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# Choice of laboratory scale reactors for HDT kinetic studies or catalyst tests

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**Abstract**

Making a choice of laboratory scale reactor for kinetic studies or catalyst tests is not an easy task above all in case of three-phase reactions. In this paper, four technologies are discussed pointing up their advantages and their drawbacks. The four technologies are packed-bed reactor in downflow or upflow modes, stirred tank reactors with crushed catalyst and stirred tank reactors with catalytic basket in batch, semi-batch or continuous modes.

Finally comparisons of the technologies in terms of gas–liquid and liquid–solid mass transfers are given. Using those criteria, we observe that slurry stirred tank reactors are the best systems to test crushed catalyst. Moreover, stirred tank reactors with catalytic basket equipped with gas inducing impeller are good tools to test shaped catalysts if operating conditions are favorable to operate the turbine efficiently.

*Keywords:* Laboratory scale reactors; Mass transfer; Trickle bed; Stirred tank; Catalytic basket

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## 1. Introduction

Due to the drastic change of oil standards in many developed countries, the emphasis on multiphase catalyzed reactions in oil fraction refining is growing. Performance improvement of actual hydroprocessing units requires determining the real limitation of this process: chemical engineering or catalyst? Too often, the chemist is focused on catalysts: their preparations, activities, kinetics, optimal forms, poisons or deactivation precursors that might deactivate them. And too often, the chemical engineer is only focused on industrial units with an obsessional idea in mind: how to improve and/or to revamp an existing process, how to bring the reactants in contact efficiently and to reduce the impact of inhibitors (in the case of hydrotreatment reactions). However, more interplays between them would lead to avoid errors done by both parts and to know, in a particular case, which of them can really improve the process. Even if chemists are only interested in improving catalyst activities and engineers in choosing the efficient catalyst form, both of them require intrinsic reaction rates: the former in order to discriminate between two mechanisms, the latter to evaluate the industrial reactor performances. But sometimes, the choice of laboratory scale reactor in order to measure intrinsic reaction rates or to test catalysts does not depend on a scientific approach but more on availabilities of an existing set-up or reactors in laboratory drawers. In the latter case, the risks to use a reactor in an inappropriate range and the resulting consequences are important for a given catalyst.

The laboratory reactor cannot be a reduced scale of the industrial device. If number like weight hourly space velocity (WHSV) may be used, they do not take into account change in hydrodynamics and particularly in turbulence. So the best way to design a new reactor for an given catalyst or a new catalyst for a given reactor is to measure intrinsic kinetics first and then to simulate the conversion using an

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|---|---|
| $a_L$ | specific gas–liquid interfacial area |
| $a_S$ | specific liquid–solid interfacial area |
| $d_p$ | particle diameter |
| $d_t$ | tube diameter |
| $k_L$ | gas–liquid transfer coefficients |
| $k_S$ | liquid–solid transfer coefficients |
| $m_c$ | catalyst mass |
| $N$ | rotation speed ($s^{-1}$) |
| $N_S$ | minimum turbine speed for two-phase stirred tank reactor ($s^{-1}$) |
| $N_{SG}$ | minimum turbine speed for three-phase stirred tank reactor ($s^{-1}$) |

industrial reactor model taking into account chemical and physical processes.

In this paper, we will focus on the points, which are important and must be looked at closely, and the traps, which must be avoided in order to obtain experimental intrinsic reaction rates for petroleum fraction hydrotreatment reactions. In general ways, whether the reactor is used to determine intrinsic kinetic parameters or simply to compare catalyst activities, the approach to choosing a ‘‘good’’ laboratory scale reactor is quite the same [1]:

- It is better to use ‘‘ideal reactor’’ (ideal plug flow or perfect mixing reactors for instance) in order to use simple mathematical models to describe mass, energy and momentum balances.
- The experiment conditions must be chosen in order that the transport resistances are insignificant and do not limit the catalyst performances.
- The thermodynamic equilibriums must also be taken into account.

Before the measurement of kinetic parameters, it is necessary to verify the ‘‘reactor ideality’’. An usual method to obtain information on macroscopic flow pattern and transfer coefficients simultaneously is to determine the residence-time distribution (RTD) using tracing method. This method has been widely detailed by Danckwerts [2]. It consists in following specific molecules introduced in reactants through the reactor flows in continuous mode. An ideal tracer should not change the flow pattern and so have physical properties the closest to those of reactants and products. In many studies, heat and mass transfers have been characterized using mock up and solvents at ambient temperature and atmospheric pressure simulating reactants in reaction conditions. Some easy tracing experiments could however be carried out on reaction conditions using few means, allowing accurate estimates of flow pattern or transport phenomena necessary to process experimental data efficiently. An easy experiment would consist in adding a normal paraffin to a gas oil (for instance to test catalyst in HDS reactions), using two pumps to feed the reactor (the first one feeding the pure gas oil and the second, the gas oil containing the normal paraffin) and following the outlet gas oil composition after switching the pump flows.

In refining, petroleum fraction hydrotreatment involves three-phase catalytic reactions (gas–liquid–solid). The three phases considered above are: the gas phase which is hydrogen containing hydrogen sulfide ($H_2S$), ammonia ($NH_3$) and some light hydrocarbons, the liquid phase which is gas oil or heavier or lighter cuts, and the solid phase which is the catalyst. Hydrotreatment reactions take place on the catalyst through the continuous liquid phase. Thus, determination of intrinsic kinetic parameters requires knowledge of liquid concentrations of reactants and products in reaction conditions. The best way is to separate liquid and gas flows in reaction conditions and to analyze compositions of each flow separately. Nevertheless, on the bench scale, it is not so easy to operate separation processes under high pressures and temperatures. Then, the separation processes operate often under high pressure but ambient temperature that changes hydrogen, hydrogen sulfide and ammonia solubilities. In that case, calculations of liquid–vapor equilibrium using state equations are required to estimate a posteriori liquid concentrations in the reactor [3]. Another method consists in sampling liquid and gas phases into the reactor. It can be used for stirred tank reactors wherein reactions are carried out under reasonable pressures but it is unrealistic for plug flow reactors. In all cases, efficient analysis apparatus and methods are required.

Moreover, determination of intrinsic kinetic parameters implies that transport times must be much shorter than reaction characteristic times. Catalyzed hydrotreatment reactions being carried out in three-phase systems on extruded catalysts, all transport phenomena into phases and between them should theoretically be considered i.e. gas–liquid, gas–solid and liquid–solid interphase limitations and intraparticle limitations. If stirred tank reactor is ideal, the macromixing inside reactor is perfect and both gas and liquid phases are homogeneous, so we can assume that the intraphase limitations are insignificant. In hydrotreatment, the phase (gas or liquid) in which the kinetics is measured is relevant; actually some differences between HDS kinetic parameters obtained from gas phase or liquid phase measurements have been explained by differences in gas–solid and liquid–solid adsorption [4]. Simultaneous gas–solid and liquid–solid contacts should be avoided. Then reactors to study HDT kinetics or to test catalysts are designed or operated in order to avoid this drawback. Consequently, only gas–liquid and liquid–solid transfers will be developed below. Regarding intraparticle transport, the problem is slightly different. Intraparticle transport is only linked to shapes, sizes and internal structures of catalyst and does not depend on neither the reactor performances, nor gas or liquid flows, contrary to extraparticle transport. Therefore, to rule out this hypothetic drawback, the main used approach is to carry out experiments using crushed catalyst. But catalyst crushing can lead to change catalytic properties: structure, composition and not to simplify the experimental processing.

Another approach is to carry out experiments using industrial or shaped catalyst, to determine apparent catalyst activity and to use classical method (Weisz modulus estimation) to estimate the transport regime in which catalyst is tested. Moreover, it is important to keep in mind that shapes and sizes of catalyst can change flow regime in small three-phase laboratory reactors, particularly the plug flow reactor.

In a general review, Perego and Peratello [5] have presented choice of laboratory catalytic reactors to estimate kinetic parameters and have classified reactors by their hydrodynamic behavior (row) and their operation modes (column) (Fig. 1). They based their analysis on a laboratory reactor classification suggested by Anderson and Pratt [6]. Regarding Perego's reactor classification, only three technologies are available for three-phase reactions: stirred tank reactors with slurry and spinning or stationary basket and fixed-bed reactor. Fixed-bed reactor operates obviously in continuous mode, but stirred tank reactors are proposed in all modes: batch, semi-batch and continuous. In the continuation, those reactors will be discussed; their general advantages and drawbacks will be underlined and some details on physical parameters (transport, wetting,. . .) will be given.

Regarding hydrotreating kinetic studies, the most used reactors are co-current upflow or downflow three-phase packed-bed reactors and three-phase stirred tank reactors with crushed catalyst [7–9]. The stirred tank reactors in batch or semi-batch mode are often preferred for their easy use and the low cost they induce, though trickle bed reactors are sometimes considered as ‘‘perfect’’ scale model of industrial unit. Those two types of reactors are specially presented afterwards. Then, some characteristics of stirred tank reactors with catalytic basket are presented. Those reactors, normally designed for kinetics studies, aren't often used in this aim. However, they can be of great interest.

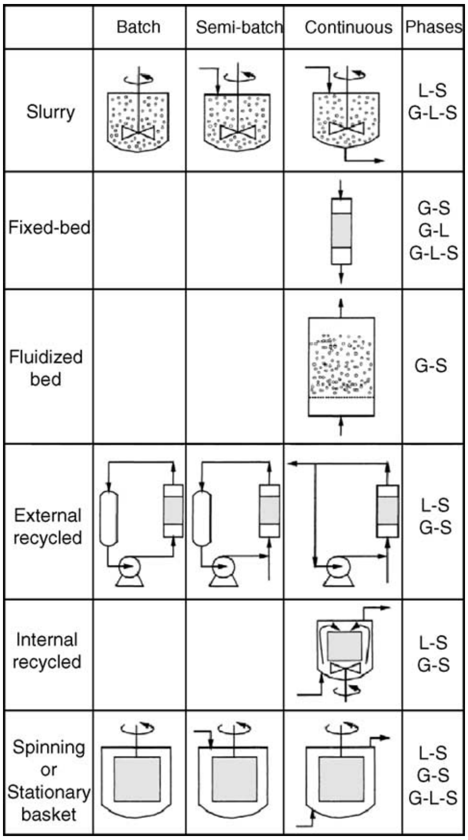

Fig. 1. Common laboratory reactors: operation modes and reacting system (L: liquid, G: gas, S: solid) [5] (Reprinted from Catal. Today, Vol. 52, Perego and Peratello, ‘‘Experimental methods in catalytic kinetics’’, Pages 133–145, Copyright (1999), with permission from Elsevier).

## 2. Catalytic packed-bed reactors for gas–liquid–solid systems

This type of reactors are often used in kinetic studies or even more catalytic tests. The catalyst weights are ranging between some dozens of grams and some milligrams (for instance about 30 g of catalyst [9], few grams of catalyst [8,10], less than 10 mg of catalyst [11,12]). Those reactors can be used in co-current upflow or downflow modes. Their main drawback for kinetics studies is the fact they are integral reactors: sampling gas or liquid fractions at several points along the catalyst bed being impossible for three-phase reactions, no direct kinetic measurements are available. However, they allow to test catalyst pellets and to follow a possible deactivation. The only way to obtain kinetics information is to assume a kinetic model, to adjust its parameters by integrating mass balance equations along the catalytic bed and to compare the computed results to experimental results (at various flow rates, pressures, temperatures, . . .). If the first kinetic model is not adequate, a second may be proposed. This method could be long and not very accurate for kinetic model determination. If trickle-bed technology is widely used in chemical industries, known to be reliable and allows to treat important flows, its use in laboratory scale is quite controversial. But due to the difference in catalyst quantity and the very low ratio $d_t/d_p$ obtained with commercial catalyst pellets in laboratory scale reactor, hydrodynamics and performances of both reactors (laboratory scale and industrial scale) are very difficult to compare. The cited reasons are poor wetting of catalyst and higher backmixing of liquid in small-scale reactors [13,14]. In order to improve trickle flow regime and to generate reliable data, some researchers proposed to dilute catalyst with smaller inert particles [13,15,16]. The use of three-phase reactor in upflow mode was also another solutions to improve catalyst wetting and obtain reliable data. But contradictions exist between two groups of researchers, in favor of bed dilution or of upflow operations. This controversy has been widely reviewed by Dudukovic et al. [17]. To bring the researchers to agreement, Bej et al. [7] have studied the effect of diluent size on the performance of a micro-scale packed-bed three-phase reactor in upflow and downflow modes of operation. The studied reaction was HDS of gas oil on a trilobe-shaped commercial catalyst. They have also used the specific procedure to load in the reactor proposed by Al-Dahhan et al. [16]. Their main results are presented in Fig. 2. Their experiments were conducted in a stainless tube with an internal diameter of 13 mm and length of 300 mm. About 5 ml catalyst and an equal volume of inert (SiC) were used in each experiment. Their conclusions were the following ones: the efficiency of a micro-scale multiphase packed-bed reactor in its upflow and downflow operations was dependent on the size of diluent used along with the catalyst, level of space velocities of gas oil and the hydrogen/gas oil ratio. Upflow operation using larger size of diluent (0.77 mm) in combination with lower space velocities of gas oil showed comparatively better performance than that with downflow operation. However, use of small size of diluent (0.19 mm) gave better reactor behavior with downflow operation. They also suggested that the increasing conversion with higher gas oil flow rate is linked to the reduction of axial backmixing of liquid. Moreover, the reactor performance for upflow operation was dependent on hydrogen/gas oil ratio whereas for downflow operation, it was almost independent on this ratio. In another papers, Castañeda et al. [18], following the same approach, using the same type of reactor but using larger diluent particles (between 1.4 and 2.3 mm in diameter), found quite similar results. They concluded also that the upflow operation is better than the downflow. But they also concluded that HDS conversions were the same for upflow and downflow operations when the reaction was studied at lower LHSV and higher temperature and that the use of the proper size of diluents can minimize the maldistribution of liquid. For Bej et al. [7], it is better to dilute catalyst with particles as small as possible to maintain low pressure drop.

Another drawback of three-phase packed-bed reactors for kinetics studies is the impossibility to vary gas and liquid flows in large ranges without risk of hydrodynamics changes in the catalyst bed. Bej et al. [7] have confirmed this fact when they concluded that the reactor performance for upflow and downflow operations was dependent on liquid flow and for upflow operation was dependent on hydrogen/gas oil ratio. Moreover, only the inlet hydrogen/gas oil ratio can be controlled, the outlet hydrogen/gas oil ratio depends on HDT conversion.

Regarding gas–liquid ($k_L$) and liquid–solid ($k_S$) transfer coefficients and interfacial area ($a_L$) and the others parameters characterizing this kind of reactors, the number of correlations available in literature allowing to estimate them is really amazing. The new review of Dudukovic et al. [17] shows clearly the difficulty to find correct correlations to estimate $k_L$ and $k_S$ for a laboratory scale reactor. Some of these correlations have been estimated using water and air as fluids in larger reactors in order to be applied in industrial reactors. For gas oil and hydrogen at HDT temperatures and pressures in small reactors (trickle-bed reactors or upflow packed bubble columns), no validated correlation exists in this system. Obviously, those coefficients should be higher for gas oil and hydrogen than for water and air (due to their physical properties). In transport correlations, any physical properties other than interfacial tension or possibly viscosity are not used to describe the foam nature of liquid phase. However, databases contain as many results with foaming compounds as with other compounds. Interfacial tension and viscosity being not enough to differentiate those liquids, results from correlations have to be used with precaution. Presently, nobody can precisely predict what are the

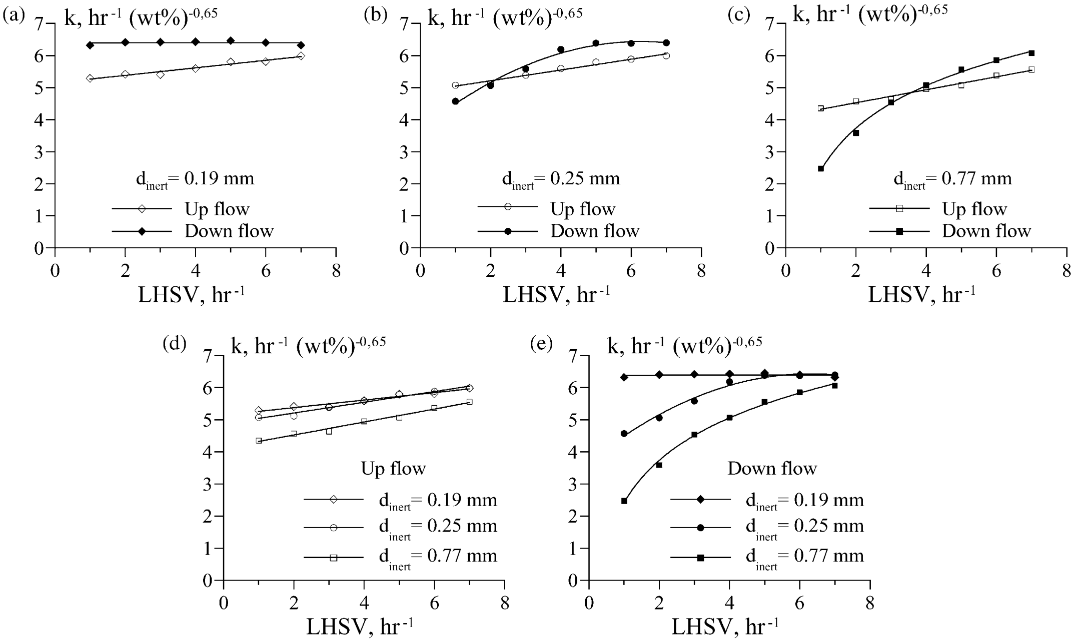

Fig. 2. Effect of LHSV on apparent rate constant of HDS in catalytic packed-bed reactor at a temperature of 340 °C and a hydrogen/gas oil ratio of 500 l/l (a) for a diluent size of 0.19 mm, (b) for a diluent size of 0.25 mm, (c) for a diluent size of 0.77 mm and (d) for upflow mode and (e) downflow mode [7].

experimental conditions to use to conduct reaction in chemical regime. However, some very useful tools are available on Larachi's web site [19]. One of them allows to estimate heat and mass transfer coefficients in upflow and downflow three-phase packed beds.

Regarding the micro-structured reactors, Losey et al. [11] measured global transfer coefficients using hydrogenation of cyclohexene in a micro-channel filled with 4 mg of a $Pt/Al_2O_3$ crushed catalyst. The order of magnitude of the overall mass transfer coefficient was between 1 and 15 $s^{-1}$. They observed the same flow patterns than in a classical three-phase packed-bed, except for the flow transition point that is moved towards low superficial mass velocities and low L/G ratios. In another work, Abdallah et al. [12] measured also global transfer coefficients performing hydrogenation of α-methylstyrene on 10 mg $Pt/Al_2O_3$ wash-coated catalyst, and they found the same order of magnitude for global mass transfer coefficients. Such values are more than two orders of magnitude larger than the values reported for laboratory trickled-bed reactor systems. Those reactors being still developed, it will be interesting to follow their technical progress in the future.

## 3. Multiphase catalytic stirred tank reactors

Multiphase catalytic stirred tank reactors can be used in batch, semi-batch or continuous modes. In those reactors, catalysts can be tested either crushed (slurry), or contained in a basket. In hydrotreating reactions, some papers can be found about kinetic studies using stirred tank reactors in all modes [20,21]. The most used reactor is the semi-batch reactor wherein pure hydrogen is introduced in continuous mode in order to maintain the total pressure constant and liquid phase and crushed catalyst are in batch mode. In all modes, the catalyst particles are totally wet and the liquid phase provides a liquid layer around them in order to avoid deactivation by fast coke formation. Moreover, for exothermic reactions, temperature is more homogeneous due to heat capacity and thermal conductivity higher in the liquid than in the gas.

In the continuation, we have not classified stirred tank reactors according to their operation modes but according to catalyst utilization (slurry or catalytic basket). Except for reactors with gas phase in batch mode, mass and heat transfers occurring in tanks can be considered independent of flow modes. In hydrotreatment, due to the $H_2S$ and $NH_3$ inhibitions, gas and liquid batch reactors are never used. Therefore, we have not dealt with this type of mode of operation in the continuation.

For kinetic studies, batch or continuous modes for liquid do not have same advantages or drawbacks. Like packed-bed reactors, batch reactors are integral reactors. But more information is available for batch reactors than for packed-bed reactors. For instance, reactant concentration profiles versus time can be obtained. Thus, to obtain instantaneous reaction rates, it is possible to derivate all concentration profiles at once. An other way consists in proceeding with the same methods as the ones used for packed-bed reactors: to speculate about an a priori reaction scheme, to assume kinetic laws, to integrate mass and heat balances, to draw a comparison between experimental and calculated data and finally, to modify reaction scheme if the results are unsatisfactory. Some difficulties are added to this drawback if catalyst induction time or deactivation takes place in the reaction scheme. To avoid this drawback, some authors prefer to estimate kinetic laws and parameters using initial reaction rates (i.e. at zero of the reaction time). Some concentrations of intermediate products being equal to zero at this time, this way allows to estimate kinetic and adsorption parameter ratios without any assumption about reaction scheme. But, the uncertainty on zero of reaction time can lead to make important error on estimated reaction rate. A crafty procedure would consist in carrying out a stirred tank reactor in continuous mode, and switching off the inlet and outlet flows after the system in continuous mode is stable. In this case, the system would be implemented in batch mode and all initial experimental data would be known. As for stirred tank reactors operating in continuous mode, they are differential. Reaction rates can simply be obtained by subtraction between inlet and outlet molecular flows. Insofar as concentrations inside the reactor are equal to outlet concentrations, the kinetic parameters can be easily estimated. Those reactors are practical for catalyst deactivation studies and might allow to show catalyst induction time. But it is not so easy to employ this kind of reactor using crushed catalyst, due to the possibly loss of catalyst in the outlet tube, its deposition on the bottom and its agglomeration behind the baffles.

In comparison with continuous mode, the batch mode has a great advantage: the cost of experiments. A liquid volume equal to the reactor volume is only consumed during each experiment, while in continuous mode, it is necessary to wait for at least five times the time on stream between two condition changes to be sure that the process is effectively stabilized. Then, the liquid volume consumed during each experiment is equivalent to five times the reactor volume. For a packed-bed reactor, it is necessary to wait for one times the time on stream approximately. Moreover, continuous mode implies to invest in added equipments like pumps, separation processes, flowmeters, ...

In spite of their respective advantages and drawbacks in modes of operation, it is interesting to show the reactor performances on the mass transport using crushed catalyst or catalytic baskets.

### 3.1. Stirred tank reactor with crushed catalyst (slurry)

The literature on stirred tank reactors with crushed catalyst is very extensive. Despite reactor widespread use and extensive literature, the research on stirred tank behaviors remains active. This is due to the fact that the available correlations are not able to exactly represent hydrodynamics and transfers in the laboratory reactor you intend to use. Correlations do not always take into account the whole structure of reactors (for example: baffle number and location, special blades on the turbine, gas inlet configuration,. . .) and they have too often been determined using mock up bigger than one liter. Moreover, correlations allowing to calculate gas holdup [22], gas–liquid [22–25] and liquid–solid [26,27] mass transfer coefficients depend on mechanical powers for mixing that are difficult to estimate or measure in laboratory scale reactors. Those correlations are useful for scaling up similar industrial stirred tanks but would only be used for a rough approximation for laboratory stirred tanks. In the end, even if the difficulties to obtain relevant properties for petroleum cuts are great, correlations do not use enough fluid properties in order to properly characterized stirring behavior if foam is formed.

The best way to obtain relevant transport coefficients, minimum rotation speeds, or gas phase holdup is to carry out their own experiments. Some experiments described in following could be easily carried out:

1. To look at the flow behaviors through transparent mock up wall. If the reaction is performed under high temperatures and pressures, other simulating fluids have to be used. The standard properties of the latter have to be close to reactant properties at reaction temperature and pressure. This visualization can give information on catalyst and gas stagnation zones in stirred tanks. Literature emphasizes advice about the choice and location of baffles, but it remains too approximate. For example, to prevent catalyst deposition on the bottom and agglomeration behind the baffles, the latter must be enough far from the wall to leave particles to flow and must be kept off the bottom [28]. The minimum rotation speed required maintaining solid in suspension can also be measured. Depending to authors, minimum rotation speed definition can however be different: it is either the condition required to ‘‘just-suspend’’ solid particles or to ‘‘completely homogenize’’ the solid in liquid phase. This parameter is important to know, due to its impact on solid–liquid transfer coefficient.
2. To carry out the α-methylstyrene hydrogenation on a Pt/$Al_2O_3$ catalyst. The reaction of α-methylstyrene hydrogenation, being so quick on this previous catalyst, allows to measure gas–liquid transfer coefficient under low pressures and temperatures [17].
3. To measure gas–liquid mass transfer coefficient ($k_La_L$) for instance by physical hydrogen absorption. It consists in following batch absorption of a soluble gas in slurry or liquid previously degassed. The volumetric mass transfer coefficient is determined by measuring the total pressure variation of the gas phase as the absorption proceeds.

A drawback of the methods 1 and 2 is that the used compounds and experimental conditions are different from the ones used in the studied reaction.

Those methods do not allow to avoid verifying if the reaction is carried out in chemical regime. Classical tests consist in varying rotation speed ($N$), particle size ($d_p$) or catalyst mass ($m_c$). If the performances of the catalyst (i.e. conversion, selectivities, . . .) do not change varying $N$ and $d_p$, then the chemical regime might be established. That is the same conclusion if the apparent reaction rate is proportional to catalyst mass. However, those methods can present some traps.

In three-phase stirred tank reactors, the turbines may provide at the same time a sufficient agitation to maintain catalyst in suspension in the liquid and good gas holdup. Some authors [29–32] have proposed correlations giving estimation of minimum rotation speed to maintain solid in slurry for liquid–solid systems without gas and to obtain a good gas holdup for gas–liquid systems without solid. As mentioned previously, the definitions depend on the authors and on used operating systems. As relevant minimum rotation speed values are difficult to estimate using correlations, we advise to carry out your own experiments to obtain experimental data. As it can be shown in Fig. 3, the turbine configuration (with or without hollow shaft) involves important differences on gas–liquid mass transfer coefficient values (Fig. 3) and on gas–liquid minimum rotation speeds. In surface-aeration reactors (i.e. turbine without hollow shaft), the increase of $k_La_L$ with $N$ can be essentially be attributed to the increase of $k_L$, the interfacial area remaining almost constant [33]. In gas-inducing reactors (i.e. turbine with hollow shaft), gas–liquid transfer coefficients are equal to the ones obtained with standard impeller when $N$ is lower than the critical mixing speed for gas induction. Above this critical mixing speed, further increase of $N$ increases the induced gas flow rate, which increases the gas holdup and the corresponding $k_La_L$ [33]. Using the latter type of turbine allows to explore a larger range of gas–liquid interface area and $k_La_L$ values. Consequently, the use of surface-aeration impeller (in comparison to the one of gas inducing impeller) can be more hazardous to detect possible

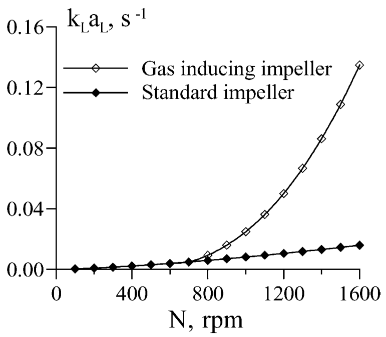

Fig. 3. Gas–liquid mass transfer coefficients vs. rotation speed in a two-phase stirred tank reactor supplied with standard or gas-inducing impellers [33].

chemical limitations by mass transfer, especially if the experimental errors linked to catalyst performance measurements are of the same order of magnitude than the variation of $k_L a_L$.

Recently, Pangarkar et al. [26] have written an excellent review on solid–liquid mass transfer coefficients in two- or three-phase stirred tank reactors. Obviously all cited works have been achieved using large tanks. Nevertheless they conclude that the key parameters are the minimum turbine speeds for complete suspension of the particles. They define two minimum turbine speeds: one for two-phase stirred tank reactor ($N_S$) and the other for three-phase stirred tank reactor ($N_{SG}$). As they have found that solid–liquid coefficients ($k_S$) are linear functions of $N/N_S$ and $N/N_{SG}$ for two-phase and three-phase stirred tank reactors respectively, a easy solution consists in measuring $k_S$ at $N_{SG}$ and then calculating $k_S$ to compare its value with apparent kinetic parameters obtained experimentally.

The effect of particles on gas–liquid mass transfer has been widely investigated, although this effect is very difficult to predict. All authors agree that effects depend on particle concentrations in liquid phase [34]. For high concentrations of particles (~10 wt.%), they observed a great decrease of $k_L a_L$ and they often put it down to an increase of the apparent viscosity. For small concentrations of particles, they have always observed an increase of $k_L a_L$. They put it down to a turbulence effect, which could reduce the gas–liquid interface thickness for large particles and effect of interface rigidity increase, which would reduce the coalescence rate for small particles. Then, effects of particle size reduction on gas–liquid transfer are difficult to predict and could give no information about chemical regime. On the other hand, catalyst mass increase could seem a good way to show gas–liquid transfer limitations. It is true in the majority of cases. But in cases in which catalyst poisoning or deactivation can happen, it would be more difficult to conclude. Moreover, to increase catalyst mass leads to increase the risk that particles stay agglomerate behind the baffles. About solid–liquid mass transfer, solid–liquid interfacial area is directly linked to particle size. The decrease of particle size, implying the increase of interfacial area, should lead to an increase of mass transfer, but the relative slip velocity between particle and fluid is decreased in the same time and reduces the mass transfer coefficient, $k_S$. That would explain why some authors have observed coefficients almost independent of particle size for particle size more than 200 μm. They explained the increase of solid–liquid mass transfer for particles smaller than 100 μm by the increase of amount of eddies which come near the surface [26].

In conclusion, the majority of authors suggest performing your own experiments to characterize your reactors. But, using those methods, experiments must be performed in large ranges of parameters to avoid concluding too quickly and badly about chemical regime.

The stirred tank reactors with slurry having drawbacks to study kinetics for three-phase reactions, we decided to characterize stirred tank reactors with catalytic basket. Those reactors have been designed to study kinetics with pellet catalysts, but as they are not often used there are not any extended characterization study in literature.

### 3.2. Stirred tank reactor with crushed catalyst

Stirred tank reactors with catalytic basket have been designed to avoid drawbacks linked to packed-bed reactors and stirred tank reactors with crushed catalyst. Those reactors have got the main advantage to ensure to perform catalytic measurements using directly industrial or shaped catalysts. Like all the stirred tank reactors, they can be operated in batch, semi-batch (specially for slow reactions) or continuous modes. Autoclave Engineers company is the most important supplier of stirred tank reactors with catalytic basket. We can notice that five types of catalytic reactors are available in their catalogue:

- The Berty Stationary Basket Catalyst Reactor which have been designed to perform gas–solid or vapor phase-solid reactions.
- The Robinson–Mahoney Catalyst Testing Reactor in which stationary basket and turbine have been designed to test catalysts for multiple phases (mainly gas–liquid–solid reactions).
- The Mahoney–Robinson Spinning Basket Reactor which is used to test catalysts for liquid–solid reactions.
- The Carberry Spinning Basket Catalyst Reactor which is another reactor designed to perform three-phase reactions. In Carberry reactor, the basket shape looks like a turbine in which the blades get trapped catalyst.
- The Harshaw Falling Basket Catalyst Reactor wherein the catalyst can be pretreated using gas phase and successively can react in a liquid reaction.

In brief, two types of stirred tank reactors with catalytic basket can be used for performing three-phase reactions either with spinning basket as the Carberry reactor or with stationary basket as the Robinson–Mahoney reactor (RMR). Even within our presentation limited to three-phase reactors, it can be mentioned that the Berty reactor has already been operated for two-phase hydrotreatment reactions [35].

As for Carberry reactors, few papers have mentioned its use. Some authors used it in a study of heavy gas oil hydrodesulfurization but have just studied intraparticular limitations [36]. Other authors hardly criticized its poor ability to transfer gas to solid through liquid phase but they studied the oxidation of aqueous organic compounds over a hydrophobic solid catalyst [37]. In the latter case, the gas forms a layer around the solid particles and the gas does not need to be transferred through the liquid phase to react. In conclusion, no useful study is available in the literature in order to evaluate the advantages or drawbacks of this kind of reactor.

As for the Robinson–Mahoney reactor, its great advantage is to maintain catalyst closed in the basket in contact with the liquid phase. Liquid and gas phases being mixed by the turbine, gas and liquid inlet flows do not change significantly hydrodynamics neither in the tank nor through the basket. Thus, it is possible to test catalyst in larger ranges of WHSV and hydrogen/HC ratio. Those reactors have already been used to perform hydrotreatment reactions [21,38], but limits of their use in order to study kinetics have never been published.

Before we tackle the important points we have observed during their characterizations, it is important to remind of the main drawback of those reactors: cost of experiment performing, due to the large volume of tanks and the mode of operation, especially in continuous mode.

We have characterized two types of ‘‘Robinson–Mahoney reactors’’: one is provided by Autoclave Engineers and the other was provided by Parr Instrument Company. In order to characterize the reactors and define their limits of use, we have studied mass transfer limitations between gas and liquid phases in the tank and between liquid and solid phases on the inside of the basket. The reactor designs are different. Their main characteristics are summarized in Table 1 and Figs. 4 and 5 (showing drawings or pictures of tanks, baskets and turbines). In the Autoclave Engineers Robinson–Mahoney reactor, the gas phase is introduced in the liquid phase at the tank bottom inside the basket and goes through the liquid phase reactor as bubbles. Under the impact of radial turbine, the gas bubbles are impelled through the basket to the reactor wall. Some of them go down and are recycled inside the basket, the others go up directly to the outlet or are recycled by the turbine at the top of impeller, following a down flow. In this system, hydrodynamics cannot be entirely independent on inlet gas flow. In fact, inlet gas flow contributes to improve liquid–solid transfer if it remains low, but above a limit inlet gas flow, it restricts liquid–solid mass transfer. On the other hand, inlet gas flow has no effect on gas–liquid mass transfer. Parr Robinson–Mahoney reactor having a gas sky, hydrodynamics does not depend on gas inlet flow. The gas bubbles in liquid phase come from the gas sky through the gas inducing impeller. However, the liquid agitation increases the foaming when gas oil is used. In the Parr RM reactor, an important gas flow is carried away to the inside of basket through the hollow shaft when the liquid level is too low. It is due to the reduced pressure drop between the gas sky and the liquid phase close to the turbine hole. The surface-aeration deformation also increases gas holdup inside the basked. Thus, low liquid level increasing gas holdup and gas flows inside the basket indirectly contributes to the foaming in the tank. Performing gas oil and hydrogen at ambient temperature and atmospheric pressure, those phenomena

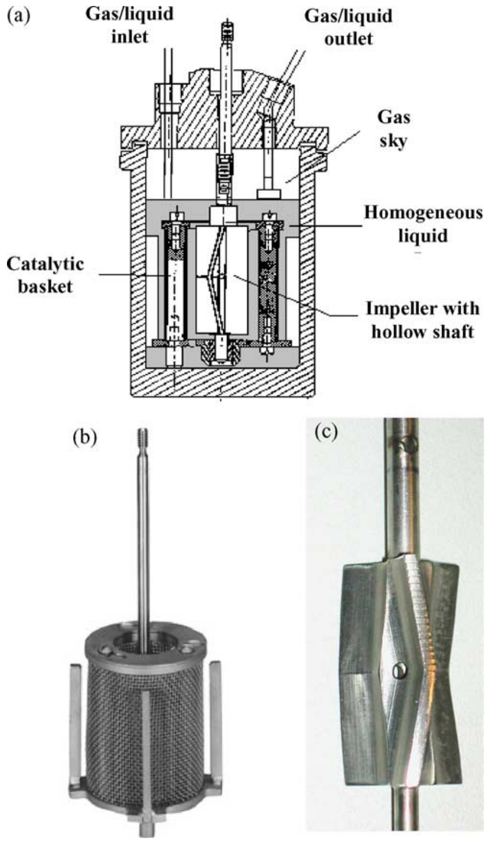

Fig. 4. Tank scheme (a), catalytic basket (b) and turbine (c) of Robinson–Mahoney reactor provided by Parr Instrument Company.

Table 1
Comparative characteristics of both Robinson–Mahoney reactors studied in this work

| Robinson–Mahoney reactors provided by | Autoclave Engineers | Parr Instrument Company |
|---|---|---|
| Tank volume (ml) | 1000 | 300 |
| Basket volume (ml) | 133 | 60 |
| Tank bottom | Curved | Flat |
| Location of gas and liquid phase inlet | Tank bottom | Tube in the liquid phase |
| Location of gas and liquid phase outlet | Tank top | Tube controlling liquid level in the tank |
| Gas sky | No | Yes |
| Impeller | Two inverse turbines with four pitched blades surrounding one turbine with six flat blades (Fig. 5) | One turbine with three curved blades and hollow shaft (Fig. 4) |
| Baffles | Four baffles outside the basket | Four baffles outside the basket |

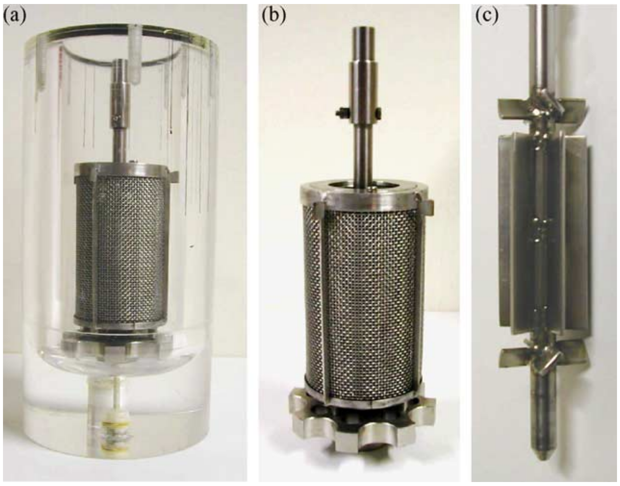

Fig. 5. Tank (a), catalytic basket (b) and turbine (c) of Robinson–Mahoney reactor provided by Autoclave Engineers.

have appeared towards 1200 rpm rotation speed. Performing water and air, they have been observed at higher rotation speeds (faster than 1600 rpm). Fig. 6 shows gas phase distributions in Parr Robinson–Mahoney reactor operated in batch mode. Pictures were obtained using radioactive gas ($^{133}$Xe) and a γ-camera. Experimental details are given by Blet et al. [39]. In summary, liquid level does not affect gas distribution for rotation speeds slower than 1600 rpm. For higher rotation speeds, if the liquid level is high, gas concentration increases inside the basket homogeneously. If the liquid level is low, gas concentration increases drastically inside the basket. The high gas concentration is showed in the bottom and profile views at 1900 rpm by the intensive white color. In fact, this limit rotation speed (1600 rpm with air + water in Parr Robinson–Mahoney reactor) is the minimum rotation speed, defined by Van Dierendonck et al. [30], for which the gas–liquid mass transfer curve versus $N$ begins to increase. Fongarland [38] has shown that this value is directly linked to the presence of basket filled with cylindrical solids. If the basket is empty or without any basket, this minimum speed becomes equal to 1000 rpm. This suggests that the suction velocity in the hollow shaft would depend on the basket presence and probably on shapes of solids inside basket. The behavior of a standard impeller is inefficient in this reactor. We have compared hydrogen holdup in gas oil at ambient temperature and atmospheric pressure using standard or gas-inducing impellers at various rotation speeds (Fig. 7). In those cases, minimum rotation speeds are approximately 1000 and 1500 rpm for gas-inducing or standard impellers, respectively. These experiments have not been performed for air and water system, the stirrer being not able to exceed 2000 rpm. Gas holdup and gas–liquid mass transfer being linked [33], the use of gas inducing impeller is consequently strongly advised to carry out experiments in Parr Robinson–Mahoney reactor, i.e. reactor with gas sky. A good adjustment of liquid level is however necessary. The Autoclave Engineers Robinson–Mahoney reactor is supplied with a standard impeller. The $k_La_L$ profiles obtained varying the rotation speeds are similar to the ones obtained by Tekie et al. [33]. The minimum rotation speed in air–water system is about 1000 rpm (it is lower than 1600 rpm for Parr Robinson–Mahoney reactor). Moreover, gas holdups remain low in comparison to the ones observed

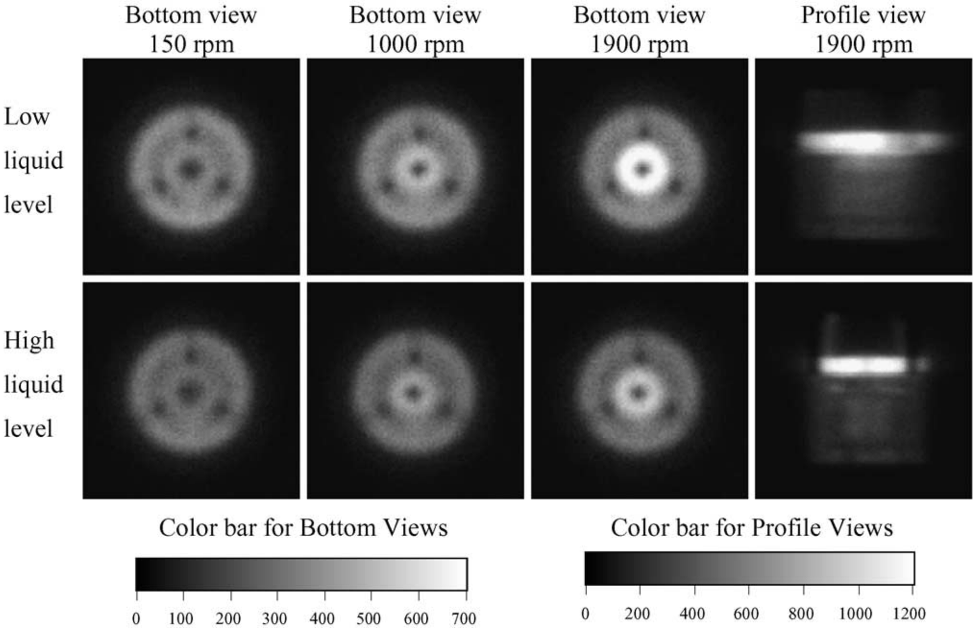

Fig. 6. Gas phase distributions in Parr Robinson–Mahoney reactor (operated in batch mode). Pictures obtained using radioactive gas ($^{133}$Xe) and a γ-camera for low and high liquid level, three rotation speeds (150, 1000 and 1900 rpm) and two locations (under the reactor: bottom view; in front of the reactor: profile view); gas phase:air + $^{133}$Xe; liquid phase:water.

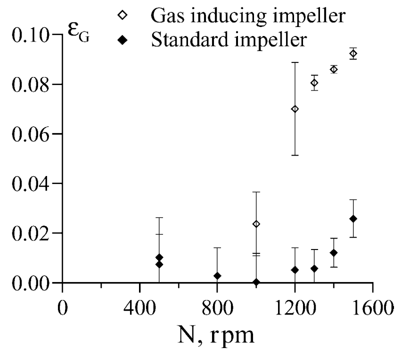

Fig. 7. Gas holdup vs. rotation speed in Parr Robinson–Mahoney reactor operated with standard or gas-inducing impellers for $H_2$–gas oil system at 25 °C and 1 atm [38].

in the other reactor (between 2 and 5% in Autoclave Engineers Robinson–Mahoney reactor for water–air and *n*-heptane–air systems). Mass transfer capacities would always be compared to actual flows transferred due to intrinsic reaction rates and reactant consumption. Then, the behavior of Autoclave Engineers Robinson–Mahoney reactor may affect the performance of reactions needing high hydrogen flow rate and high gas holdup, like hydrocracking.

As mentioned previously, the turbines in both RM reactors are radial impellers. Thus, we could expect to have liquid–solid transfer profiles along the basket. In order to determine those profiles and minimum and maximum values of $k_S$ that will be compared to HDT kinetic parameters, we have carried out experiments using naphtol pellets putted inside the basket and water or *n*-heptane as liquid phase. From the evolution of naphtol concentration in liquid phase versus time, the solid–liquid mass transfer coefficients have been estimated. We have found that the $k_S$ profiles and values are similar in both reactors (relative deviations are about 20%). For low rotation speeds, the profiles are practically flat. But for high rotation speeds, $k_S$ at the basket center is about two times greater than $k_S$ at the top and bottom of basket. Thus, liquid–solid mass transfer hardly depends on rotation speeds. We will give some values in the last part of this paper and give quantitative comparison of performances for previously described reactors.

## 4. Comparison between mass transfer coefficients estimated or measured in catalytic packed-bed and stirred tank reactors

In the previous parts, only qualitative characteristics and performances of reactors are discussed. In this part, we are going to try to compare quantitatively the performances of previously described reactors: trickled-bed reactor, stirred tank reactor with crushed catalyst and both Robinson–Mahoney reactors. The reactors are compared one with the others using gas–liquid and liquid–solid mass transfer coefficients. All the data are summarized in Table 2.

For both Robinson–Mahoney reactors, the data are directly issued from experiments carried out by Mitrovic [40] and Fongarland [38]. The others data are issued from correlations in literature. Due to the difficulty in choice of appropriate correlations, we have restricted this comparison to water-air system for $k_La_L$ and gas holdup and *n*-heptane–air system for $k_S$.

In slurry reactor, liquid–solid specific interfacial area is far larger than the ones in the others reactors. Thus, only $k_Sa_S$ can be compared. Specific interfacial area ($a_S$) is taken equal to 57,000 m$^{-1}$ in slurry reactor and equal to 920 m$^{-1}$ in the trickle-bed and RM reactors. All estimations and measurements are performed at 25 °C and 1 atm. The characteristic sizes of the stirred tank reactor with slurry are the same as the ones of Autoclave Engineers Robinson–Mahoney reactor (tank volume: 1 l; tank diameter: 0.08 m; six-blade impeller diameter: 0.03 m; inlet gas flow: $10^{-6}$ Nm$^3$ s$^{-1}$). The rotation speed is the same for all the stirred tank reactors: 1000 rpm. The characteristic packed-bed sizes to simulate the mass transfer coefficients are 0.03 m for reactor diameter and 0.376 m for reactor length. The gas and liquid superficial velocities are $2.78 \times 10^{-3}$ and $1.57 \times 10^{-4}$ m s$^{-1}$, respectively. They have been chosen in order to simulate an $H_2$/HC ratio in order of magnitude of 250.

As it can be seen on Table 2, slurry stirred tank reactor would be the best reactor relatively to global mass transfers. But drawbacks of this reactor wouldn't be forget specially when the reactor is operated in continuous mode. Moreover, the high liquid–solid mass transfer coefficient is due to low solid superficial area. Comparing the reactors performing shaped catalysts, we can observe better liquid–solid and gas–liquid mass transfer coefficients for stirred tank reactor

Table 2
Comparison of mass transfer coefficients for water–air systems in four three-phase reactors

| Reactors | *n*-Heptane–air system | | Water–air system | |
|---|---|---|---|---|
| | $k_S$ (m s$^{-1}$) | $k_Sa_S$ (s$^{-1}$) | $k_La_L$ (s$^{-1}$) | $\varepsilon_G$ |
| Trickle-bed reactor | $8.6 \times 10^{-6}$[a] | $7.9 \times 10^{-3}$[a] | $2.7 \times 10^{-4}$[a] | n.e. |
| Slurry stirred tank reactor | $11.3 \times 10^{-5}$ [27] | 6.44 [27] | $4.4 \times 10^{-3}$ [22] | $4.5 \times 10^{-3}$ [22] |
| Parr Robinson–Mahoney reactor | $8.8 \times 10^{-5}$ | $8.1 \times 10^{-2}$ | $1.3 \times 10^{-3}$ | n.e. |
| Autoclave Engineers Robinson–Mahoney reactor | $8.5 \times 10^{-5}$ | $7.8 \times 10^{-2}$ | $2.0 \times 10^{-3}$ | $5.3 \times 10^{-2}$ |

n.e.: non-estimated.

[a] Estimated using the Larachi's spreadsheet program.

with catalytic basket. Mass transfers in catalytic basket reactors are ten times as great as the ones in packed-bed reactors. The Parr Robinson–Mahoney reactor is however, operated in worse conditions for gas–liquid mass transfer because rotation speed is about 1000 rpm in air–water system and in those conditions, the gas inducing impeller behaves like a standard one. To really compare the four reactors, we should measure gas–liquid mass transfer coefficients using a system for which the gas inducing impeller is really efficient. But we can think that Parr Robinson–Mahoney reactor would be more efficient than Autoclave Engineers Robinson–Mahoney reactor for gas-liquid mass transfer but similar to it for liquid–solid mass transfer.

To study gas oil hydrodesulfurization on $CoMo/Al_2O_3$ catalyst (30 g), we have used a Parr Robinson–Mahoney reactor. In this particular study, no problem about reactor performances has been observed. The reactor was operated in gas and liquid continuous flow mode with $N$ higher than 1000 rpm, temperatures were between 320 and 360 °C and the total pressure was 3.3 MPa, gas oil liquid flows and hydrogen flow were between 0.75 and 2 ml $min^{-1}$ and fixed to 3.3 Nl $h^{-1}$, respectively. The acceleration factors estimated from experiments were between $4 \times 10^{-4}$ and $2.2 \times 10^{-3}$. In our experiments, gas–liquid mass transfer does not affect reaction rates. But the operating conditions were soft in comparison to the ones necessary to perform hydrocracking reactions and some problems could probably appeared using more active catalysts.

## 5. Conclusion

A targeted but rapid study of reactor hydrodynamics is advised in order to operate accurately HDT reactions. This study can be realized either a priori using simple techniques like hydrogenation of α-methylstyrene or a posteriori comparing apparent reaction rates to mass transfer rate. In this last case, the correlations have to be used cautiously.

Our experiments on Robison–Mahoney reactors show that they may have better performances than the catalytic packed-bed reactor. Nevertheless, small changes in catalytic basket reactor operations (rotation speed, liquid viscosity, foam formation, . . .) may greatly reduce their performances. In this case, we also strongly recommend measuring mass transfer coefficients under reaction conditions before performing kinetics measurements.

If no deactivation is observed and/or the reaction rates are too slow, the Robison–Mahoney reactors may be immediately transformed in semi-batch reactor by stopping inlet liquid flow, saving time and reactants.

Finally, the important and obvious points which must be taken into account in the choice of laboratory scale reactors are: the aim of the study (comparisons of catalytic activity and selectivity or determination of kinetic models and their parameters), the catalyst stability, the time necessary to the study (not to neglect the time to reach catalyst and reactor stationary state) and reactant volumes necessary to perform experiments and analysis. All those points are important to evaluate the cost of study.

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