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Wax composition transients during Fischer–Tropsch synthesis

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Abstract

The temporal evolution of the composition of the products collected from a slurry reactor during Fischer–Tropsch synthesis over a Co/Al_2O_3 catalyst is studied, in order to rationalize the time required for a complete renewal of the liquid phase used to initially dilute the catalyst. The transients are well described by a simple equation with no assumption on the phase repartition of the hydrocarbons in the reactor, which also provides an estimate of the time constant of the system. The mathematical model can be used to predict the time necessary to reach steady state of the composition of the reactor outlet and hence collect reliable data for product selectivity in a slurry reactor. The change in the composition at the outlet of a fixed bed reactor after step changes of a co-fed liquid olefin is also approximately analyzed: it is shown that the transient is much faster for a fixed bed reactor than for a slurry reactor.

Keywords: Fischer–Tropsch synthesis; Slurry reactor; Fixed bed reactor; Unsteady mass balance

1. Introduction

The catalytic conversion of synthesis gas into hydrocarbons (Fischer–Tropsch synthesis, FTS) is recently receiving great attention, as a powerful way of exploiting natural gas wells located in remote areas [1–3]. Syngas, produced from natural gas by partial oxidation or steam reforming, is transformed into a complex mixture of gaseous, liquid, and solid hydrocarbons and alcohols that can be further processed to maximize the liquid product yield [3]. In general heavy paraffins (waxes) are the preferred products of FTS, since they can be easily hydrocracked to liquid fractions (gasoline and diesel fuel), whereas light hydrocarbons are undesired products.

The renewed interest in FTS has led to many works relative to investigation of the process variables. In particular, various experimental studies were performed to accurately describe activity and product selectivity over different catalysts [4]. Both fixed bed and slurry reactors were widely used to test the performance of catalysts, the former system being easier to operate, the latter allowing a better temperature control. Yet the performances of these types of reactor may be different, due to the fluid dynamic and dimensional characteristics of the two systems. In fact it is common practice to initially load a slurry reactor with a liquid, to suspend the fresh catalyst, before the start-up of the unit. For this reason, if heavy product selectivity is a variable of interest, the time required to collect reliable data is longer for a slurry reactor rather than for a fixed-bed reactor. Indeed the presence of the liquid wax in the reactor (either if initially contained in the slurry reactor, or if produced by the reaction and retained in the system) may in principle modify the hydrocarbon distribution in the effluent, by diluting the real liquid products. The replacement of wax during the reaction is a matter of great interest in the operation of both laboratory and industrial scale units, being crucial in one case to collect reliable data, in the other to control and predict the specifications of the products.

The problem relative to the wax renewal and its consequences on reaction selectivities has been approached in different ways in the literature. Some authors explicitly considered the dilution of the produced wax with the initial liquid, by taking into account the time necessary to remove the old wax by the newly synthesized one; some others just considered the gaseous products, whose transient is much faster.

Gormley et al. [5], in their study on the effect of the initial wax media on FTS in a slurry reactor, corrected the heavy products distribution by considering the daily disappearance

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of the initial liquid from the system. In developing a detailed kinetic model for hydrocarbon selectivities Schulz and Claeys [6] utilized data collected in a slurry reactor maintaining the same reaction conditions for about 60 days to be sure of attaining steady state for the condensed products. Schulz and Claeys also [7] performed catalytic activity tests in a slurry reactor: they investigated the role of secondary reactions of olefins in the FTS mechanism and reached the conclusion that heavier olefins exhibit longer residence time in the reactor, due to their higher solubilities in the liquid wax. Bukur et al. [8] reported steady state conversions and light compound selectivities, obtained from a 1-L slurry reactor during very long runs (up to 730 h), after only 16–20 h on stream, but detected slight changes in heavier products selectivities. In this case, however, the study was focused on a general comparison of the performances of fixed bed and slurry reactors and not on the development of a complete model for hydrocarbon distribution. Oukaci et al. [9] compared activity and selectivity of a Co catalyst supported on different materials in both a fixed bed and a slurry reactor, in terms of rate of CO consumption, methane selectivity, and chain growth probability (α). For the slurry system the collection and analysis of liquid products were performed every 24 h. The change in the composition of the liquid in the slurry with time, however, may have only slightly affected the chain growth probability since its values were estimated from hydrocarbons having 4 to 14 carbon atoms. Zimmerman et al. [10] developed a complex kinetic model accounting for heavier hydrocarbons from data collected in the vapor phase only in a slurry reactor every only 6–8 h. In this case the change in composition of the wax contained in the reactor could modify the vapor–liquid equilibrium and affect the measured selectivity. Also Withers et al. [11] measured selectivities to liquid products collected from a slurry reactor every 14–16 h. The analyses of the vapor and liquid phases were used not only to derive a kinetic expression for CO consumption, but also to compare activity and selectivity of different catalysts. Yet the estimates of the productivities of heavy hydrocarbons might be influenced by the presence of the initial slurry in the reactor. Huff and Satterfield [12] tested an iron catalyst in a slurry reactor for 680 h by changing the operative conditions several times and analyzing the gaseous products. Still they recognized that high-molecular-weight products are retained in the liquid phase initially loaded to dilute the fresh catalyst, and tend to build up in the reactor. The authors used this argument to explain the negative deviations of this class of products from the classic Anderson–Schulz–Flory distribution for chains with more than 20–25 carbon atoms, by calculating the time required for molecules of different chain length to appear as a vapor. A similar approach was adopted by Dictor and Bell [13]: the authors wrote the nonstationary mass balance for component n under the hypothesis that the species can be found in both the vapor and the liquid phases, considered at equilibrium, but that it is removed only as a vapor. Solubility values were taken from the literature [14,15]. The change of shape of ASF plots during the first period of reaction was then attributed to holdup of heavy compounds in the molten waxes contained in the reactor and continuously formed. The authors reported that some time is necessary for heavy products to become visible in the analysis of the vapor phase. The simple equation derived was proposed as a tool to predict the time required for heavier product to appear in the vapor phase and to adopt optimal conditions to minimize it. However, no comparison of the model to experimental data was presented in the paper. Furthermore the authors did not consider the possibility of collecting liquid products, where the most desirable FTS products are to be found. Only later Caldwell and van Vuuren [16] restated the problem by applying nonstationary mass balances to species containing n carbon atoms, assuming vapor–liquid equilibrium and considering that every component leaves the ambient in both a vapor and a liquid stream. The solubility was supposed to vary with n according to an exponential law. Aim of the work was to model the change in the composition of the liquid and the vapor phases at reaction conditions inside the reactor. As for the vapor phase, the numerical solution of the relevant differential equations led to results similar to those of Huff and Satterfield [12]. However, the data collected from a laboratory unit are usually relative to the *total* productivity, summing the amount of a species in the liquid as well as in the vapor phase. Thus the mathematical complication introduced by considering the vapor and the liquid phase individually could in general be avoided, unless particular interest is set on the phase repartition inside the reactor at synthesis conditions.

It is clear then that a reliable model for a priori estimation of the time necessary to achieve steady state for heavy molecule productivities, avoiding the influence of previously present wax, is still lacking. In this study the problem was quantitatively approached, with the final objective of developing an effective yet simple method for the determination of the optimal conditions for the operation of a slurry reactor, in order to collect reliable data on selectivity to heavy products.

For this purpose a slurry reactor was chosen to measure activity and selectivity of FTS over an alumina-supported cobalt catalyst at high pressure and temperature. In particular the distribution of products contained in the wax collected from the system was monitored as a function of time on stream in order to determine the time required to collect data on *real* productivity of heavy hydrocarbons. The experimental data for various compounds are reasonably fitted by a simple transient model, without any assumption on the compositions of the vapor or of the liquid phase. The equation so derived is also compared to experimental transient data collected in a fixed bed reactor upon changing the concentration of an olefin co-fed with syngas at reactor inlet.

2. Experimental

Catalytic activity runs were performed in a 490-cm^3 continuously stirred tank reactor, shown in Fig. 1, at Eni-Tecnologie laboratories. A sketch of the unit is reported in Fig. 2. The reactor is of cylindrical shape and is equipped with a rotating impeller, which guarantees that the reaction medium be properly mixed. Fresh syngas enters the autoclave through a dedicated line (sparger) at the reactor bottom, while nonconverted reactants and gaseous and liquid products leave the reactor through the filter F, which prevents any catalyst loss during the runs, and are sent through a heat-traced line to a separation section. The reactor level is self-controlling through this continuous outlet stream, which maintains a constant volume of the reaction mixture inside the reactor. The heavier products (waxes) are condensed in a vessel (V103A in Fig. 2) kept at ca. 403–413 K, whereas the organic and aqueous products are separated in a second bottle at 275 K (V105A in Fig. 2). Light hydrocarbons, CO_2, and unreacted syngas are depressurized up to atmospheric pressure through a back pressure regulator, sent to a volume totalizer, and vented. The collection of condensed products is possible during the run without depressurization of the unit and without loss of the products by a system that switches from the separation stages V103A and V105A to V103B and V105B, or vice versa.

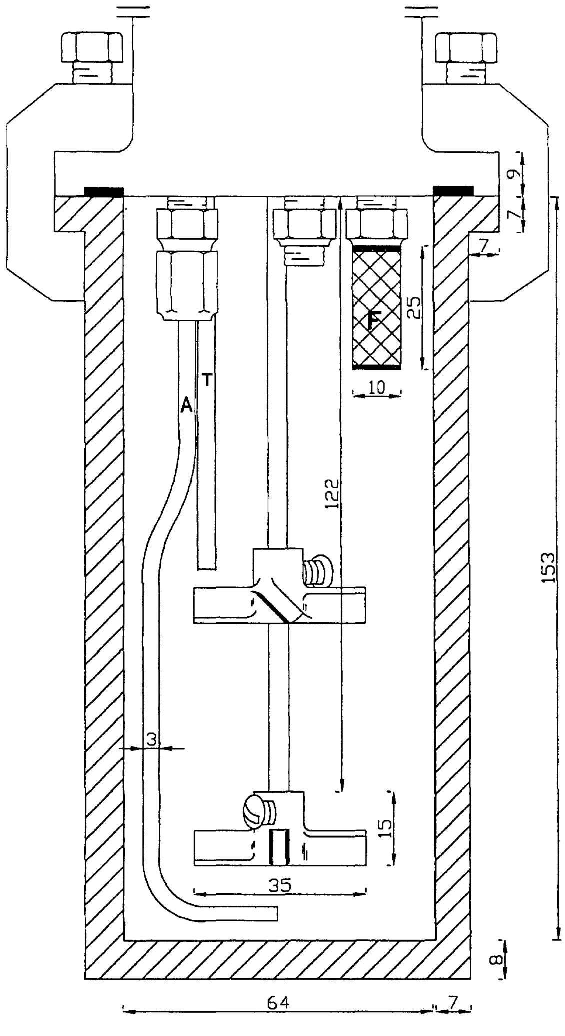

Fig. 1. Slurry reactor used for experiments SL-1 and SL-2. Measures are given in mm. A: sparger; T: thermocouple; F: filter.

The noncondensable gases are first analyzed on line by a gas chromatograph (mod. HP 5890) equipped with an HP Porapak Q column in series with a column Supelco Carboxen 1000 and a capillary column HP Al_2O_3-plot. The Porapak Q column is connected to a thermal conductivity detector to measure H_2, O_2, N_2, CO, CO_2, and CH_4. The column Supelco Carboxen 1000 and the capillary column HP Al_2O_3-plot are connected to a flame ionization detector to analyze olefins and paraffins in the range C_1–C_9. A sample of wax (ca. 30 g), and one of the liquid phases (ca. 0.5 cm^3) is collected periodically and analyzed off line with a gas chromatograph (mod. HP 5890 Series II), equipped with a capillary column Supelco SPB-1 for the wax and the liquid hydrocarbons, and a Chromapack fused silica column for the aqueous phase, connected to two flame ionization detectors. The waxes are dissolved in CS_2 before the analysis, whereas the aqueous phase is added with acetonitrile as an internal standard (7.5 μl per g of aqueous phase). This analysis procedure permits to collect and take into consideration all the FTS products.

Two experiments, named SL1 and SL2 were considered in this work: For run SL1 the reactor was loaded with 36.3 g of a 14.2% w/w Co/Al_2O_3 catalyst, suspended in 313 g of a commercial wax (SX70, provided by Shell). For run SL2 the reactor was loaded with 45 g of the same catalyst, initially suspended in 255 g of a C_{18} paraffin.

Before use, the catalyst is prereduced with pure H_2 (flow $= 5.56\ nm^3/s/g_{cat}$, 0.083 K/s from 398 K to 673 K, hold for 16 h) in a fixed bed reactor external to the slurry reactor and then loaded in the slurry reactor. Particular care is used not to reoxidize the catalyst with air during the loading operations. The CO stream is purified from the Fe carbonyls by adsorption on a molecular sieve trap and then mixed with H_2 and, during the startup procedure, with N_2, before entering the reactor.

A similar experiment was carried out on a fixed-bed reactor in an analogous rig operated at Politecnico di Milano (run FB1). In particular a co-feed experiment with 1-octene was performed and the presence of 1-octene and n-octane in the effluent stream was monitored during the run. Co-fed 1-octene was first purged from oxygen traces by a flow of Ar for ten minutes, kept in an inert atmosphere during the run, and then sent to the top of the reactor with an HPLC pump (Gilson mod. 302). The co-feeding line was heat-traced at 308 K. The gaseous and liquid mixture was then fed to the reaction section. The reactor was a stainless steel tube (ID = 10 mm, length = 0.8 m), internally coated with copper to prevent the formation of Fe-carbonyls, loaded with 3 g of the same Co-based catalyst, diluted 1:1 (vol/vol) with α-alumina. The reactor was placed inside a

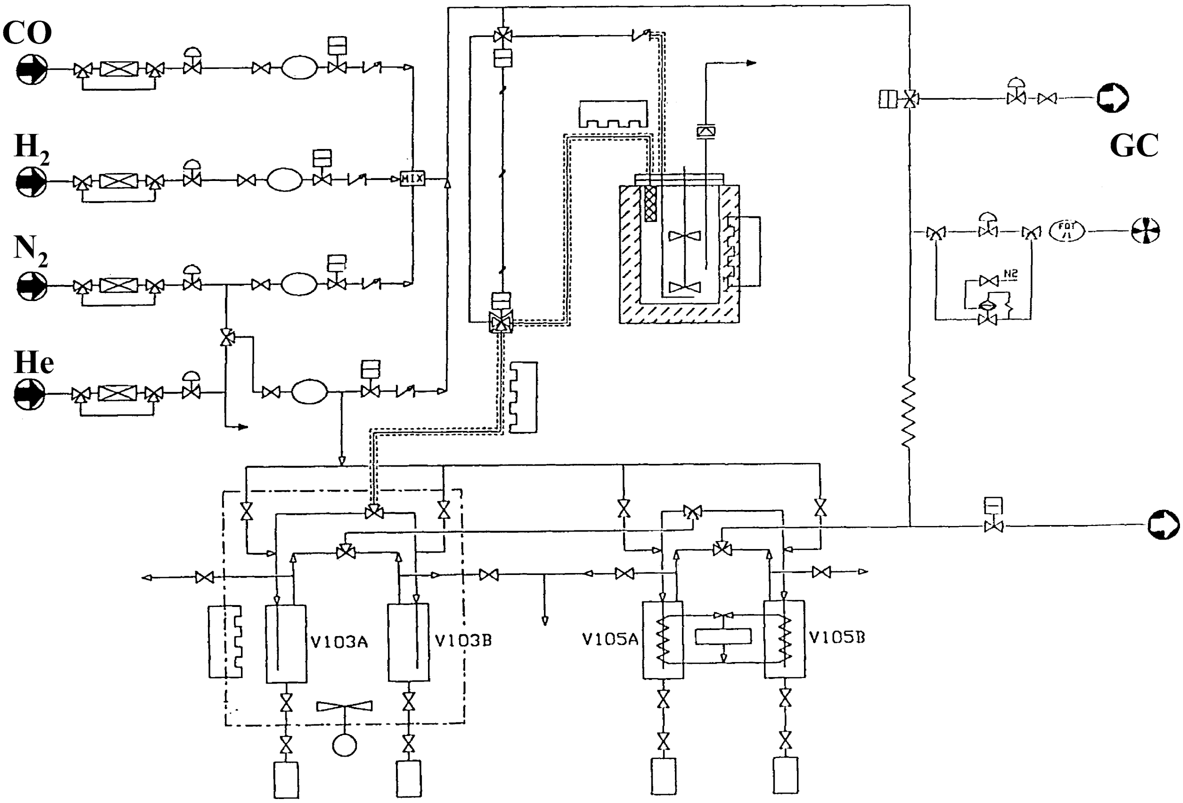

Fig. 2. Schematic of the unit used to collect experiments SL-1 and SL-2.

three-zone furnace to ensure an isothermal profile in the catalytic bed. In the upper part of the furnace the liquid vaporizes before entering the catalytic bed. The products and the nonconverted gases leaving the reactor are sent to the separation section. Water and the heavy hydrocarbon products are separated in a first separation stage, held at 378 K. Light hydrocarbons, the remaining water, and the alcoholic products are blocked in a second vessel, kept at 273 K. The noncondensable gases are sent to an on-line gas chromatograph (mod. HP 6890), whereas the solid and liquid products are analyzed off-line periodically on a dedicated gas chromatograph (mod. HP 6890). The on-line gas chromatograph is equipped with a molecular sieve (5 Å), an HP Al_2O_3-plot, and an HP Porapak columns. The columns are connected to a flame ionization detector and to a thermal conductivity detector. The off-line gas chromatograph is equipped with two capillary columns (HP-5) connected to a flame ionization detector. The analysis methods are similar to those described for the slurry unit.

The kinetic experiments were performed at 2.0 MPa, 490 K, GHSV = 2.5 $\mathrm{Nl/h/g_{cat}}$ for run SL1, GHSV = 2.0 $\mathrm{Nl/h/g_{cat}}$ for run SL2, and GHSV = 2.5 and 5.0 $\mathrm{Nl/h/g_{cat}}$ for run FB1, with an inlet H_2/CO molar ratio of 2, at a pressure of 2.0 MPa and temperature of 493 K. The units were operated for a total time of 895 h (run SL1), 1002 h (run SL2), and 2612 h (run FB1), during which CO conversion and product selectivity data were collected periodically. In particular the temporal evolution of the composition of the heavier hydrocarbons was monitored. Table 1 reports the operative conditions for the three experiments.

3. Results and discussion

The chromatogram representative of the initial liquid slurry loaded in the reactor before starting run SL1 is shown in Fig. 3a. The distribution presents a maximum in correspondence of the paraffin C_{33}, with a retention time of ca. 44 min. After 19 h of operation under reaction condi-

Table 1
Operative conditions for FTS runs

Run	GHSV ($\mathrm{Nl/h/g_{cat}}$)	H_2/ CO (mol/mol) at inlet	P (MPa)	T (K)	Duration (h)	Catalyst loading (g)	Initial liquid loading
SL1	2.5	2.0	2.0	493	895	36.2	SX70 (313 g)
SL2	2.0	2.0	2.0	493	1002	45.0	C_{18} paraffin (255 g)
FB1	2.5; 5.0	2.0	2.0	493	2212	3	

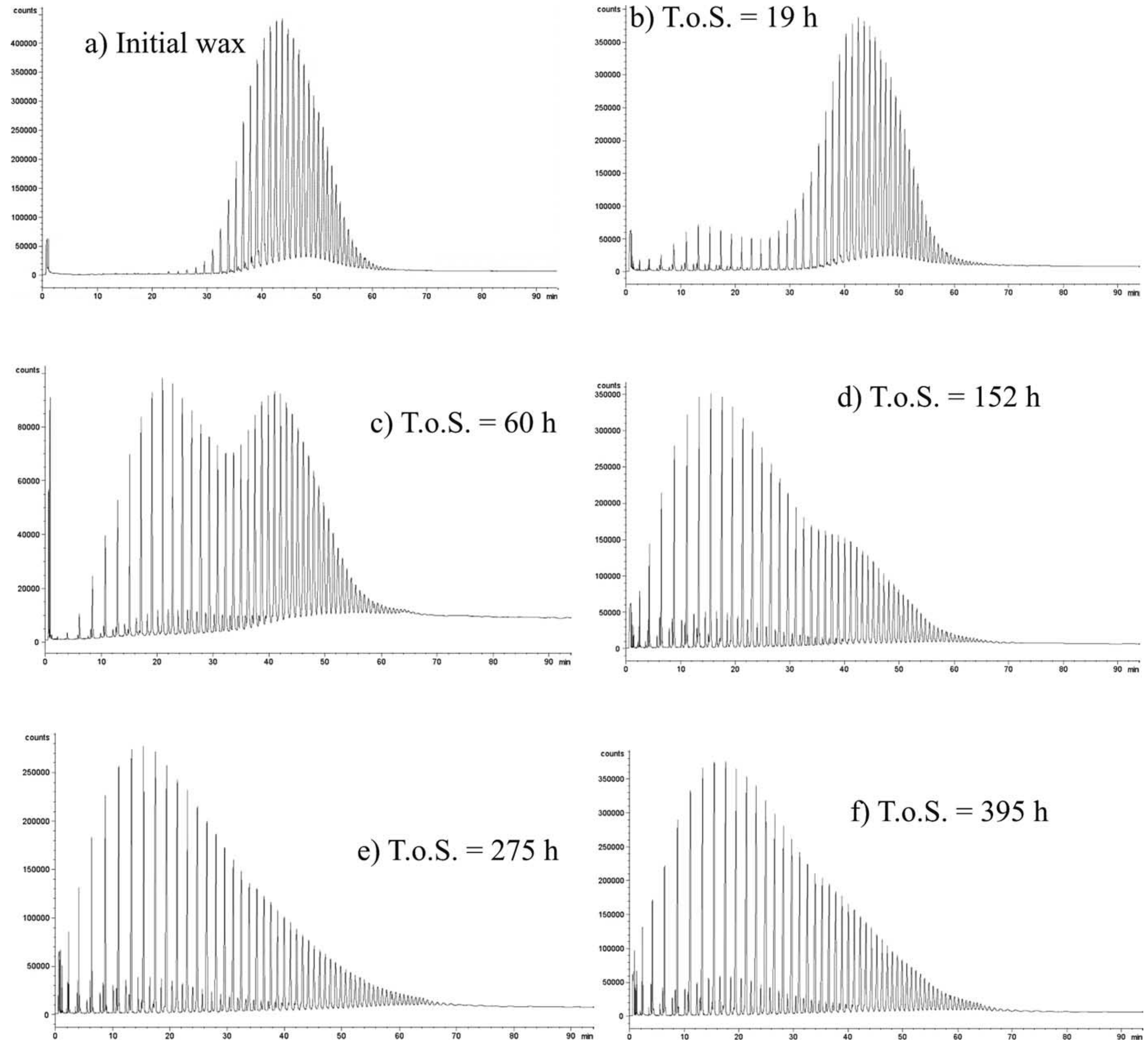

Fig. 3. Chromatograms of the wax collected downstream from the reactor for run SL1.

tions, the chromatogram of the condensed heavy products changes: in fact the obtained bimodal distribution derives from the superimposition of the initial slurry, with a maximum at C_{33}, and the wax produced in the first 19 h of reaction, with a maximum peak at ca. 15 min corresponding to C_{13} (Fig. 3b). At these conditions the CO conversion is 33.6% and the methane selectivity, estimated from the gas phase is 3.3%. The analyses of waxes collected after 60, 152, 275, and 395 h on stream confirmed that the longer the time on stream, the higher the dilution of the initial slurry with the new wax produced by the reaction (Figs. 3c–3f). After 60 h on stream the two peaks corresponding to the maxima of the distribution of the initial slurry and of the produced wax are of similar height (Fig. 3c). Only after 395 h of reaction does the wax analysis resemble the real distribution of heavy products, leading to a chromatogram with just one maximum at the retention time of ca. 15 min (Fig. 3f). The Anderson–Schulz–Flory distribution for heavy hydrocarbons is reported in Fig. 4 for different times on stream, which emphasizes the change in the wax composition with time. At the same time activity and selectivity data were collected, which are reported in Table 2. CO conversion achieves rapidly steady state (after 60 h), and then it begins to decline, probably due to a deactivation process; methane selectivity also reaches rapidly a constant value. On the contrary a longer time is necessary (about 440 h) for C_{5+} selectivity to achieve a constant value, its estimation being affected by the presence of the initial wax in the reactor. Table 2 also shows that the concentration of C_{33} paraffin in the

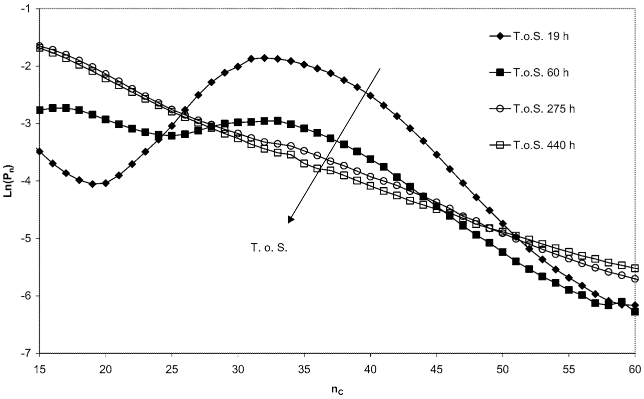

Fig. 4. Hydrocarbon distribution in the condensed solid product for run SL1 at different times on stream: (◆) 19 h; (■) 60 h; (○) 275 h; (□) 440 h.

total hydrocarbon products (w_{33}) decreases gradually with time on stream.

In a similar way, during run SL2 the presence of C_{18} paraffin, initially loaded in the reactor, was followed after startup of the unit. The chromatograms relative to collection of waxes at different times on stream, reported in Fig. 5, demonstrate that the peak relative to C_{18} paraffin (at retention time of about 24 min) decreases with time on stream and reaches its steady state value after 350–400 h. Kinetic data for run SL2, presented in Table 3, show that both methane and C_{5+} selectivities, as well as CO conversion, reach steady state rather quickly. As during run SL1, the slight decay of the CO conversion with time indicates deactivation of the catalyst. In this case in fact the presence of C_{18} only slightly affects the wax distribution. Hence the use of a single liquid product as a suspending medium for the catalyst in the slurry reactor seems to be a good technique to rapidly collect *total* selectivity to condensed products (C_{5+}), after the unit startup. Yet the concentration of *single* hydrocarbons changes with time on stream (as shown for instance in Table 3 for the concentration of paraffin C_{18} in the total amount of hydrocarbons products, w_{18}), due to the slow dilution of the C_{18} paraffin during the reaction (see Fig. 5). Hence monitoring the replacement of the initial liquid can be still utilized to gather important information for the understanding of the phenomena governing such a transient, as it will be shown in the following.

Table 2
Kinetic data for run SL1

Time on stream (h)	CO conversion (%)	CH_4 selectivity (%)	C_{5+} selectivity (%)	w_{33} (%)
0	–	–	–	6.9
19	33.6	3.3	89.3	5.1
60	43.0	7.4	58.7	1.7
107	44.9	7.0	67.1	0.8
152	42.3	6.8	63.2	1.4
223	37.9	8.1	70.6	1.0
275	38.6	7.6	70.8	1.2
319	39.1	7.6	75.6	0.9
395	36.2	8.1	70.1	0.9
440	35.4	8.2	75.5	1.0
463	34.9	8.1	75.7	1.1

Table 3
Kinetic data for run SL2

Time on stream (h)	CO conversion (%)	CH_4 selectivity (%)	C_{5+} selectivity (%)	w_{18} (%)
0	–	–	–	100.0
18	30.0	13.7	69.2	46.8
42	37.6	8.7	76.7	29.9
64	37.5	8.9	79.0	26.2
162	35.5	10.1	75.0	8.6
210	34.6	9.9	72.9	4.4
234	33.3	9.7	76.3	3.3
258	32.4	10.2	75.3	3.2
329	33.4	9.7	73.8	2.6
376	34.4	8.8	74.5	2.5
402	30.5	10.3	72.8	2.4
425	31.2	10.2	74.5	2.5
497	29.4	10.6	73.1	2.3
522	30.6	10.6	75.5	2.1

The time necessary to totally replace the initial liquid with the wax produced by FTS and thus collect *real* selectivity data can be modeled by a simple unsteady mass balance on the continuously stirred tank reactor for a single species, either if present in the initial liquid or not. For instance, consider a hydrocarbon product containing n carbon atoms,

$$\frac{\mathrm{d}m_n(t)}{\mathrm{d}t} = P_n - q_n(t), \tag{1}$$

where $m_n(t)$ is the mass of the species considered (g), present in the reactor at the time t (day), P_n its total productivity at steady state (g/day), and q_n the total amount of component n withdrawn from the reactor per unit time (g/day). It should be noticed that Eq. (1) holds *whatever liquid–vapor repartition* is attained inside the reactor.

The further development of the model is based on some simplifying assumptions, listed in the following.

(1) The transient is much longer than the time required for the rates of the reactions to adjust to the new conditions; in other words, the temporal evolution of the system is governed primarily by the replacement of the product mass contained in the reactor volume. Also, rates are almost independent of the liquid product composition.
(2) The productivity of any single species P_n (g/d), as well as the total hydrocarbon productivity P_{tot} (g/d), is regarded as constant during the transient, despite the slight deactivation of the catalyst.
(3) The total mass m_{tot} (g) (vapor and liquid) inside the reactor is constant in time. Since during the run the volume of the reaction medium is kept constant, as well as the catalyst load, this hypothesis is valid if liquid and gas holdups are constant, and if changes in the composition do not significantly modify the density of the liquid throughout the transient.

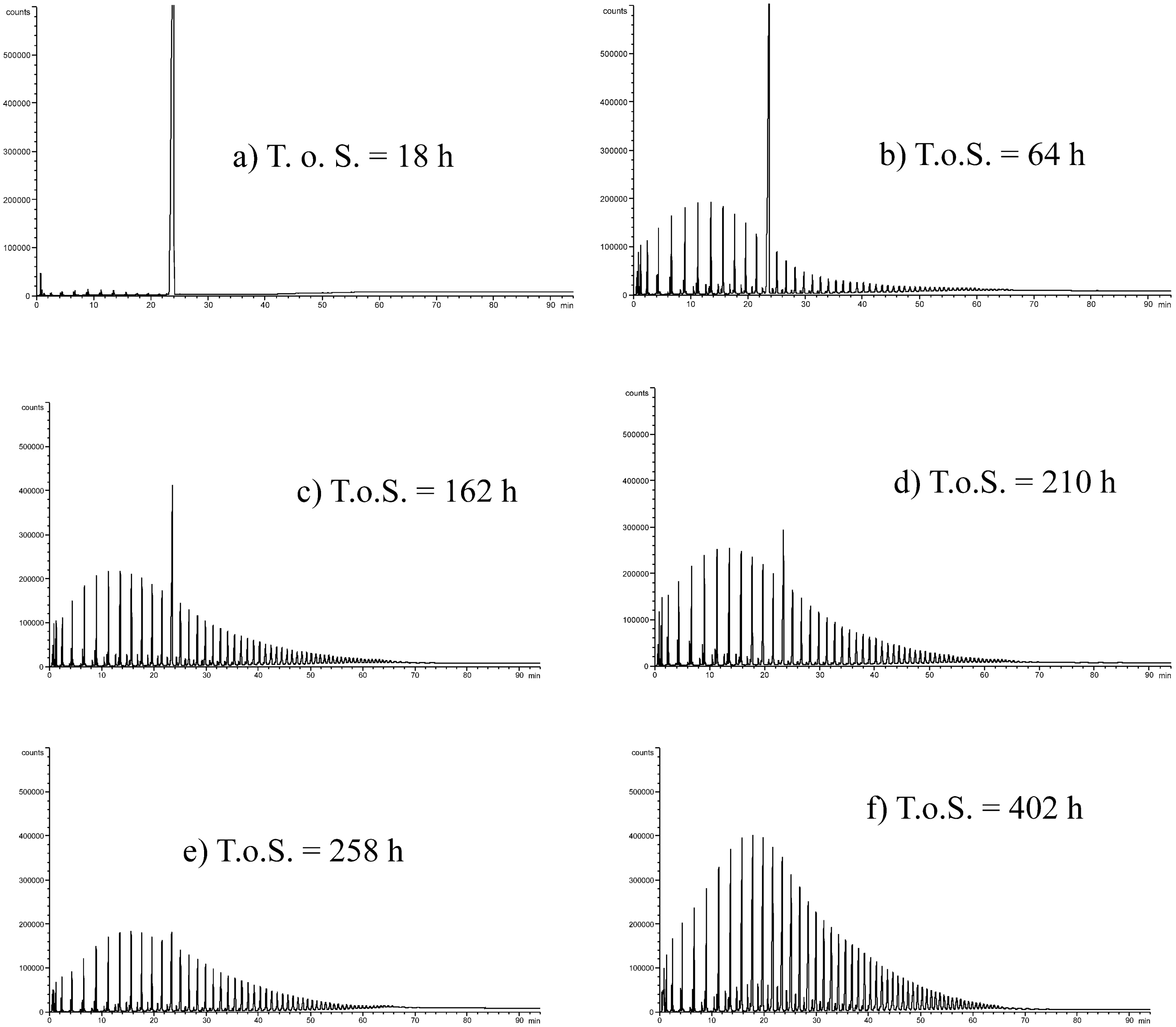

Fig. 5. Chromatograms of the wax collected downstream from the reactor for run SL2.

(4) The mass of gaseous hydrocarbons in the reactor is negligible with respect to the mass of the liquid ones. The mass of gas in the system is the sum of the gas dispersed in the liquid phase plus the gas in the upper part of the reactor, not occupied by the liquid. The two contributions has been evaluated separately:
   (a) The estimate of gas holdup in the liquid, according to [17], is less than 1%;
   (b) The liquid volume (360 cm^3) is one order of magnitude greater than the one occupied by the gas (36 cm^3). Even considering that all the gas volume is not composed by a mixture of hydrocarbons and unreacted CO and H_2, but is completely filled with a heavy gas, such as propane, the resulting gaseous mass (0.5 g) is much smaller than the liquid one (290 g).

   Being the gas holdup both in the liquid phase and in the upper part of the reactor much smaller than the liquid amount in the reactor, neglecting the vapor phase in the total evaluation of the total mass of hydrocarbons seems reasonable.

Under these assumptions, if $w_n\ (t)$ is the mass fraction of the component with n carbon atoms in the products, m_L (g) and m_V (g) are the total amount of liquid and vapor products, respectively, in the reactor at reaction conditions, and P_{tot} (g/day) is the total productivity, $m_n(t)$ and $q_n(t)$ become

$$m_n(t) = w_n(t) \cdot m_{tot} = w_n(t) \cdot (m_L + m_V) \cong w_n(t) \cdot m_L \quad (2)$$

(since the gas holdup is negligible)

$$q_n(t) = w_n(t) \cdot P_{tot}. \quad (3)$$

Eq. (1) then becomes

$$\frac{\mathrm{d}[m_\mathrm{L} \cdot w_n(t)]}{\mathrm{d}t} = P_n - P_\mathrm{tot} \cdot w_n(t). \tag{4}$$

Since m_L is regarded as a constant, Eq. (4) can be rewritten as

$$\frac{\mathrm{d}w_n(t)}{\mathrm{d}t} + \frac{P_\mathrm{tot}}{m_\mathrm{L}} w_n(t) = \frac{P_n}{m_\mathrm{L}}, \tag{5}$$

with the initial condition

$$w_n(t=0) = w_n^0. \tag{6}$$

The analytical solution of Eq. (5) with the initial condition (6) is

$$w_n(t) = \left(w_n^0 - \frac{P_n}{P_\mathrm{tot}}\right) \mathrm{e}^{-(P_\mathrm{tot}/m_\mathrm{L})t} + \frac{P_n}{P_\mathrm{tot}}. \tag{7}$$

It should be noted that when the transient is over $(t \to \infty)$ the concentration approaches the steady state concentration $P_n/P_\mathrm{tot} = w_n^\mathrm{SS}$, which can be deduced from the ASF plot at steady state. Accordingly the final form of the mass balance is conveniently rewritten as

$$\frac{w_n(t) - w_n^\mathrm{SS}}{w_n^0 - w_n^\mathrm{SS}} = \mathrm{e}^{-t/\tau}, \tag{8}$$

where the time constant τ is given by

$$\tau = \frac{m_\mathrm{L}}{P_\mathrm{tot}}. \tag{9}$$

It can be assumed that the transient is over when $w_n(t_\mathrm{TR}) - w_n^\mathrm{SS} = 0.01(w_n^0 - w_n^\mathrm{SS})$, leading to the calculation of a total transient time t_TR

$$t_\mathrm{TR} = 4.6 \cdot \tau. \tag{10}$$

Values of initial and steady state concentrations for species with different carbon numbers are reported in Tables 4 and 5 as derived from our experiments in the slurry reactor (runs SL1 and SL2). The total productivity P_tot is the one obtained at steady state, whereas m_L is the real mass of liquid present in the reactor, which is in principle different than the amount of liquid initially loaded in the reactor. The amount of liquid calculated from the dimensions of the reactor reported in Fig. 1, considering that the catalyst is suspended in the liquid, is about 360 cm^3, which, assuming a density of about 0.8 g/cm^3 leads to $m_\mathrm{L} \sim 290$ g in the reactor during the transient. A similar liquid holdup was also estimated by linearizing Eq. (8) for given species, evaluating τ from the slope of the plot

$$\ln\left[\frac{w_n(t) - w_n^\mathrm{SS}}{w_n^0 - w_n^\mathrm{SS}}\right]$$

versus time, and calculating m_L through Eq. (9), once the value of P_tot is known. The values of P_tot measured, the estimates of τ and the resulting values of m_L for the runs SL-1 and SL-2 are listed in Table 6. It is worth noticing that the masses of liquid estimated for the two experiments are very similar and consistent with the amount calculated on a geometric basis only. Table 6 also shows the time of the transient t_TR calculated from Eq. (10).

Table 4
Parameters for Eq. (8) for run SL1

n	w_0 (%)	w_n^SS (%)
15	0.00	2.79
20	0.04	2.18
30	5.19	1.15
33	6.88	0.99
40	4.40	0.67

The estimates of the concentration transient in the products of species having different chain lengths for run SL1 and for run SL2, given the values of τ reported in Table 6, at different times are reported in Figs. 6 and 7 respectively, and compared with the experimental values. The agreement between calculated and experimental concentrations for both experiments is confirmed by the low values of the average relative errors (average $|(w_n^\mathrm{CALC} - w_n^\mathrm{EXP})/w_n^\mathrm{EXP}|$) being 23.3% for run SL1 and 17.8% for run SL2. It should be stressed that the reported errors derive from calculated values of concentrations, on *a purely predictive basis*. The slight overestimation of the concentration of C_{18} in the first period of the transient for run SL-2 can be ascribed to the fact that at the startup the reactor was loaded with 255 g of liquid only, instead of 324.2 (see Table 6): in fact in this short period the synthesis products do not leave the reactor but build up in the system, filling the reactor and diluting the species C_{18}.

Given these premises Eq. (8) can be used to estimate the time needed to collect reliable data for heavy products selectivity in a slurry reactor, when m_L, P_tot, w_n^0, and w_n^SS are known. In general, according to Eq. (9), the time t_TR needed to reach a steady value of concentration increases with the constant τ. Hence the transient will be faster for a smaller amount of liquid present in the reactor (m_L) and for a greater total productivity (P_tot). The values of t_TR estimated for run SL1 and SL2 are 9.3 days and 10.7 days respectively. Since the equation here presented accounts for the *total* productivity of a condensable species, it can be applicable to describe startup transients, as well as transients following a change in reaction conditions, which result in a modification of product selectivity, regardless of the liquid and the vapor phases being at equilibrium or not.

In view of the results herein presented, it is clear that a lab-scale slurry reactor operated under typical FTS

Table 5
Parameters for Eq. (8) for run SL2

n	w_0 (%)	w_n^SS (%)
15	0.00	2.82
18	100.00	1.97
20	0.00	1.97
30	0.00	0.90
40	0.00	0.53

Table 6
Parameters for Eq. (8) for runs SL1 and SL2

Run	P_{tot} (g/d)	τ (d)[a]	m_{L} (g)	t_{TR} (d)
SL1	156.8	2.0[b]	317.5	9.3
SL2	139.5	2.3[c]	324.2	10.7

[a] τ was estimated by the slope of the linearized plot of Eq. (8).
[b] Estimated from the transient of C_{33}.
[c] Estimated from the transient of C_{18}.

conditions (i.e., $m_{\text{L}} = 350 - 700$ g, $P_{\text{tot}} = 100 - 400$ g/d) the time necessary to gain data representative of FTS products after startup or after a change in the reaction conditions is very likely to be about one week.

On the other hand, it is evident that, when a fixed-bed reactor (FBR) is used on a laboratory scale to collect data relative to high molecular weight hydrocarbons, the time t_{TR} to reach steady state after a variation in the reaction settings must be much shorter than that in a slurry reactor because the volume to be replaced by the liquid products is significantly smaller. In order to evaluate the response time for this system, two-step changes to the feed composition of the FBR unit were applied during run FB1, and the corresponding composition transient at the reactor outlet was monitored. The results are shown in Fig. 8. The first step was a change in the set of the inlet concentration of co-fed 1-octene, obtained by increasing the syngas space velocity from 2.5 to 5.0 Nl/h/g_{cat}, while keeping the 1-octene flow constant (5 µl/min). The second step change resulted from the shut off of the 1-octene stream. It is apparent from Fig. 8 that the response in the fixed bed system is much faster than in the slurry system, the 1-octene outlet concentration reaching a steady state level after about two days. A rough estimate of the response to such an instantaneous change can be made assuming differential plug flow fluid dynamics, and applying Eq. (8). Figure 8 shows a comparison of the experimental concentrations of 1-octene in the total products with the ones predicted by Eq. (8). The resulting average relative error is 8.2%. The liquid mass (m_{L}) used in Eq. (8) was conservatively calculated by supposing that all the inter and intraparticle voids of the bed are completely filled with wax. Given a bed void fraction of 0.4, a catalyst pore volume of 0.35 $\text{cm}^3/g_{\text{cat}}$, and 30 cm of the reactor filled with nonporous alumina, a value of $m_{\text{L}} = 1.3$ g results. Also the liquid holdup of the lines downstream the reactor before the wax collection point was taken into account, since it is comparable with the amount of liquid in the bed. An estimate of such a holdup leads to a total value of $m_{\text{L}} = 4.6$ g. Also in this case, the vapor mass was neglected, being the liquid density two orders of magnitude greater than the vapor one. The resulting t_{TR} is 1.9 days, consistently with the experimental data. The transient time estimated for run FB1 is indeed much smaller than the ones calculated for runs SL1 and SL2. As a matter of fact an FBR presents a lower liquid holdup per gram of catalyst than a slurry reactor, so that a lower t_{TR} derives. Table 6 compares the values of m_{L}, P_{tot}, τ, and t_{TR} for runs SL1 and SL2. The use of fixed-bed reactors seems therefore to be preferred when heavy product selectivity is the most important response expected for the experiment.

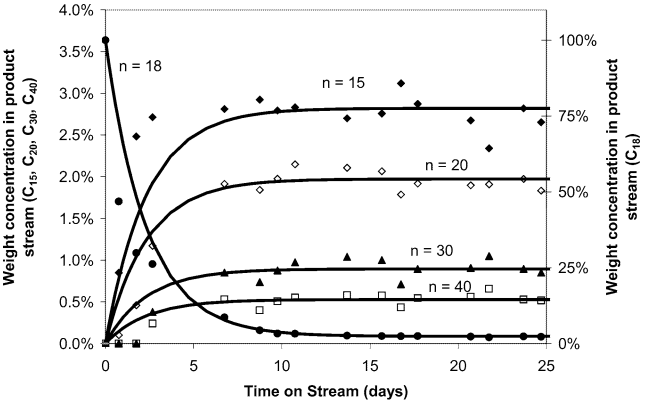

Fig. 7. Evolution of paraffin C_{15} (◆), C_{18} (●), C_{20} (◇), C_{30} (▲), C_{40} (□) in the waxy products with time, for run SL1. Solid marks experimental, line calculated.

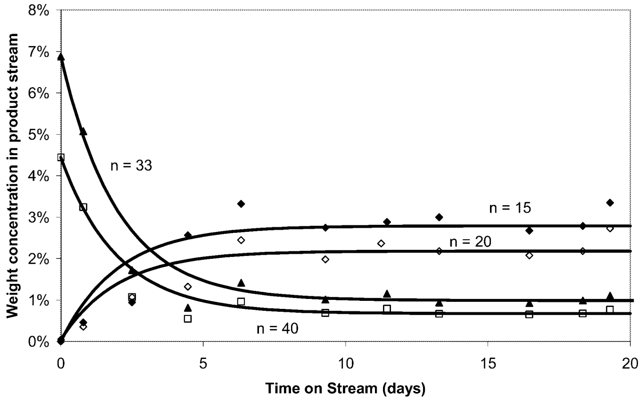

Fig. 6. Evolution of paraffin C_{15} (◆), C_{20} (◇), C_{33} (▲), C_{40} (□) in the waxy products with time, for run SL1. Solid marks experimental, line calculated.

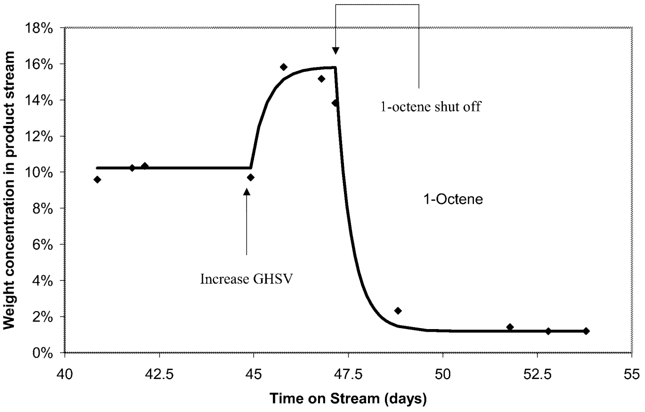

Fig. 8. Evolution of olefin C8 in the products with time for run FB1 after two step changes at the inlet for 1-octene. Solid marks experimental, line calculated.

4. Conclusions

The problem of collecting data relative to heavy products selectivity during Fischer–Tropsch synthesis in a continuously stirred tank and in a fixed bed reactor was here assessed and studied. The time necessary to achieve steady state selectivity to long chain molecules was monitored and modeled. The application of unsteady mass balances to one species only leads to a simple yet effective equation to estimate the transient time, needed to completely replace the liquid. The model herein presented does not imply any assumption on the phase repartition of the products inside the reactor, since it accounts for the total productivity of a considered species. The model was validated by applying it to two experiments carried out in a slurry reactor loaded with two different amounts of catalyst and with two different kinds of liquid used to initially suspend the catalyst. Furthermore the model approximately predicted fixed-bed reactor data as well, proving to be a powerful tool for the comparison of the two systems in the estimate of the time necessary to reach steady state.

The application of this equation shows that, on a laboratory scale, collection of data relative to high-molecular-weight products is much more rapid in a fixed-bed reactor rather than in a slurry reactor, since the ratio of the amount of liquid to be replaced to the total hydrocarbon productivity during the experiments is usually much smaller.

The approach herein presented can find important applications also in the evaluation of transient times associated with startups and changes in the operating conditions of industrial scale slurry reactors.

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