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The hydrogenation of isophorone to trimethyl cyclohexanone using the downflow single capillary reactor

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Abstract

Despite many innovations in the intensification of catalytic multiphase reactors for the small and medium scale manufacture of chemicals, there have as yet been relatively few commercial successes. One reason for this might be that many of these developments inherently incorporate a fixed catalyst, which may not suit an industry that is based on principles of batch manufacture and multi-product plant. This study evaluates an intensified reactor that encompasses the opportunities demonstrated from structured flows and thin channels, together with a mobile, slurry catalyst, namely a capillary reactor with gas/liquid/suspended catalyst flow. A downflow single capillary reactor (SCR) was designed, built and evaluated for the selective hydrogenation of isophorone to trimethyl cyclohexanone using commercial Pd- and Rh-based catalysts. Using the single capillary arrangement, the reaction was shown to be operating under kinetic control.

Comparison of the rate of hydrogenation with autoclave showed a significant increase of the reaction rate when capillary reactor was used. The temperature of reaction is a crucial factor in tuning the reaction towards different products. The constant relative reaction rate obtained for different catalyst loading as well as the calculated value of the apparent activation energy show that the reaction of hydrogenation of isophorone is not mass transfer limited in the single capillary reactor.

Keywords: Multiphase reactions; Thin channel reactors; Slurry catalyst

1. Introduction

Multiphase reactions are very common in the chemical industry. Many of the industrial reactions, such as hydrogenation, oxidation, carbonylation and hydroformylation [1] take place in two or even three phase conditions. Such processes have to deal with diffusion (or mass transport) limitations. The workhorse of the fine chemicals industry is the stirred batch reactor, also known as autoclave. This is a versatile reactor and can be used for more than one reaction. But despite advances in the design of the impeller and of the gas sparge pipe, this reactor still presents some disadvantages. They can be inadequately mixed and frequently mixing or mass transfer or heat transfer steps govern the reaction rate. The net result of this is that reaction times tend to increase significantly with increasing scale, leading to reduce operating and thus capital efficiency. They are difficult to scale-up as the critical dimensions associated with a multiphase reaction (reactor dimensions, bubbles size, micro-mixing scale and kinetic-related distances) do not scale in proportion. Increasing the reactor size often increases the limitations due to mass transport [2].

The trickle bed and pulsed trickle bed reactors are used mainly in the refinery and petrochemical industry for hydrogenation-based reactions. This reactor type is continuous in operation and is regarded as a plug flow reactor [3,4]. These reactors have not, however, found favour in the fine chemicals sector because it is inherently a continuous reactor and, with the fixed bed of catalyst, is not suited to multi-product applications.

The slurry bubble column reactor employs energy input into the column via the gas sparge [5]. With the exception of the oleochemicals processing sector, this reactor also has not

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found favour in the small to medium scale chemicals manufacturing industry sector. While relatively simple in concept, the reactor is not simple to scale-up and therefore there is an inherent risk and difficulty in transferring new chemistries from the laboratory bench to production. Jet or loop reactors use an eductor, such as a venturi, or a nozzle to obtain a good dispersion of the gas phase into the liquid [6–8]. These reactors create a very intense phase dispersion in the region of the discharge from the eductor and thus achieve very good mass transfer. These types of reactors have found application in the small to medium scale industry sector, especially in uncatalysed applications and those with homogeneous catalysts, such as mineral acids or bases. There has recently been significant attention to the potential of structured reactors and catalysts to achieve increases in volumetric productivity and controllability [5,9]. This is exemplified by the micro-channel reactor concept. In this case, each channel is an independent plug flow reactor and scaling-up simply becomes an issue of increasing the number of channels (scaling-out) as long as flow is equally distributed over all channels [10]. Even these latest developments have overlooked a crucial point. The fine chemicals sector is driven by the need to retain flexibility of operations, that the inherent need for a production unit to have a multi-product capability. This is a key reason for the near total adherence to homogeneous and slurry catalysts. There is therefore potential interest for the fine and intermediate scale manufacturing of chemicals in an intensified reactor that retains the use of a mobile or slurry catalyst. This is the driving force behind this study, which evaluates an intensified reactor that encompasses the opportunities demonstrated from structured flows and thin channels, together with a mobile, slurry catalyst, namely a multi-capillary reactor with gas/liquid/suspended catalyst flow.

2. Experimental

The reaction test system used for most of the data reported herein is the catalytic hydrogenation of isophorone. There are four possible reaction products: 3,3,5-trimethyl cyclohexanone (TMCH-one), *trans* 3,3,5-trimethyl cyclohexanol (*trans* TMCH-ol), *cis* 3,3,5-trimethyl cyclohexanol (*cis* TMCH-ol) and 3,3,5-trimethyl cyclohexene-1-ol (TMCH-ene-ol). We have to state at this point that no trimethyl cyclohexene-1-ol was observed as reaction by-product at any stage of the reaction.

The reactor used for these studies is shown schematically in Fig. 1. The liquid-catalyst suspension from the receiver was circulated through the reactor by a pump. The reactor was a tube 6.35 mm o.d. with an internal diameter of 3.86 and 500 mm length, placed vertically. Consequently, the total volume of the tube-reactor was ca. 6 cm^3.

A thermocouple was placed at the top of the reactor and connected with a PID control unit. This controller was linked with the heating tape placed on the tube before the reactor and had the role to pre-heat the liquid feed to the reaction temperature. A second thermocouple was used to measure the outlet reactor temperature and it was connected to a second PID controller. This second controller was linked with a second heating tape, which was used to heat the reactor itself. Both controllers were set to the same temperature during the reaction to ensure accurate control and monitoring was maintained.

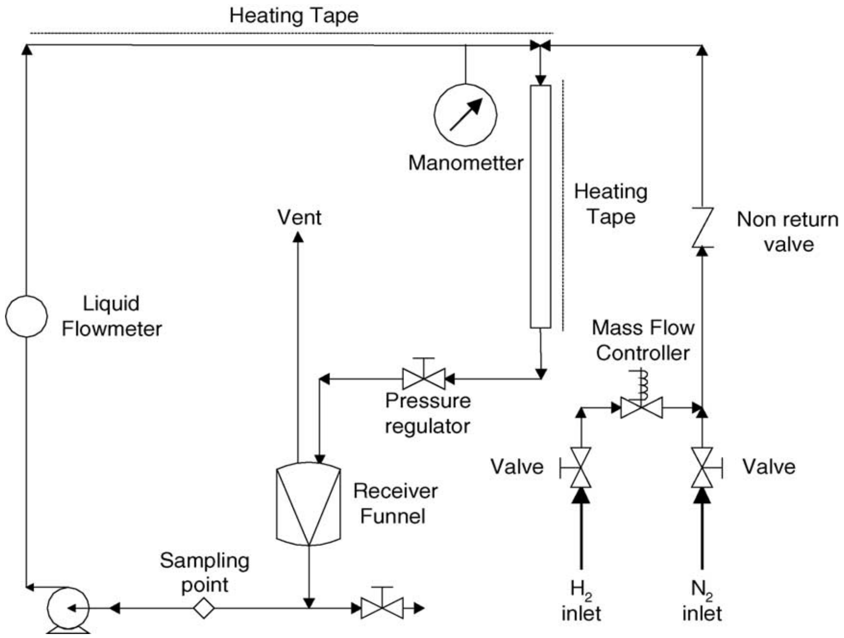

Fig. 1. Scheme of the reactor system employed for this study.

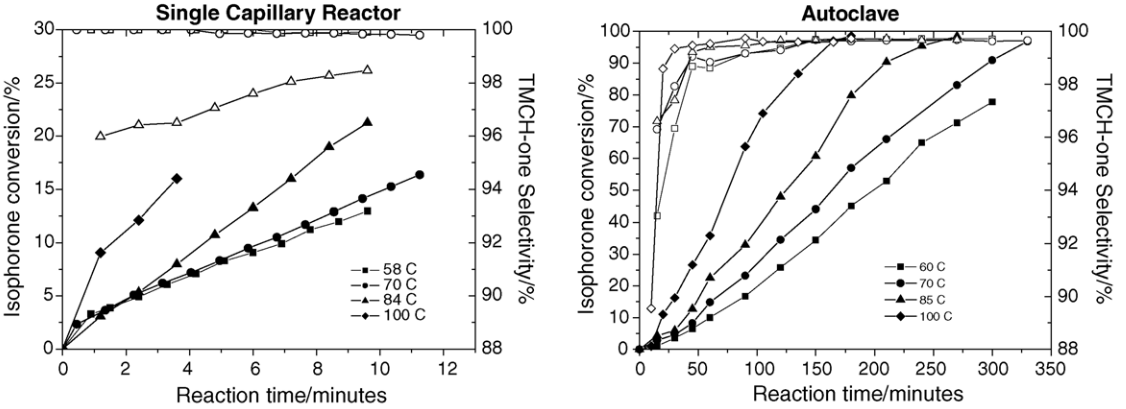

Fig. 2. Reaction profiles obtained at different working temperatures in the single capillary reactor and stirred autoclave; full symbols refer to the isophorone conversion, open symbols refer to the selectivity in trimethyl cyclohexanone (TMCH-one).

The hydrogen gas at constant flow (regulated by a Brooks mass flow controller) was injected into the flowing liquid at the top of the reactor through a capillary 1.59 mm o.d. After passing through the reactor, the mixture of solid, liquid and gas was decompressed and passed to the receiver vessel where the unreacted hydrogen was separated and vented. This depressurisation and degassing was carried out as close as possible to the reactor in order to minimise end effects. The manual backpressure regulator had to deal with three phases and consequently there were minor oscillations in the reactor pressure. Therefore, the reaction pressures quoted are the average pressure over the time period of the experiment.

The operating procedure of the rig for these tests was the following: 100 ml of isophorone are introduced in the receiver and then 1 g of humid catalyst (5%Pd/C–87L or 5%Rh/C, both supplied by Johnson-Matthey) is added (equivalent of 0.409 g dry catalyst). Both catalysts were made using the same support and have a surface area of 950 m^2/g. The particle size of the slurry was $d_{10} = 2.68$ μm and $d_{50} = 18.28$ μm. The mixture liquid-catalyst is circulated at high flow rates (300 ml/min) for 5 min to achieve a good dispersion of the catalyst into the liquid phase. At the same time, the hydrogen flow is started (280 (ml N)/min). The liquid flow rate is then reduced to 40 ml/min, the heating is started and the pressure is increased in the reactor to the desired value. Samples of about 0.5 ml each were taken periodically with a syringe and analysed by gas chromatography, Varian 3800 equipped with an Omegawax capillary column (30 m, 0.32 mm, 0.25 μm film thickness) and flame ionisation detector (FID). The results obtained by GC analysis were represented as a function of reaction time. The reaction time was calculated via a procedure described elsewhere [2].

For comparative purposes, reactivity data was compared with isophorone hydrogenation in an Autoclave Engineers 100 ml stirred autoclave equipped with downflow turbine and sampling pipe. The stirrer speed was set at 1500 rpm, temperature was maintained in the range 60–100 °C. Product analysis was performed using the same procedure detailed previously.

3. Results and discussion

Fig. 2 presents the variation of the isophorone conversion and the variation of the selectivity in TMCH-one with the reaction time in both systems used in the study: single capillary reactor (SCR) and autoclave. As expected, the reaction rate increases with the increase of the temperature for both systems. However, the increase of the reaction rate with the temperature is more pronounced for the SCR system. Indeed, the ratio between the reaction rates (rate SCR/rate autoclave) increases from 5.4 at 60 °C to 5.5 at 70 °C, then 6.7 at 85 °C and finally to 7.4 at 100 °C. These results show that in the capillary reactor, we achieve an enhanced mass transfer. Capillaries are believed to lead to improved mass transfer due to the minimisation of transport distances. The literature focuses on the specific application of the catalyst coated onto the channel wall, where the postulation is that in Taylor or slug flow, the thin film thickness between the bubble and the catalysed wall allows rapid transport. Most of the published regime-mapping work (Delft group and others) infers that at our superficial velocities, we are not in Taylor flow (although there are exceptions to this). Our case is, however, somewhat different in that the catalyst is suspended presumably within the liquid slug. In our operation, Taylor flow is therefore not a prerequisite for enhanced mass transfer as the catalyst is now suspended within the liquid. Presumably, the enhanced transport in this instance arises from the wall-induced local circulation patterns and that the configuration maintains the catalyst in the proximity of the bubbles.

The value of the apparent activation energy (E_a) was calculated for both reactors by plotting logarithm of the reaction rate (% isophorone converted per minute) versus T^{-1}. In this case, we found a value of 32 kJ/mol for the SCR and 22 kJ/mol for the autoclave. In the case of the SCR

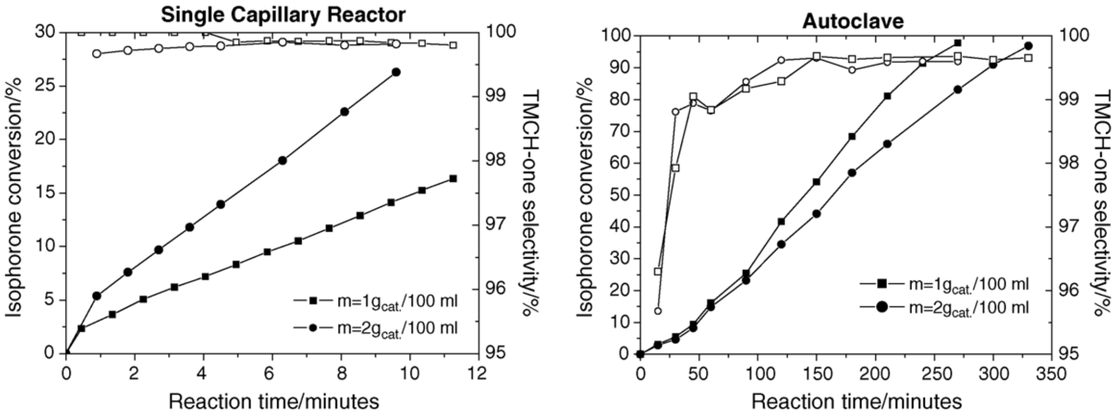

Fig. 3. Reaction profiles obtained at different working catalyst charge in the single capillary reactor and stirred autoclave; full symbols refer to the isophorone conversion, open symbols refer to the selectivity in TMCH-one.

system, the reaction takes place faster at the very beginning of the reaction, then it stabilises. This is also the period when by-products were formed. Consequently, the higher the temperature, the higher the initial reaction rate and the higher the amount of by-products formed at the beginning of the reaction. After this first period, the synthesis of by-products is suppressed and the value of selectivity in the TMCH-one (desired product) increases continuously. However, if the temperature of reaction is low enough (70 °C or below), the amount of by-products formed is either blocked or at traces level. If we consider the rate of apparition of each product for the first intervals and we use these data to calculate the apparent activation energy (E_a) for each one of the parallel reactions, we find a value 25 kJ/mol for the synthesis of TMCH-one, 112 kJ/mol for the synthesis of *trans* TMCH-ol and 223 kJ/mol for the production of *cis* TMCH-ol. These results suggest that the production of by-products is enhanced and consequently the selectivity in TMCH-one is decreased with the increase of the temperature, especially at the beginning of the reaction.

In the case of the reaction carried out in the stirred autoclave, an induction time is present always at the beginning of the reaction (lower reaction rate for the first intervals). That is in contrast with the SCR system, for which a higher reaction rate was determined at the beginning of the reaction. At the same time, by-products are always formed in small quantities at the beginning of the reaction, indifferent of the temperature of reaction used. However, the differences in the selectivity in TMCH-one for different temperatures are marginal and for high conversions, they are always very high (above 99.5%).

In order to establish if the reaction is mass transfer limited in these conditions of reaction or not, we carried out an experiment using the double of the amount of catalyst used previously. The results obtained at 70 °C and 6 bar pressure are presented in Fig. 3 for both reactor systems used in the study (5%Pd/C–87L, Johnson-Matthey). In the case of the single capillary reactor, the 100% increase in the catalyst charge (concentration) leads to a 100% increase in the reaction rate without a decrease in the selectivity in TMCH-one for high conversions. This result suggests that the reaction is not mass transfer limited in these conditions.

The same experiment was carried out for the autoclave and the experimental result presented in Fig. 3 suggest that

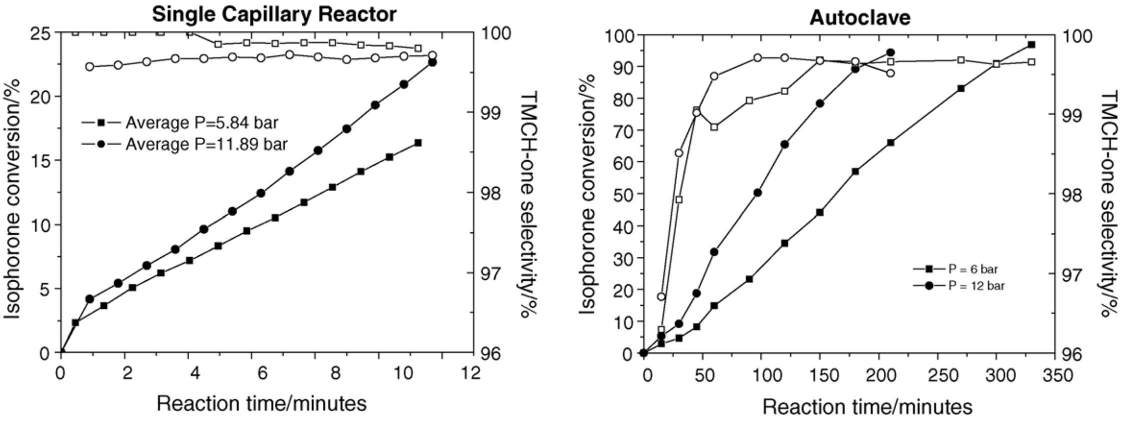

Fig. 4. Reaction profiles obtained at different working pressures in the single capillary reactor and stirred autoclave; full symbols refer to the isophorone conversion, open symbols refer to the selectivity in TMCH-one.

in this case, the reaction is mass transfer limited, as the reaction rate is just marginally increased for a 100% increase of the catalyst concentration. Just like in the case of the SCR system, the catalyst charge seems to have no effect over the selectivity in TMCH-one. However, at iso-conversion values (for the range of conversions studied in the SCR), the selectivity in TMCH-one seems to be higher for the capillary reactor.

Fig. 4 presents the reaction profiles obtained at different working pressures for the two reaction systems used in the study. For the SCR system, the back-pressure regulator had to deal with three phases. This is the reason why the pressure was not constant, but had fluctuations. The higher the targeted average pressure, the higher the fluctuations. In these conditions, it is possible that in reality, we did not reach the desired average pressure. This is the reason why when the SCR system is used, the partial order of reaction with respect of hydrogen appears to be less than 1. Consequently, we ascribe this result to the error in the calculation of the average pressure. We can also note that the selectivity in TMCH-one at the beginning of the reaction is affected by the increase of the pressure. As the reaction takes place faster, the apparition of by-products at the beginning of reaction is enhanced. However, the overall selectivity in TMCH-one remains very high and its trend is increasing.

In the case of the stirred autoclave, for which the pressure is very easily maintained at the desired value, the partial order of reaction with respect of hydrogen is 1 (when the pressure is doubled, the reaction rate is doubled). In this case, there is no effect of the increase in the working pressure over the selectivity in TMCH-one.

At the end of our study, one last experiment was done at 70 °C, 6 bar hydrogen pressure using 1 g of wet 5%Rh/C catalyst, Johnson-Matthey. The reaction rate in the SCR system increased from 1.6% isophorone converted per minute to 2.9% isophorone converted per minute. However, the increase in the reaction rate came with the price of lower selectivity in TMCH-one. Indeed, for a conversion of isophorone of about 18%, the selectivity in TMCH-one was 0.8% lower for the Rh-based catalyst.

4. Conclusions

These experiments show that the capillary reactor concept (that encompasses the advantages of the plug flow continuous reactors) can be applied successfully with slurry type catalysts. In these conditions, increases of more than seven times in the reaction rate were observed, compared with the stirred autoclave. In terms of selectivity in the desired product, as long as the reaction is performed (especially at the beginning) at low temperature (below 70 °C), the selectivity in TMCH-one appears to be higher than in the autoclave system reactor. The reaction in SCR appears to be not mass transfer limited, as the increase in the catalyst concentration leads to an increase in the reaction rate in the same ratio. The selectivity in the TMCH-one for the SCR system is strongly dependent on the temperature, as the energy of activation for the parallel reactions that produce by-products are higher than the apparent activation energy of the desired reaction. Consequently, for high selectivity in TMCH-one, it is necessary to work at temperatures below 70 °C.

Higher reaction rates can be achieved with Rh-based catalyst, but on the expense of lower selectivity in TMCH-one.

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