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Multiphase hydrogenation of resorcinol in structured and heat exchange reactor systems
Influence of the catalyst and the reactor configuration

Dan I. Enache [a], Graham J. Hutchings [a], Stuart H. Taylor [a], Sugat Raymahasay [b], J. Mike Winterbottom [b], Mick D. Mantle [c], Andy J. Sederman [c], Lynn F. Gladden [c], Chris Chatwin [d], Keith T. Symonds [d], E. Hugh Stitt [e,*]

[a] *Cardiff University, School of Chemistry Main Building, Park Place, Cardiff, CF10 3AT, United Kingdom*
[b] *University of Birmingham, Department of Chemical Engineering, Edgbaston, Birmingham B15 2TT, United Kingdom*
[c] *Magnetic Resonance Research Centre, Department of Chemical Engineering, University of Cambridge, New Museums Site, Pembroke Street, Cambridge, CB2 3RA, United Kingdom*
[d] *Chart Energy & Chemicals Inc., The Creative Industries Centre, Glaisher Drive, Wolverhampton, WW10 9TG, United Kingdom*
[e] *Johnson-Matthey Technology Centre, P.O. Box 1, Belasis Avenue, Billingham, Cleveland, TS23 1LB, United Kingdom*

This paper is dedicated to the memory of Chris Chatwin who died during the project on 6 May 2003, aged only 41.

Abstract

This study addresses the intensification of heterogeneously catalysed multiphase reactions using thin flow channel approaches, where the gas liquid and slurry catalyst are all circulated through the reactor, in contrast to the wall coated and packed bed approaches generally used. Resorcinol hydrogenation is used as an example reaction. Catalyst screening and process parameter investigations were carried out using a representative single capillary. The main objective of this paper is however to evaluate the scalability of this ‘‘structured slurry bubble column’’ concept through the use of heat exchange (HEx) reactors, and particularly exploring the various process channel design features made possible by the ‘‘shim’’ mode of construction. Hydrodynamic studies of gas, liquid and solid transport using magnetic resonance imaging and video-graphic techniques are reported. Twelve prototype HEx reactors were manufactured, and seven of these were selected for testing under reaction conditions. The results presented are discussed in terms of the observations of phase transport characteristics. This study shows the viability of implementation of a structured slurry bubble column using a heat exchange reactor design approach.

Keywords: Multiphase reactions; Microreactor; Thin channel reactor; Scale-out

1. Introduction

Multiphase catalytic reactions are common in the fine chemicals and pharmaceutical industry [1] and are usually carried out in a batch stirred tank reactor. The susceptibility of these reactors to heat and mass transfer limitations, especially on scale-up is well known, as are the generally deleterious effect of these transport limitations on reaction rate, selectivity and product yields.

There is an enormous body of work devoted to reasoned proposals and experimental investigations of alternative reactors [2–4], targeting cost savings via the inherent capital benefits of continuous processing and through process intensification. Reactors proposed include variously the trickle bed, eductor based jet and loop type reactors and most recently, structured reactors. In the last category the catalysed monolith and micro-channel type reactors are particularly prevalent in terms of publications. While the technical and occasional cost arguments for a switch away from the batch stirred tank are often very persuasive, they have hitherto had little impact in industry: as yet very few non-stirred tank installations are to be found in the fine chemicals and pharmaceutical industry for

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* Corresponding author. Tel.: +44 1642 522 704; fax: +44 1642 522 606.
E-mail address: hugh.stitt@matthey.com (E.H. Stitt).

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multiphase reactions. It is possible that a significant reason behind this reluctance to switch reactor technologies is the inherent flexibility of the batch stirred tank.

Reaction operations in the fine chemicals and pharmaceutical industry are largely multi-stage, and frequently the same reactor may be used for different reactions. Additionally, the typical ‘‘campaign’’ approach of batch manufacturing and plant scheduling to maximise capital productivity dictate that a given plant will probably be used for more than one product. That is, the manufacturing plant, including the reactor, is multi-product. This makes the flexibility, and suitability to multi-purpose and multi-product operation of the batch stirred tank almost irresistible; hence its prevalence as the reactor of choice in intermediate and small scale chemicals manufacture.

A fixed bed reactor, such as a trickle bed and a catalysed monolith are of course inherently reactors dedicated to a given reaction. While the ‘‘monolith loop reactor’’ [5,6] offers some flexibility if configured such that the catalyst filled tubes in the recycle loop can be interchanged, even this has not breached the barrier to progress beyond the stirred tank. There are a few examples also of installation of continuous traditional fixed bed approaches for fine chemicals manufacture—see Clay for example [7].

Some intensified reactors have been installed or trialed at ‘‘pilot’’ scale in the intermediate and fine scale chemicals manufacturing sector. These include the oscillatory flow baffled reactor [8] and BHR Group’s FLEX reactor [9] and the variable residence time reactor [10]. These differ significantly from the trickle bed and monolith reactor in that they are suited to operation with a slurry catalyst. This is true also of the slurry bubble column reactor, which has found limited use (at a scale smaller than many of the Fischer Tropsch ‘‘pilot’’ units) for the hydrogenation of vegetable oils [11].

This emphasises that in equipment selection for the fine and intermediate scale chemical manufacturing sector, a key criterion is unit flexibility. Packed and fixed beds are thus an anathema, with the specific exception of where the production rate of a given product regularly and consistently exceeds that required to make a dedicated, and possibly a continuous plant the unit of choice.

There is therefore scope within the needs of the fine scale chemicals manufacturing sector to consider process intensification routes that allow use of a slurry catalyst, and thus enable multi-process and multi-product reactor use.

It was based on this rationale that Enache et al. have previously investigated the application of three phase flow (gas bubbles, liquid continuum, dispersed slurry catalyst) through capillary channels to the hydrogenation of resorcinol [12] and isopherone [13]—a so-called ‘‘structured slurry bubble column’’. While a commercial installation would comprise many channels, by following the same scale-out concepts used in micro-channels and monolith type designs [14], a single capillary channel was largely used as representative in these studies. For both chemistries significant increases in the reaction rate were observed irrespective of whether comparison was based on rate referred to mass of catalyst or effective reactor volume. For a larger scale installation this would require attention to the heat transfer availability. This begs the question of how one would scale out a reactor based on capillary-type flow channels of nominally 0.5–5 mm diameter. One simple approach would be a shell and tube type arrangement based on tubes of a commensurate diameter. This approach might however miss a trick, and given the likely heat transfer coefficients of such equipment the operation and design might still be heat transfer constrained resulting in larger than necessary equipment.

Solvents are commonly used in intermediate and fine scale multiphase reactions. While in some cases this is required to assist in the chemistry, in many cases a key role of the solvent lies in mitigating the potential effects of the adiabatic temperature rise in the presence of inadequate heat transfer. In such cases the loading of catalyst may also be restricted in order to limit the maximum heat generation rate; matching it to the available heat transfer rate. By using a reactor design where heat transfer is not limiting there is potential for process intensification by eradication (or minimisation) of the solvent and increased catalyst loading both of which will lead to kinetically enhanced reaction and peak heat generation rates.

Reactor designs with intensified heat transfer have been available for a number of years, based in many cases on the concepts of compact heat exchangers [15,16]. Use of this type of reactor, generally featuring narrow flow channels and large heat transfer areas, has previously been proposed for single phase liquid reactions [17,18], for liquid–liquid reactions [19] for gas–liquid reactions [20,21] and for heterogeneously catalysed gas liquid reactions with the catalyst either adhered to the channel walls [22], or packed within the flow channels [23–25].

The scale up of thin channel type reactors has traditionally been assumed to follow the simple rules of ‘‘scale out’’ [14], whereby scaling is simply by assuming all channels are identical and thus, for example, 1000× on the number of channels leads to 1000× on the throughput. More recent work has exposed this as something of a simplification. Magnetic resonance imaging studies were amongst the first to indicate less than perfect spatial and temporal flow distribution, showing distributions in bubble sizes and flow velocities across the channels [26]. Indeed, some channels in negative flow were observed. Recent developments in this technique have enabled improved spatial and temporal resolution and allowed detailed confirmation of these observations [27]. Kreutzer et al., using pressure drop measurements, has demonstrated the critical effect of distributor design [28] and showed also that significant residence time distributions do occur in multi-channel units (10 cm diameter 200 cpsi monolith) [29]. This study notes a finite operating window of gas and liquid velocities where reasonable flow distribution can be achieved, a conclusion also reached using time averaged gamma ray tomography by Roy and al-Dahhan [30]. al-Dahhan et al. extend this technique to a 0.6 m diameter cold-flow monolith unit and note that reasonable flow uniformity can indeed be achieved, but that much attention is required to the design of the reactor internal features [31]. Thus scale out, while not as simple as originally perceived, can be satisfactorily achieved with due care and attention to design.

The objective of the present study is to explore whether this type of reactor might be applicable to the structured slurry bubble column design concept, and what design features are applicable. Specifically, a variety of custom built laboratory scale heat exchange (HEx) reactors supplied by Chart Energy & Chemicals, for the hydrogenation of resorcinol have been tested, installed on the same experimental set up used in previous work [12].

Results are thus presented for the selection of the catalyst system for resorcinol hydrogenation using a single capillary reactor, in which the liquid, the finely divided solid catalyst and the gas phase are circulated through the reactor section in a down flow orientation. For two different catalysts the effect of loading was evaluated, also using the single capillary reactor. Different flow channel designs of HEx reactors were used in order to assess the ease of the scaling-up/scaling-out process.

The proposed outcome of this development was a multiphase reactor based on multiple channels, which features excellent heat transfer, and thus temperature control as well as intense gas–liquid–solid dispersion, and consequently the elimination of bulk mass and heat transfer resistances. Applying such a reactor to catalytic reactions in the fine chemicals industry should enable:

- A modular reactor of simple construction that can be piped into existing infrastructures;
- A flexible installation that can operate in once through, plug flow continuous, or in recycle mode for batch operation and that is compatible with multi-step and multi-product requirements;
- Simple scale up of laboratory developments for homogeneous and slurry catalysis facilitated by the multi-channel configuration;
- High heat transfer giving facile temperature control, allowing a reduction in solvent usage and thus faster reaction rates for the same selectivity;
- Intense phase intermixing giving excellent mass transfer and thus elimination of bulk transport resistances, hence increased rates and true kinetic control;
- This in turn reduces equipment size or increases productivity of a given manufacturing asset;
- Higher rates and thus smaller, cheaper equipment. An operating advantage that will promote the move from stoichiometric to molecular hydrogen and oxygen.

2. Experimental

2.1. Test reaction

The test reaction used for the data reported herein is the catalytic hydrogenation of resorcinol to 1,3-cyclohexanedione [12]. The reaction occurs in a basic aqueous solution and proceeds via three steps (Fig. 1): The first step is the acid–base reaction between resorcinol and NaOH. The methodology is to protect the two C=C bonds of the aryl group during the hydrogenation reaction. The second step is the catalytic hydrogenation of the sodium salt of resorcinol. Finally, the product obtained in the second step is reacted with HCl and the final product is cyclohexanedione that is obtained after the rearrangement of the double bonds. The 1,3-cyclohexanedione is used as an intermediate in the synthesis of a number of important industrial materials, which are used for applications including cosmetics, agrochemicals, polymer additives and pharmaceuticals.

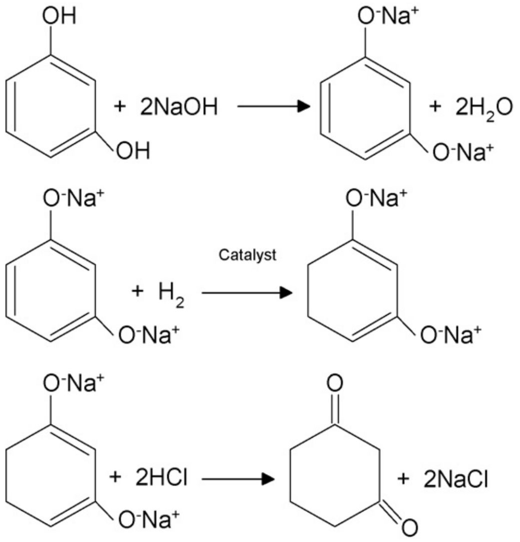

Fig. 1. Synthesis pathway for the obtaining of 1,3 cyclohexanedione from resorcinol.

2.2. Reactor design

The reactor set up used for these studies has been described in detail previously [12]. For the experiments involving a micro-structured reactor, the single linear vertical tube used in the previous study was replaced by a HEx reactor from Chart Energy & Chemicals (Fig. 2).

These integrated heat exchange reactors [32–34] are manufactured from a plurality of etched or cut plates, joined by diffusion bonding or brazing technology, as appropriate, to give an integrated heat exchanger reactor body. These reactors feature vertical or horizontal process flow channels of 1–10 mm width and rectangular cross-section, and heat transfer fluid channels, cross-flow between each process channel. Design pressures of greater than 50 bars are possible. Materials of construction used include aluminium, stainless steel, inconel and hastelloy. They can be manufactured up to 1 m in length.

The heat exchanger reactors manufactured by Chart Energy & Chemicals used in this study had channels of rectangular cross-section 1 or 2 mm in width, and heat transfer fluid flow adjacent to each channel. The total process volume of the reactors tested was 3 cm^3.

2.3. HEx reactors for visualisation experiments

Chart Energy & Chemicals prepared special units for the purposed of flow visualisation. For MRI a small number of Perspex units were made, while for video imaging, stainless steel units with a transparent Perspex faceplate were manufactured. Experiments were carried out on these units

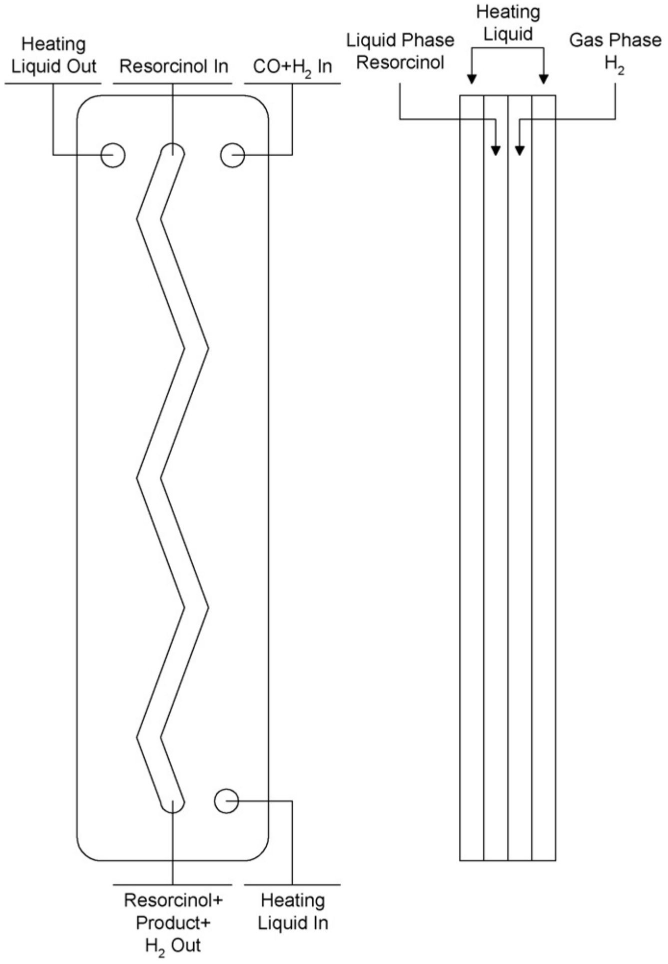

Fig. 2. Flowchart diagram of one of the reactors used in this study (KTS10437-38).

to look at phase distributions and flows, flow regime and particulate transport, water and alumina powder or fibre support (Smopex 105).

2.4. Visualisation experiments using MRI

All experiments were performed on a Bruker DMX 200 MHz NMR spectrometer operating at a proton frequency of 199.7 MHz. A 63 mm diameter birdcage radiofrequency coil was used for signal excitation/detection. Spatial resolution was achieved using a 3-axis orthogonal shielded gradient system, capable of producing a maximum gradient strength of 0.14 T/m. The field of view of the images is 3.5 mm × 70 mm with 64 pixels × 64 pixels, i.e. giving a resolution of 547 microns in the x (horizontal) direction and 1094 microns in the z (vertical, and direction of liquid/gas flow). The slice thickness was 2.4 mm and four successive images, each spaced 140 ms apart were acquired following a single excitation using the SEMI-RARE pulse sequence which is described elsewhere [35,36]. Thirty sets of four images were acquired. Each group of four images were taken 10 s apart thus allowing sufficient time for complete T_1 relaxation between successive radiofrequency excitation. A liquid flow rate of 2.0 ml min^{-1} was chosen and the gas-to-liquid ratio was approximately 1:1 for the results presented here.

A near identical cell to that depicted in Fig. 2 was used for MRI visualisations. Flow visualisations were performed on a Perspex cell containing 2 mm × 2.0 mm diameter channels. The inlet and outlet were connected to the gas/liquid flow using silicon tubing and the whole system was then placed into the centre of the MRI magnet. A 2:1 gas:liquid feed was introduced into the cell at the inlet in a Taylor flow regime. This was achieved using a T-piece connector situated some 2.0 m upstream before the inlet. Note that the system was operated in batch mode and not re-circulating.

2.5. Catalyst testing procedure

Sodium hydroxide (11.75 g) was dissolved in distilled water (53 ml). Resorcinol (28.4 g) was added to the solution and stirred for ca.15 min in the cooling bath. The solution (75 ml) was introduced to the receiver with the catalyst and the reaction was started. Samples (1 ml each) were taken periodically with a syringe, neutralised with HCl (0.45 ml, 37% Fischer Chemicals), and then mixed with acetone (2 ml). The mixture of resorcinol and cyclohexanedione was extracted with acetone and analysed by gas chromatography. (Varian 3800) equipped with a DB-Wax capillary column and flame ionisation detector. For comparative purposes reactivity data was compared with resorcinol hydrogenation in a Baskerville 100 ml stirred autoclave, equipped with a Buchi Press Flow Controller, which allowed continuous monitoring of hydrogen uptake.

2.6. Data interpretation for the capillary reactor

The results obtained by GC analysis were represented as a function of reaction time. For the capillary reactor, the reaction time was calculated via a procedure described below. The total volume of the single capillary reactor system used was 6 ml (3 ml for the HEx reactor). As the volumetric ratio gas/liquid used was 1/1, it means that inside the reactor there is 3 ml of liquid and 3 ml of gas for single capillary (1.5 ml of liquid and 1.5 ml of gas for HEx reactor). In these conditions, the reaction time is obtained by multiplying the reaction time with 3 (volume of liquid in the reactor) and divided by 75 (which is the total volume of the solution) (or multiplied by 1.5 and divided by 75 for HEx reactor). This methodology of calculating the reaction time was imposed by the fact that only a small volume of liquid was present at any time in the reactor.

3. Results with the single capillary reactor

3.1. Influence of the catalyst

In a previous study [8] results for the hydrogen uptake, which is a measure of the resorcinol conversion, as a function of reaction time in an autoclave reactor were presented. The same result was obtained using either 5%Rh/Al_2O_3 or 5%Pd/C catalysts. The reaction was carried out at 100 °C at 10 bar hydrogen pressure, while the stirrer was set at 1400 rpm. The reaction proceeded with a constant rate until it approached total conversion. After the point of equivalence, the reaction rate

Table 1
Results obtained under optimum conditions (flow rate resorcinol solution: 15 ml $\min^{-1}$; flow rate H_2: 150 mlN $\min^{-1}$) with various catalysts in the CRS

Catalyst	Commercial name	Temperature (°C)	Average pressure (bar)	Relative reaction rate (mmol h^{-1} $g_{cat.}^{-1}$)
5%Rh/Al_2O_3	Rh/Al_2O_3-524	100	8.62	366
5%Pd/C	Pd/C-87L	100	7.33	710
5%Pd/C	Pd/C-369	100	7.49	610
Ni/Raney	Acticat 1000	100	8.75	154
Ni/Al_2O_3	CP304	100	9.75	44
Ni/Al_2O_3	CP306	100	9.77	20
5%Rh/C	Rh/C-20A	100	8.21	546

Rh/Al_2O_3-524: 16% < 25 micron, 53% < 45 micron, 98% < 90 micron 99.7% < 150. Rh/C-20A and Pd/C-87L: 10% < 3 micron, 50% < 15 micron, 90% < 98 micron. Pd/C-369: 4% < 3 micron, 50% < 20 micron, 90% < 61 micron (Ceca L4S).

Table 2
Effect of flow rate in the single capillary reactor on observed performance for Pd/Al_2O_3 and Pd/C catalysts

5%Pd/Al_2O_3			5%Pd/C		
$m_{cat.}$ (g)	Absolute reaction (rate/mmol h^{-1})	Relative reaction (rate/mmol h^{-1} $g_{cat.}^{-1}$)	$m_{cat.}$ (g)	Absolute reaction (rate/mmol h^{-1})	Relative reaction (rate/mmol h^{-1} $g_{cat.}^{-1}$)
0	0	–	0	0	–
0.25	141	566	0.25	176	702
0.5	284	568	0.5	363	725
1	301	301	1	709	709
2	370	185	1.5	763	508
4	355	89	2	800	400.2

decreased considerably as further hydrogenation of the substrate was much slower. The same kind of reaction profile was also obtained in the single.

Table 1 presents the results obtained in the single capillary reactor for various catalysts. The highest value of the reaction rate was observed for the Pd catalysts supported on charcoal, followed by the Rh supported on charcoal, and then Rh supported on alumina and finally the Ni based catalysts. From these results it is evident that the most active metal is Pd, followed by Rh and then by Ni. This is in agreement with earlier findings by Bond [31]. It should be noted however that using the recirculating capillary, the density of the support of the catalyst plays a very important role [12]. Catalysts 5%Rh/Al_2O_3 and 5%Rh/C had the same active phase and similar dispersion. However, the catalysts supported on charcoal presented a higher reaction rate than the catalysts supported on alumina (Table 1). The difference in the reaction rate observed experimentally can be ascribed only to the difference of the density of these catalysts. The difference in the density of the supports used for these catalysts caused different transportability of these solids and thus variability of the actual catalyst loading in the reactor section. The transportability is related to the density of the support in relation to the density, the viscosity and the velocity (flow rate) of the liquid phase. For a given liquid and a given flow rate, the lower the density of the catalyst, the higher the observed reaction rate. Starting from this explanation, the lower reaction rate obtained for the Ni/Raney catalyst (if compared with noble metal supported catalysts) is also caused by the fact that this catalyst is the densest used in the present study. However, it is important to note that the reaction rate obtained with the Ni/Raney catalyst in the single capillary reactor was 154 mmol h^{-1} $g_{cat}{}^{-1}$ and this was 3 times superior to the reaction rate observed in an autoclave for 5%Rh/Al_2O_3-524, which was 52 mmol h^{-1} $g_{cat}{}^{-1}$ [8].

3.2. Influence of the catalyst loading

A volume of 75 ml of resorcinol solution was introduced into the receiver and various quantities of catalyst were added, ranging from 0.25 to 4 g of 5%Rh/Al_2O_3. Fig. 3 shows the variation of the resorcinol conversion with the reaction time and the results are presented in Table 2. For a low concentration of the catalyst the increase of the catalyst charge led to an increase of the absolute reaction rate in a similar ratio. But a further increase of the catalyst concentration, above 1 g, resulted in a constant absolute reaction rate. Consequently, the value of the relative reaction rate started to decrease for catalyst charges above 0.5 g. This behaviour could be taken as suggesting a

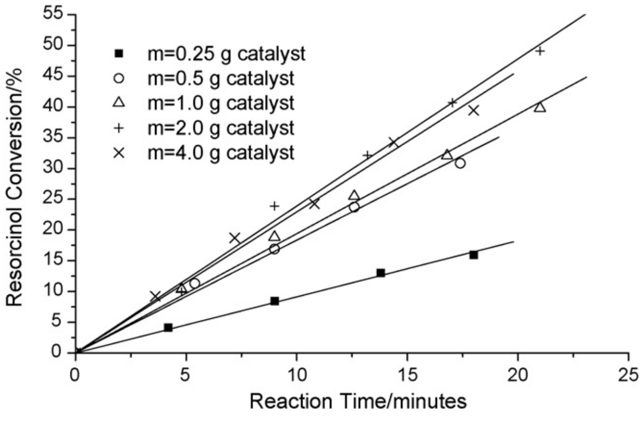

Fig. 3. The variation of the absolute reaction rate with the catalyst loading for 5%Rh/Al_2O_3 catalyst.

mass transfer limited reaction. If the reaction were mass transfer limited however, higher reaction rates would not be observed with other catalysts. But as mentioned above, higher reaction rates were measured for 5%Rh/C and 5%Pd/C catalysts. The effects observed here are attributed to the limitations of hydraulic catalyst transfer of the catalyst in the recirculating system. That is, the catalyst charge in the reactor is not the same as the average value loaded because catalyst deposits occured in the reciculation loop at higher catalyst charges. This was confirmed by examination of the system, as after catalyst testing with a higher charges deposits were evident through the system, notably inside the backpressure regulator and in the dead-end of the pump head. Against this background the study was repeated using a 5%Pd/C catalyst.

The best catalyst, determined using the single capillary reactor, was 5%Pd/C—and it has a lower density than 5%Rh/Al_2O_3. If the hypothesis is correct, then the carbon supported catalyst should reach the plateau of constant absolute reaction rate for a higher catalyst loading. The experimental results confirmed this supposition (Table 2). The absolute reaction rate increased in the same ratio as the catalyst charge, while the relative reaction rate remained constant up to 1 g catalyst in 75 ml of resorcinol solution. There was no difference between the absolute and relative reaction rates of resorcinol hydrogenation for these catalysts in the autoclave; however, in the case of the micro-structured reactor there was a significant difference in the measured reaction rates. These results confirm that the reaction in the single capillary reactor is not mass transfer limited but rather that the decrease of the observed reaction rate constant with the increase of the catalyst loading was caused by the different quantities of catalyst settling in the system.

The deposition of dense catalyst at high flow rates is clearly a fault in the design of the reactor peripherals—primarily the pump and let down valve. Use of relatively smaller pipe work may help—but only up to a point because this is not the root cause of the particle deposition. Detailed consideration should be given to their design, and the avoidance of flow constrictions and pipe diameter changes in any future rig improvement or new build—whether at laboratory or plant scale.

4. Results with the heat exchange reactors

4.1. Flow visualisation experiments

Visualisation with water only showed that bubbles broke up into smaller bubbles and flowed through the channels in Taylor flow (Fig. 4). Flow through channels was not uniform. At the exit point these smaller bubbles coalesced together and formed bigger bubbles.

The MRI visualisation experiments were carried out using geometrically identical units at a lower liquid flow rate of 2.0 and 4.0 ml/min and a gas to liquid ratio of 2:1 and 1:1, respectively. At the lowest liquid flow rate the flow through channels was less uniform (Fig. 5A) than at higher liquid flow rate (Fig. 5B).

The video imaging experiments with water and alumina were carried out at two levels of concentration for alumina: 0.5 and 1.0%. There was no problem with fluid flow through the channels with 0.5% solids. With 1.0% solids, solids deposited at the entry point for gas injection and eventually the channel became blocked. This blocking was more apparent with low liquid velocities. Solid deposits in the reactor could be removed by reversing the fluid flow and passing gas bubbles through the reactor.

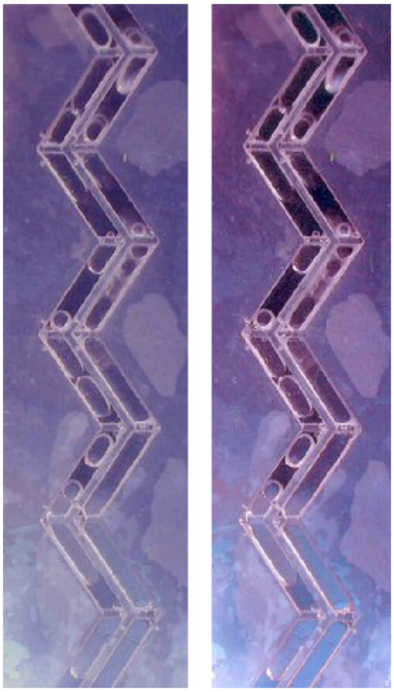

Fig. 4. Water–air flow visualisation through chart heat exchanger units.

In addition to traditional ceramic oxide and carbon supports, polymeric fibres were also investigated. The motivations for this were essentially twofold. First, these commercial supports offer significant interest as supports for heterogeneous and immobilised homogeneous catalysts. Second, given the solids transport issues in the peripherals, these presented and alternative low-density support to carbon.

The experiments using the fibre support were performed at three concentrations: 0.1, 0.3 and 1.0%. There were no blocking problems with the 0.1 and 0.3% solids in the Perspex Herringbone Units. Both the 1 and 2 mm channels were used.

Blocking of the channels occurred with the use of 1.0% solids loading. Liquid flow rates used were 40, 65, 110 and 150 ml/min. With the 1 mm channels and liquid flow rates of 110 and 150 ml/min, 1% loading did not have blocking of the channels. At these higher flow rates slug/Taylor flow was not obtained with the formation of very small bubbles and high flow velocity, which was not suitable to obtain pictures. However, when lower flow rates were used—initially there was no blocking but with time, blocking started. It was observed that the outer channels first get blocked and thereafter the inner channels. This was due to the velocity distribution between channels.

For the 2 mm channels there was much less blocking and only after a much longer time and mainly in the initial entry section.

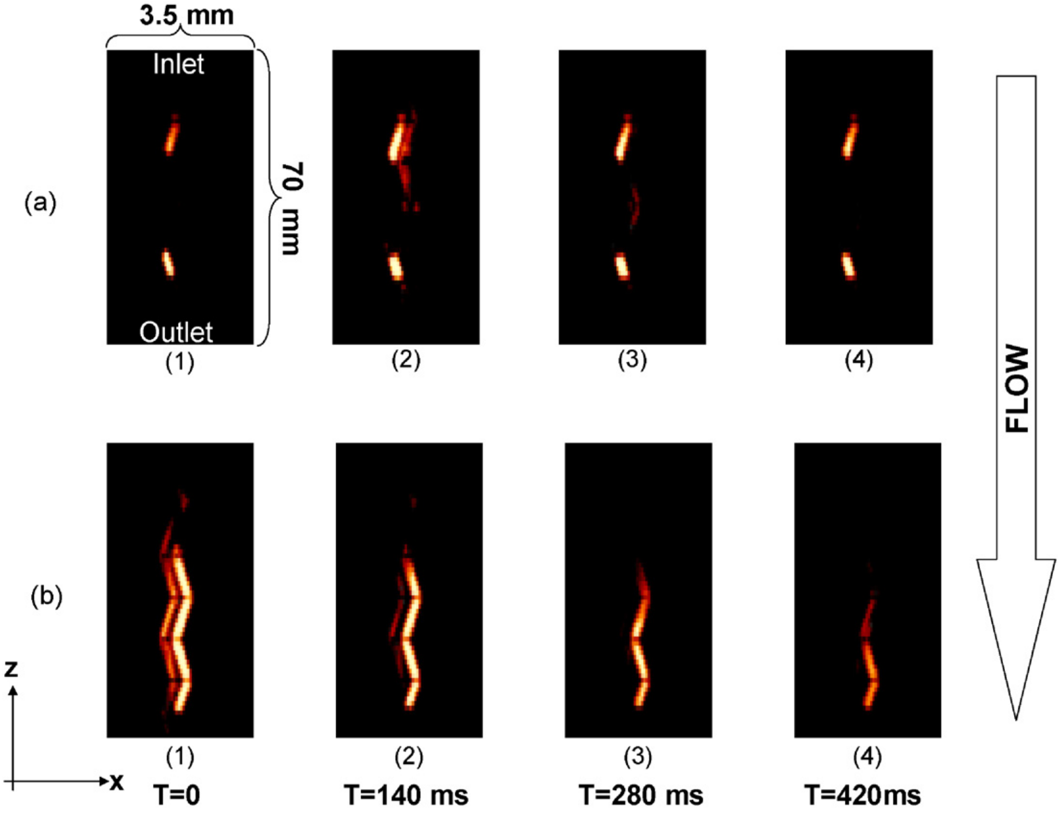

Fig. 5. MRI visualisation of the water–air flow through a HEx reactor.

It was concluded that in order to eliminate blocking of the channels with solids higher liquid flow rates and bigger diameter channels (2 mm) were better suited for reaction with slurry catalyst.

For three model reactors, visualisation experiments were carried out.

- The Model A reactor design used pin injection and splitter bars. In this model formation of gas/bubbles with biphasic flow occurred. With 1% solids there was a problem of blocking with both the 1 and 2 mm channels. It was noted that the gas inlet pressure had to be much higher than in normal gas injection systems used in earlier experiments.
- The Model B design had a perforated plate and splitter bars. The gas bubble flow obtained was similar to Taylor flow. Solid deposition occurred much quicker than in units without splitter bars, both in the 1 and 2 mm channels, though it took a longer period of time in the 2 mm channels.
- The Model C design was constructed with a perforated plate and no splitter bars. Gas distribution appeared to be much better than for Model A, and it was similar to that observed for Model B. Furthermore, there was no problem of solids depositing/blocking in either the 1 or 2 mm channels.

4.2. *Reaction testing of HEx reactors*

A series of experiments was performed in seven different HEx reactors, using a 5%Pd/C catalyst. These are capillary heat exchangers (1 or 2 mm wide with rectangular cross-section) with the channels forming a zigzag shape. The seven heat exchangers have a range of different characteristics, which can be summarised as follows:

- Manufactured with 8 channels 1 mm wide or 2 channels 2 mm wide, in order to achieve the same flow section and the same reaction volume.
- The presence or absence of splitter bars—these devices have the role to support the blades of the heat exchangers and to create a better mixing of the phases inside the reactor and a better heat transfer.
- Injection through a 1/16″ capillary injector (noted as no injection in Table 3), pin injector or via perforated plates.

The viscosity of the solution and the catalyst loading used in previous studies resulted in a large pressure increase when using the capillary heat exchanger reactors. Consequently, this study was performed in slightly different conditions. The concentration of the resorcinol solution was decreased to 24% and the catalyst loading was also decreased from 1 g in 75 ml of solution, to 0.15 g in 75 ml of resorcinol solution. For the same reason, the study was carried out at lower flow rates than the optimum value previously determined, the conditions used were; liquid flow rate = 10 ml min^{-1}, gas flow rate = 100 mlN min^{-1}. At the same time, technical constraints of a secondary pump, which was used to circulate the heating agent (liquid paraffin) through the heat exchanger, forced us to work at a lower temperature of 85 °C. The results obtained when the reaction was carried out in the heat exchangers are presented in Table 3.

Table 3
Results obtained in the HEx reactors: catalyst Pd/C-87L, 0.15 g catalyst/75 ml solution, 24% resorcinol concentration at 10 ml min^{-1} liquid flow rate, 100 mlN min^{-1} H_2 flow rate at 85 °C

Reactor	Channel W. × H.	Description	Average pressure (bar)	Reaction rate (mmol h^{-1})	Reaction rate (mmol h^{-1} $g_{\text{cat.}}^{-1}$)
KTS10437-7	1 × 1	No injection*–splitter bars	6.96	39.8	264.8
KTS10437-8	2 × 2	No injection*–splitter bars	6.13	47.0	313.8
KTS10437-16	2 × 2	Pin injection–splitter bars	6.30	51.4	343.2
KTS10437-24	2 × 2	Injection via perforated separating plate–splitter bars	6.33	53.2	354.6
KTS10437-28	2 × 2	No injection*–no splitter bars	6.19	42.4	282.4
KTS10437-37	1 × 1	No splitter bars–injection via perforated separating plate	6.27	41.4	276.2
KTS10437-38	2 × 2	No splitter bars–injection via perforated separating plate	6.41	57.6	384.6

No injection*—uses the same 1/16″ capillary injector as the single tube 1/4″ reactor.

The experimental values of the reaction rate show little difference between the values measured in the presence or absence of the splitter bars and also little influence of the system of injection used. The differences measured were within ±10% range for most of the results, which is the accepted experimental error. The only significant difference noted was when the size of the channels decreased from 2 to 1 mm. A decrease of the reaction rate with the decrease of the size of the channels was observed. This was an unexpected result, and contrary to the observations made in the first series of experiments using a vertical capillary tube reactor. The explanation of this behaviour is given by the results obtained in specially manufactured visualisation units.

4.3. Discussion

There are three factors that have to be discussed about the configuration of the HEx reactor, namely the size of the channels cross-section, the type of injector and the presence/absence of splitter bars.

- By comparing the results obtained using HEx Reactors KTS40437-7 with KTS10437-8 (entries 1 and 2 in Table 3) and KTS10437-37 with KTS10437-38 (entries 6 and 7) the differences between the measured reaction rates are well above the experimental error, and are in favour of the 2 mm × 2 mm channel reactors. This is explained by the results obtained in the visualisation units (see above, paragraph 4.1) for the experiments carried out in solid/liquid/gas flow. The use of HEx reactors with 1 mm × 1 mm cross-section channels lead to blockage of some channels quicker and to a greater extent compared with the 2 mm × 2 mm channels reactors. This result in the number of active channels, allowing the fluid to pass through, to decrease and thus an increase of the superficial velocity and a decrease of the residence time. Consequently, as demonstrated by previous results [12], if the residence time is too short, the reaction rate decreases up to the point of having no reaction at all. This was explained by the kinetics of hydrogen mass transfer and its chemisorption on the catalytic active sites.
- The ‘‘no injection’’ consists actually of a 1/16″ capillary inserted into a 1/4″ tube prior to the HEx reactor. That means that the gas bubbles and the liquid slugs are pre-formed before entering the reactor and consequently it can lead to a non-homogeneous distribution of the gas and liquid between the channels. The ‘‘no injection’’ type of reactor lead consistently to lower reaction rate (see for comparison entries 2, 3, 4, or entries 5 and 7 in Table 3), though in the first series, the difference is within the experimental error. However, the pattern: lower rate for ‘‘no injection’’ type reactor and higher rate observed for the perforated plate injector is always observed. These results are consistent with the visualisation experiments, which showed that in the case of the injection performed via perforated plates, better gas distribution was achieved.
- Finally, the presence/absence of splitter bars (entries 2 and 5, or 4 and 7) show that there is not much difference in the results obtained. Despite beneficial contribution for the local mixing and thus increase in the mass and heat transfers, the presence of splitter bars act as ‘‘nucleation’’ sites for the blockages with solid, according with the visualisation experiments.

As a result, the best reaction rate was obtained using a 2 mm × 2 mm cross-section channel reactor, with no splitter bars (both of these features helps decrease the blocking of the channels) and with injection performed via a perforated separating plate (which gives the best gas distribution).

It appears that the diameter of the capillary reactor plays an important role, and it an optimum value of between 2 and 3.5 mm is apparent [12]. When the channels are too small, some channels may be blocked by particles of settled catalyst. Consequently the hydraulic diameter of the reactor decreased, the velocity of the fluids was increased whilst the residence time in the reactor decreased. If the residence time in the reactor becomes lower than the induction time for the reaction, then no reaction would be observed. The induction time for the reaction could be related to the kinetics of hydrogen mass transfer and its chemisorption on the catalytic active sites. Blocking some of the channels will also lead to the decrease of the effective reactor volume to less than 3 ml, affecting the value of the reaction time.

An attempt to carry out the reaction at higher flow rates was made. The same behaviour as in previous studies [12] was observed when the flow rates were increased to the optimum values as can be seen in Table 4. Optimum flow rates were 15 ml min^{-1} for the liquid and 150 mlN min^{-1} for hydrogen.

Table 4
Catalytic results obtained at various liquid flow rates in the HEx reactors (catalyst Pd/C-87L, 0.15 g catalyst/75 ml solution, 24% resorcinol concentration at 85 °C)

Reactor	Average pressure (bar)	Liquid flow rate (ml min^{-1})	Reaction rate (mmol h^{-1})	Reaction rate (mmol h^{-1} $\text{g}_{\text{cat.}}^{-1}$)
KTS10437-16	6.30	10	51.4	343.2
KTS10437-16	6.43	15	79.0	526.4
KTS10437-16	6.24	20	20.2	134.2

Further increase of the liquid flow rate to 20 ml min^{-1} resulted in a decrease of the reaction rate, most likely caused by the decrease of the residence time in the reactor. The increase of the liquid flow rate should have also increased the quantity of transported catalyst, and consequently an increase of the reaction rate may be expected. This behaviour can also only be explained by the presence of an induction time for the reaction, which is most probably related to the time needed by hydrogen to reach the active sites of the catalyst.

5. Conclusions

A structured slurry bubble column concept for heterogeneously catalysed multiphase reactions in which all of the gas, liquid and slurry catalyst are circulated through thin channels has previously been reported, and significant rate benefits relative to a laboratory autoclave demonstrated [12,13,21] using a variety of chemistries. The effects of the main process parameters have also been explored. In this study, using resorcinol hydrogenation as a test reaction again, catalyst screening and catalyst loading effects have been examined using a representative single capillary reactor. The best catalyst of those tested for this reactor plus reaction combination was shown to be 5%Pd/C. The low density of the carbon support is favoured by the laboratory set up, because at high densities and high catalyst loading the operation becomes limited by the recirculating liquid's ability to transport the catalyst particles; this is however not necessarily a key issue with a scale process where design could be specifically to circumvent this problem.

The main objective of this paper has been to demonstrate the scalability of the structured slurry bubble column concept into compact heat exchange (HEx) reactors. In a production installation these reactors would mitigate the commonly limiting effects of heat generation on achievable rate and potentially allow minimisation or even eradication of solvent usage.

A number of prototype compact heat exchange reactors have been built and tested for gas, liquid and solid flow characteristics using MRI and video-graphic techniques. The key observations from this work were that Taylor or segmental gas–liquid flow is likely to prevail at the chosen liquid and gas rates, and that channel sized below 2 mm are generally unsuitable for the required gas–liquid–solid three phase flow. Based on these studies a number of the unit designs were selected for reaction testing.

Reaction testing showed that special channel design features such as flow splitter bars for flow disruption and distributed gas injection have little if any beneficial effect on the reactor performance. Using the best performing reactor, further studies investigated the effect of total flow rate, at the same phase flow ratios. These data confirmed a significant effect of flow rate on reactor performance.

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