plant, enhancing the chances for a loss of efficiency.

In principle the heat of reaction can be supplied either to the gas feed before entering the reactor or directly to the reacting system using a suitable type of reactor (e.g., a multitubular reactor), or to the solid catalyst.

Preheating the feed gas to such temperatures in a furnace can push undesired thermal cracking reactions with loss of selectivity and potential fouling. In spite of the presence of the catalyst, even heating through the walls of a multitubular reactor has drawbacks: a radial temperature profile will establish inside the tubes, with the highest value at the wall, to allow the passage of the necessary heat flux. Again, side reactions at the tube wall can affect the yield.

The regeneration of the catalyst, i.e. the combustion of the coke deposited on its surface, is a fairly exothermic reaction and it can be exploited to supply the heat of reaction. If this concept is adopted in a fixed bed reactor, reaction and regeneration must take place in the same vessel. Many reactors working in parallel are needed and each of them alternates reaction and regeneration in cyclical operation requiring a well-sequenced isolation valve system. The heat of reaction is supplied to the catalyst in the regeneration step conveying hot air in excess. Each reactor is operated batchwise from the view-point of the solid phase, and the temperature in the reaction zone is not stationary, but decreases during the reaction step and its profile is continuously changing while the catalyst is deactivating. In this way the optimal conditions can be maintained for only a small part of the reaction period and the resulting yield is averaged over a wide range of operating conditions.

A fluidized bed system is the only way to achieve steady process conditions supplying the heat of reaction to the catalyst. Fluidized solids can easily be transferred in huge quantity in a closed loop, offering the opportunity to operate reaction and regeneration in two separate vessels with pneumatic conveying of solids between them: a completely continuous process can be thus obtained. The heat produced in the regeneration raises the temperature of the catalyst, which is immediately transferred back to the reactor. Heat is exchanged between the hot catalyst particles and the surrounding gas in the efficient way allowed by fluidized beds with a high heat-transfer coefficient: indeed, the whole surface area of the catalyst forms the heat transfer surface.

4. FBD technology

A dehydrogenation technology employing a fluidized bed reactor was developed in the former Soviet Union during the fifties, to supply C_4–C_5 olefins to the production of synthetic rubbers.

In the last decade, Snamprogetti and the Russian company Yarsintez have further developed this technology improving both chemical and engineering sides to make it economically competitive in the Western markets [7].

A new technology for the production of the catalyst was developed, enhancing its chemical activity and improving dramatically its mechanical resistance, a

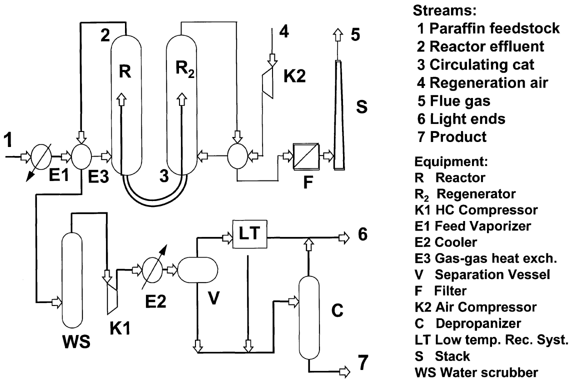

Fig. 2. Flow-sheet of FBD technology.

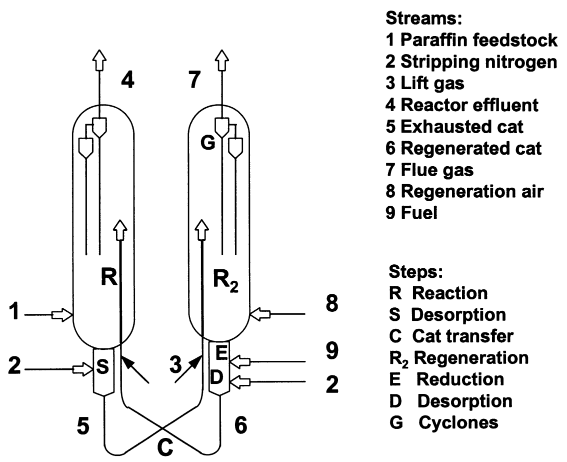

Fig. 3. Reactor–regenerator assembly.

particularly important feature in fluidized bed system: the consumption of the catalyst by attrition has been decreased by a factor of thirty in comparison with the original Russian catalyst. The result of this joint effort is the FBD (fluidized bed dehydrogenation) technology that is now commercialized by Snamprogetti for the dehydrogenation of C_3, C_4 and C_5 paraffins (FBD-3, -4 and -5).

In the FBD technology, the reaction section is based on a two units reactor–regenerator assembly similar to that used in the FCC process [8]. The dehydrogenation step occurs in a staged fluidized catalytic bed, without diluents, operating at pressure slightly above atmospheric. A typical process scheme is detailed in Fig. 2: it is common to the dehydrogenation of all other paraffins, except for the separation section.

Fresh feed is vaporized, mixed with a recycle from an olefins user unit (e.g. MTBE), preheated by cross-exchange with the reactor effluent, then fed to the reactor vessel from the bottom of the catalytic bed. Reaction products are separated from the entrained catalyst powder by means of high efficiency cyclones and, after a complete dust elimination in a suitable scrubbing system, are sent to compression and separation sections to separate C_4 stream from hydrogen and by-products. The heart of the process is the reactor–regenerator system, described more in detail in Fig. 3.

Catalyst circulates continuously from the reactor vessel to the regenerator and vice-versa by means of pneumatic transfer lines, originating a countercurrent movement of gas and solid both in the reactor and in the regenerator. In the regenerator vessel the catalyst restores its initial activity by combustion of the low amounts of coke deposited on its surface: additional fuel is catalytically burned directly on the catalyst to satisfy the overall thermal balance, as will be detailed later. The heat developed in the regenerator is stored by the catalyst itself and then released to the reaction environment. Before being conveyed to the regenerator, the catalyst is stripped with nitrogen to avoid loss of adsorbed products.

The same operation is performed on the bottom of the regenerator to avoid oxygen transport to the reactor vessel, with loss of selectivity.

5. Fluidized beds and optimal yields

Because the reactions of dehydrogenation are limited by equilibrium, the achievement of higher conversion per pass, reactor volume being equal, is favored by a plug-flow movement of the gas phase. On the contrary the high intensity of mixing in a fluid bed results in a closer approach to a perfectly mixed reactor (CSTR).

The necessity of careful control of the temperature has already been emphasized: the suitable range of reaction temperatures is quite narrow. Low temperatures slow the reaction and strengthen the equilibrium burdens, while high temperatures push side reactions. Fig. 4 shows equilibrium conversion vs. temperature for the dehydrogenation of isobutane. The other curves show conceptual profiles of conversion vs. temperature that can be established in the reactor following the path of the reacting gases.

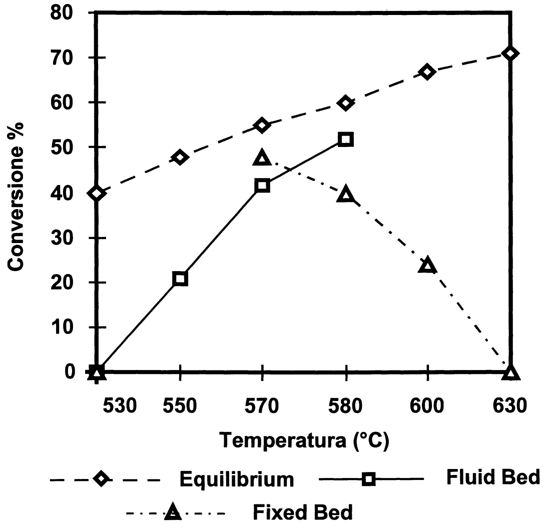

Fig. 4. Achievable conversion vs. temperature in different types of reactor.

A profile with gas temperature increasing along the reactor is the most desirable, because it allows to approach the equilibrium at higher temperature, maximizing the attainable yield, while the mean reaction temperature is kept acceptably low to minimize the formation of by-products. To reach the same conversion to isobutylene with an isothermal or, even worse, decreasing temperature profile would require a much higher mean reaction temperature increasing the rate of thermal cracking reactions. Summarizing, the ideal dehydrogenation reactor should be a plug-flow unit, with increasing gas temperature along the catalytic bed. It is well known that horizontal baffles with suitable openings can be inserted in a fluid bed to limit the free movement of solids, and therefore, the phenomena of backmixing.

The catalytic bed is split into a series of stages, each one comparable to a CSTR. Using a sufficient number of grids, the fluidized bed reactor approaches very closely the behavior of a plug-flow reactor from the view-point of the gas phase. In this way, the bed is no longer isothermal, but an axial increasing temperature profile is established with the highest temperature at the gas outlet, where hot catalyst arrives from the regenerator.

The two aforesaid conditions to optimize the conversion of the paraffin and the selectivity to the olefin have been met and it must be stressed that no other type of reactor can meet both of them simultaneously.

The flow rate of circulating catalyst is determined by the large amount of heat required by the reaction rather than by catalyst de-activation: therefore the temperature profile created by the insertion of baffles allows a substantial reduction of this flow rate in comparison with isothermal conditions.

The high heat-transfer coefficient between gas and solid, typical of a fluidized bed, ensures that no interphase temperature differences can exist at any level in the reactor. The temperature of the catalyst decreases along the bed and more heat per unitary weight can be transferred to the reacting gas. Consequently, the mechanical life of the catalyst, largely depending on the required circulation flow rate can be increased.

The low pressure drop associated with fluid beds allows to keep a slightly over-atmospheric pressure in the reactor: a fixed bed would require a much larger cross-section or the addition of a diluent to maintain such a low partial pressure of the reactants.

Another much favorable feature of fluidized beds is the chance to substitute part of the catalyst while the plant is running. In this way the problem of catalyst ageing with variation of yields is eliminated: periodical substitutions are made, also allowing for the fines lost through the cyclones, so that the average age of the catalyst remains constant in time.

6. Scale-up procedure

The ideal scale-up procedure should consist in the development of reliable kinetic and hydrodynamic models to be combined in a reactor simulation model. In this way the very expensive scale-up steps of pilot units of increasing size could be avoided and the industrial plant could be designed directly from laboratory data. However, despite large efforts of academic researchers, none of the many hydrodynamic models proposed for fluid beds can be reliably applied "a priori" without experimental check at a large scale. The scale-up procedure must therefore include experimentation at a scale that can be considered hydrodynamically homologous to the industrial scale.

In the case of the FBD technology the "hard job" of building pilot plants of increasing size was performed by Russian engineers in the 1950s and a process demonstration unit (PDU), a reactor–regenerator system with 1 m internal diameter, was available for further experimentation. Consequently the improved catalyst, after screening at the lab-scale, was thoroughly tested in the PDU. The influence of catalyst ageing and operating conditions on paraffin conversion and selectivity to olefins and by-products was studied. An empirical polynomial model was determined by regression of experimental data and implemented in a design software performing thermal and material balance of the reactor–regenerator system.

The hydrodynamic optimization of the technology, mainly concerning catalyst circulation system, gas distribution and internal baffles was performed on large scale "cold" (ambient temperature) equipment ("mock-ups"). Since in fluid beds visual observation is very important to assess hydrodynamic behavior, "mock-ups" are made from transparent acrylic sheets in a half-circular shape: visual observation is possible on the flat side.

The scale-up of the FBD technology was performed without a rigorous mathematical model of the fluid bed. However, the availability of a large number of significant data from the PDU, including temperature profiles along the bed, pushed the development of such a model, because its availability should allow extrapolation to different hydrodynamic conditions and different reactions (only substituting kinetics): future optimizations and scale-ups could be much cheaper.

7. Kinetic model

The network of chemical reactions involved is extremely complex, resulting in a wide range of light and heavy by-products. Besides the main reactions of dehydrogenation, reactions of thermal cracking to lighter hydrocarbons and consecutive dimerizations and aromatizations, finally leading to coke deposition, take place. The kinetic experimentation was performed on laboratory fluidized bed reactors. In principle, this is a questionable choice, since a fixed bed experimentation should allow to decouple hydrodynamic effects related to fluid bed. In this case, the necessity to operate the reaction at atmospheric pressure makes fixed bed operation impractical (pressure drop of the gas phase too high).

Several different reaction schemes have been tested and the simplified one reported below was found to provide the best fit to experimental data.

- Dehydrogenation reactions:

$$i\mathrm{C_4H_{10}} \leftrightarrow i\mathrm{C_4H_8} + \mathrm{H_2} \tag{1}$$

$$\mathrm{C_3H_8} \leftrightarrow \mathrm{C_3H_6} + \mathrm{H_2} \tag{2}$$

- Cracking reactions:

$$i\mathrm{C_4H_8} + \mathrm{H_2} \leftrightarrow \mathrm{C_3H_6} + \mathrm{CH_4} \tag{3}$$

$$\mathrm{C_3H_6} + \mathrm{H_2} \leftrightarrow \mathrm{C_2H_4} + \mathrm{CH_4} \tag{4}$$

- Aromatization reactions:

$$i\mathrm{C_4H_8} \leftrightarrow \mathrm{Xylene} + 3\mathrm{H_2} \tag{5}$$

$$\mathrm{C_3H_6} \leftrightarrow \mathrm{Benzene} + 3\mathrm{H_2} \tag{6}$$

- Coking reactions:

$$\mathrm{Xylene} \leftrightarrow \mathrm{Coke} + 5\mathrm{H_2} \tag{7}$$

$$\mathrm{Benzene} \leftrightarrow \mathrm{Coke} + 3\mathrm{H_2} \tag{8}$$

The laboratory reactor has been assumed to behave as an ideal plug-flow and simulated as a series of ten CSTR stages at fixed temperature. The steady-state material balance for each stage results in the following expression:

$$y_i = y_{i(\mathrm{feed})} + \sum_{i=1,n\mathrm{comp}}^{j=1,n\mathrm{react}} v_{i,j} r_j \times GG, \tag{9}$$

where y_i are the moles/time of component i, GG is the mass of catalyst in each stage of the reactor, $v_{i,j}$ are the stoichiometric coefficient of component i in the reaction j, r_j are the rate of reaction j based on unit weight of catalyst.

For the general reaction j ($aA \Rightarrow bB + cC$) analysis of laboratory rate suggested the following kinetic model:

$$r_j = k_j \times P_A^a \tag{10}$$

which becomes

$$r_j = \vec{r}_j \times \left[1 - \frac{P_B^b \times P_C^c}{K_{\mathrm{eq}} \times P_A^a} \right] \tag{11}$$

for reactions [1,2] where the equilibrium has to be accounted for.

K_{eq}'s, the equilibrium constants, have been calculated from the data given by Kjær [9], while the kinetic constants k_j's are expressed as

$$k_j = \exp\left(A_j + \frac{B_j}{T}\right), \tag{12}$$

A_j and B_j being parameters.

The resolution of the mathematical model of the CSTR requires the numerical integration of a non-linear system of algebraic equations. The parameters A_j's and B_j's for all reactions are computed by means of a non-linear estimation program seeking the minimum of a weighted residual sum of squares between the measured and computed value of outlet gas composition:

$$\mathrm{RSS}(K,E) = \sum_i w_i(\hat{y}_i - y_i)^2. \tag{13}$$

On the basis of the statistical analysis performed on the regressions of the data produced it has been possible to discriminate between different reaction schemes.

Fig. 5 reports experimental and calculated values of conversion vs. selectivity for the dehydrogenation of isobutane to isobutylene on the basis of the reaction scheme reported above.

8. Reactor model

Many hydrodynamic models were proposed for fluid bed reactors. The common feature of all of these models is the hypothesis of the existence of a multi-phase system in the reactor.

Two phase models assume that a dilute phase (usually pure gas in the form of bubbles) and a dense phase (usually an emulsion of gas and solid in conditions of minimum fluidization) are present in the bed. Reaction takes place in the dense phase, while mass transfer takes place between the two phases. Gas in the bubbles rises faster than gas in the emulsion.

Typical pure two phase models were developed by May [10], later modified by Van Deemter [11], and by Davidson and Harrison [2]. Other two phase models assume that some solid is also dispersed in the bubble [12] or immediately surrounding the bubble forming a cloud, which is, however, treated as part of the bubble itself, i.e. with the same gas composition [13].

In three phase models the cloud is treated separately from both bubbles and the remaining dense phase [14]. Other models proposed (two or three phases) propose a dilute phase shaped differently compared to the traditional bubbles (e.g., the "snakes" proposed by Carberry and Pigeon [15]. For general reviews see

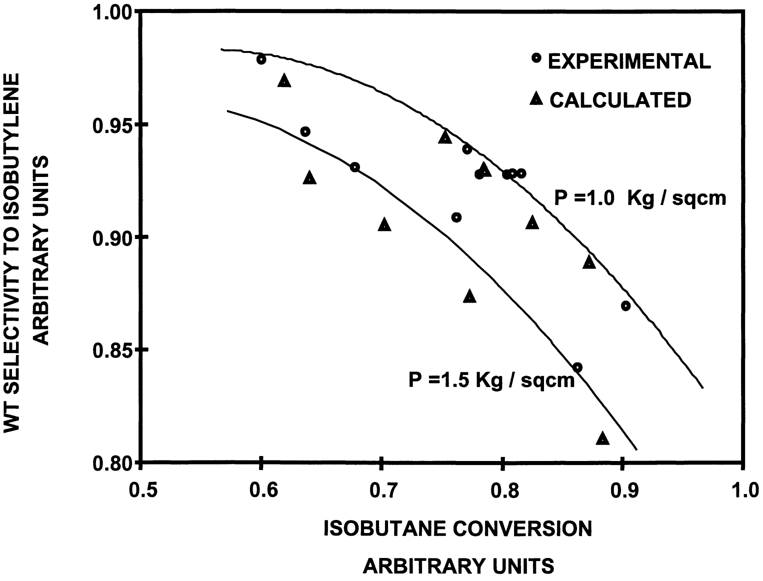

Fig. 5. Experimental and calculated selectivity and conversion (laboratory data).

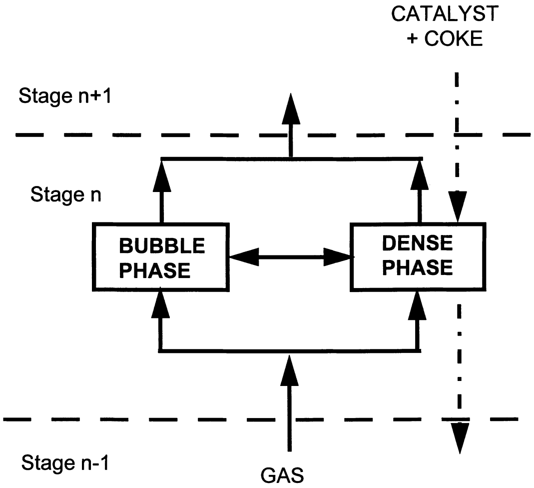

Fig. 6. Schematic diagram of the hydrodynamic model of the reactor.

Geldart [3], Kunii and Levenspiel [4], Grace [16], Yates [17], Donati and Dapelo [18].

The two phase model by Davidson was chosen as a basis for our treatment, since it remains quite simple, even including the fundamental hydrodynamic feature of the two phases.

To simulate the reactor–regenerator system in the FBD technology the following complications must be considered:

- Horizontal baffles are inserted in the bed at various heights.
- The fluid bed is not stationary, but an overall countercurrent flow of gas and solid phases is achieved.
- Baffles break the bubbles of gas and provide a discontinuity in the bed.

The approach chosen, schematized in Fig. 6 considers perfect mixing for each phase in the zone between two grids.

At the level of the grid a perfect mixing of the gas between the two phases is considered, so that a new bubble and a new emulsion phase are formed. Each zone between two grids is considered as a stage with the gas phase entering at the bottom and leaving from the top and the solid phase entering at the top and leaving from the bottom. The model is also provisional of mass transfer between bubble and emulsion phase.

The material balances around each stage are simultaneously solved as a non-linear system of equations using an algorithm specialized for the solution of sparse systems of non-linear equations [19]. The experimentally measured axial temperature profiles are used to determine the temperature of each stage, while rigorous heat balances are not included in this preliminary model.

9. Results of the simulations

The results of the simulation performed by means of the above described model have been compared to outlet experimental data for conversion and selectivity obtained on a process demonstration unit (capacity more than 3000 metric tons per year). Calculations have been performed in order to test the sensitivity of the model to the assumptions made on the hydrodynamics and on the kinetics

9.1. *Influence of bubble diameter and bubble flow rate*

Hydrodynamic parameters needed for the model are calculated from equations available from the literature and from measured bed and catalyst properties.

The bubble diameter is kept constant along the bed and affects the calculated fraction of the bed occupied by bubbles.

As defined by Davidson and Harrison [2] the bubble flow rate is estimated as the excess gas flow above that required for minimum fluidization. In practice the gas flowing in the bubble phase is less than this and a parameter Y is introduced in the model according to Eq. (14)

$$\frac{Q_b}{A} = Y(U - U_{mf}), \tag{14}$$

where Q_b is the bubble flow rate, A the section of the bed, U the gas velocity and U_{mf} the gas velocity at minimum fluidization.

The influence of bubble diameter and of the parameter Y on conversion and selectivity is shown in Fig. 7(a) and (b).

Conversion is more sensitive than selectivity to the hydrodynamic parameter and the stronger the effect of variation in the bubble diameter the higher the bubble

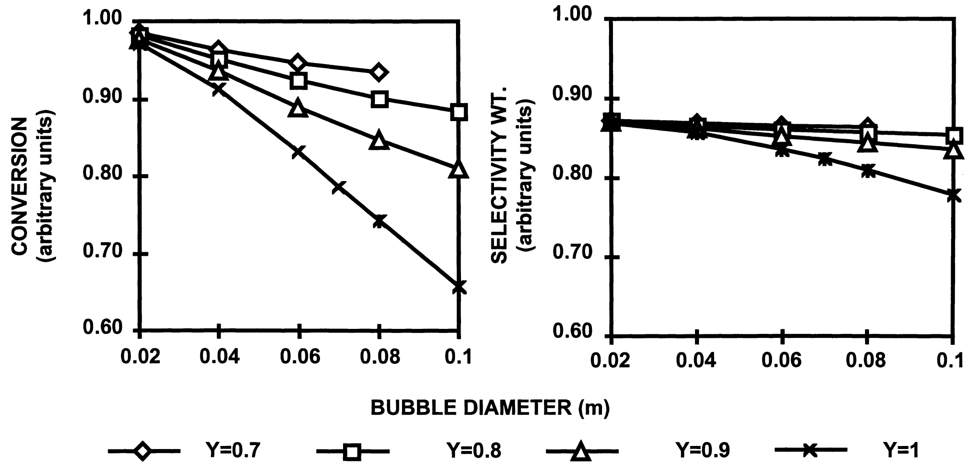

Fig. 7. Effect of variation of bubble diameter and bubble flow rate on coversion of isobutane (a) and weight selectivity to isobutylene (b).

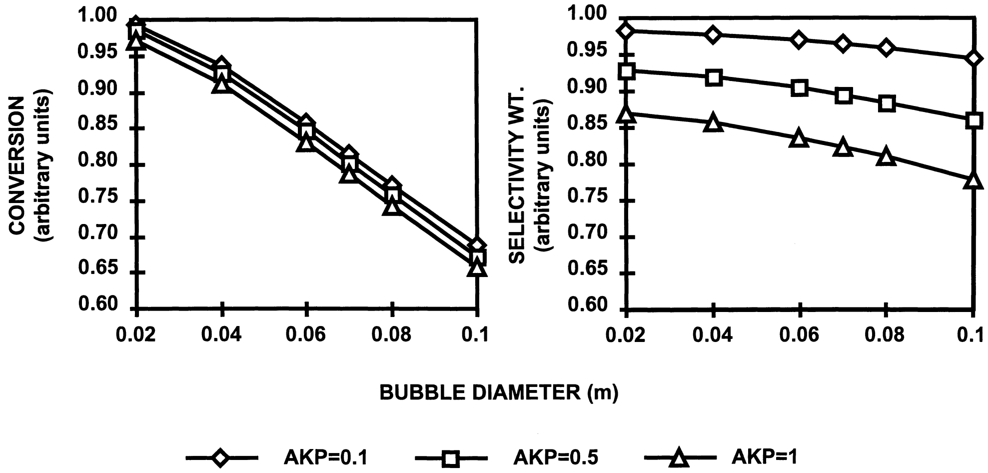

Fig. 8. Effect of variation of kinetic rate constants for secondary reactions on conversion of isobutane (a) and weight selectivity to isobutylene (b).

flow rate. Considering that the gas flow rate increases through the bed due to reaction, an improvement of the predictions of the model could derive by accounting for bubble growth, instead of assuming a constant bubble diameter.

9.2. Influence of kinetic rate constants

As already mentioned catalyst kinetic parameters estimated from fluid bed reactor data are subject to considerable error and uncertainty, particularly for secondary products.

To illustrate what the effect of these uncertainties can be, the kinetic pre-exponential parameters for the secondary reactions (4–8) have been multiplied by a correcting factor (AKP). The predictions of the model, particularly in terms of selectivity, as shown in Fig. 8, are extremely sensitive to variations in the kinetic rate constants.

The results obtained from the simulation performed assuming a constant bubble diameter of 0.1 m, a parameter Y equal to 0.9 and reducing the kinetics of the secondary reaction to 10% of that calculated on the basis of laboratory results, are compared to the

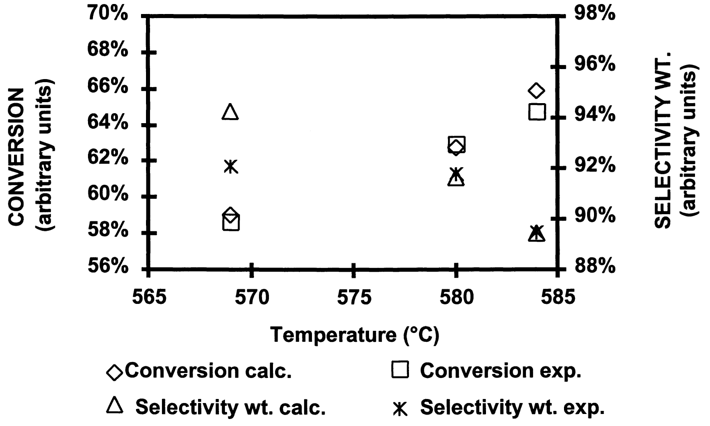

Fig. 9. Experimental and calculated selectivity and conversion vs. reactor top temperature (pilot plant simulation).

experimental ones obtained on the pilot plant unit for runs with different temperature profiles. From Fig. 9 it can be seen that the model is able to reproduce satisfactorily the dependence of isobutane conversion on temperature, while it fails in predicting the experimental selectivity to isobutylene when operating with a lower temperature profile. The reason for this behavior can again be ascribed to the kinetic expression employed, particularly for secondary products, rather than to the hydrodynamic expressions.

From the analysis conducted it is clear that further improvements of the model will need to test different kinetic expressions for the secondary reactions and will require the evaluation of the kinetic properties of the catalyst using gradientless reactors or reactors with well characterized hydrodynamics.

Further work must also be devoted to the implementation of the hydrodynamic behavior of the reactor, including the influence of the distributor zone, showing an higher turbulence than the rest of the bed, and the freeboard zone.

Finally the model excludes every phenomenon of backmixing, i.e. gas flowing down or solid flowing up through the grid. Some solid is really entrained by the upflowing gas from one stage to the next one. This phenomenon can be taken into account considering that the net downward flow rate of solid results from the difference between an upward flow rate and a gross downward flow rate.

10. Conclusions

The FBD technology was successfully scaled-up through an expensive path including large-scale pilot units and acrylic equipment for hydrodynamic tests.

The preliminary bubbling-bed model used represents a sound basis for the rational scale-up of fluidized bed, but further improvements on the kinetic expressions for secondary reactions and on the description of the hydrodynamic behavior of the reactor are necessary.

Work is still in progress to develop a physically meaningful model able to simulate PDU tests and consequently to be extrapolated for further optimization of the technology.

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