



Separation studies in a continuous flow fluororous biphasic system

Proof of concept

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Abstract

A proof of concept study was undertaken for the separation of the fluororous solvent from the organic reactants/products of a fluororous biphasic system, in the absence of fluororous modified Rh catalyst. Fast and efficient separation of the two phases was observed. The more polar products were present in the organic phase—i.e. the higher the simulated conversion level—the less was the leaching of the fluororous solvent in the organic phase.

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1. Introduction

Heterogeneous catalytic systems are successfully used in many industrial processes, especially in the mineral oil industry. Although vigorous conditions are needed for industrially important conversion levels to be achieved and often selectivity is far from optimum, the successful performance of heterogeneous catalytic reaction without losing any solid catalyst to the product streams has advanced their industrialisation [1]. Homogeneous catalysts can provide very high activity and selectivity towards industrially desirable products under relatively mild conditions but their commercialisation has been so far hampered by the problem of their separation from the reaction products and solvent and hence the difficulties associated with their recycling [1,2]. To date many strategies and techniques for product separation from the catalyst in homogeneous systems have been developed, leading to an extensive use of organometallic complexes in homogeneous catalysis [1].

The new concept of fluororous biphasic systems (FBS) has been developed for the easy separation and recycling of the

homogeneous catalysts. A fluororous biphasic system consists of a fluororous phase containing preferentially a fluororous soluble catalyst and a second organic phase containing reactants and products with limited solubility in the fluororous phase [2,3]. The term fluororous was first introduced by Horvath and Rabai [2] as the analogue to the term aqueous to emphasize the fact that the reaction is mainly controlled by a reagent or a catalyst designed to dissolve in the fluororous phase. Fluororous phase is defined as the rich in fluorocarbon phase [2,4]. FBS are well suited for converting apolar reactants to products of higher polarity, as the partition coefficient of reactants and products is high and low respectively in the fluororous phase. The net result is little or no solubility limitation of the reactants in the fluororous phase and easy separation of the products. Furthermore, as the conversion level increases, the amount of polar products increases, further enhancing their separation efficiency.

One of the most important advantages of the fluororous biphasic catalysis concept is that many well-established hydrocarbon soluble reagents and catalysts can be converted to become fluororous soluble by the addition of fluororous ponytails [3]. The main advantage of FBS lies on the fact that with appropriate choice of organic and fluororous phases, by increasing the temperature and/or pressure the two phase system becomes a single phase, eliminating possible mass transfer

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limitations. Thus, catalysis occurs under genuine homogeneous conditions, with the advantages of high conversion and selectivity. After completion of the reaction, the system is cooled and the two phases are quickly re-established, for facile catalyst–product separation [5].

Fluorous biphasic catalysis is a generic technology that is applicable to a wide variety of homogeneous catalytic systems [2,6–12]. This work is focused on applying the technology on the hydroformylation of higher alkenes, a reaction system of great industrial importance [1,13].

Hydroformylation is the reaction between alkenes and a mixture of hydrogen and carbon monoxide (synthesis gas), which leads to linear (l) and branched (b) aldehydes as primary products. This reaction is the oldest and most widely used homogeneous catalytic reaction of alkenes [14]. The produced linear aldehydes are used as intermediates in manufacturing many different compounds, such as alcohols, diols, carboxylic acids, acroleins, acetals, ethers and amines. Alcohols are by far the largest group in the range of such products and are mainly consumed as plasticizers in the polymer and detergent industry [1]. Thus, high selectivity towards linear aldehydes is desirable.

Currently, the hydroformylation process for long chain alkenes is carried out industrially using cobalt-based catalysts, which require very harsh operating conditions. Considerable advantages in selectivity and operating conditions can be obtained using rhodium based catalysts, but conventional separation of the products by distillation is impossible since the boiling points of the products are well above the decomposition temperature of the catalyst. Various new approaches have been published for the rhodium catalysed hydroformylation of light and heavy alkenes [15–23]. Hydroformylation of higher olefins in fluorous biphasic systems using a rhodium modified catalyst has been successfully studied in batch experiments [6,7] but no continuous studies have yet been reported. A reactor for continuous flow Lewis acid catalysed reactions has recently been published [24].

In this work for the first time a pressurised continuous reaction system has been developed that enables catalyst separation and recycling. We developed this system for the long term testing of hydroformylation in an FBS. Besides the chemical reactor it includes a heat exchanger at the reactor outlet and a separator at its end. The phase behaviour and the mass transfer characteristics of the system are essential for the design of the reactor and separator. Approximate first order kinetics with respect to the substrate concentration, observed in batch experiments, [6] was used for the initial design. However, studies of the phase behaviour of the perfluoromethylcyclohexane/octene/nonanal fluorous system have shown that, because of the incomplete miscibility of the product aldehyde with the fluorous solvent even under the reaction conditions the substrate is reversibly transferred between the two phases [25]. Such behaviour complicates the reactor modelling.

We report here initial tests of the separation efficiency in the absence of chemical reaction. In these experimental runs

the fluorous solvent, perfluoromethylcyclohexane (PFMCH), substrate, 1-octene, and product, *n*-nonanal, were fed into the system. The ratio of octene to *n*-nonanal was varied, thus simulating different conversion levels. CO and H₂ were used to pressurise the reactor. These experiments have verified the separation concept principle of the system providing very useful observations as well as very encouraging results. Moreover, we report the results of liquid–liquid equilibrium batch experiments with PFMCH, 1-octene and nonanal under the conditions pertaining in the separator. The results are in good agreement with those obtained from the continuous experiments, verifying further the concept principle of the designed system.

2. Experimental

2.1. Materials

Perfluoromethylcyclohexane (PFMCH, 90% pure), 1-octene (98% pure) and nonanal (95% pure) were all used as purchased from Aldrich without further purification.

2.2. Equipment

All the continuous separation experiments were performed in the system shown schematically in Fig. 1. The continuous flow system is comprised of a continuous stirred tank reactor (CSTR), a glass separator, a heat exchanger, two HPLC pumps, a pressure controller, two mass flow controllers for gases and a mass flow meter for liquids. Fig. 2 is a photograph of the experimental set-up.

2.2.1. Reactor

The CSTR (S.S. 100 cm³, Parr) is fitted with an outside heating mantle, a thermocouple, a pressure gauge, a stirrer (1800 rpm), a gas/liquid inlet, an outlet port and a bursting disc. It was operated under high pressure, usually 20 bar.

2.2.2. Separator

The separator (glass, 100 cm³) is a simple settler of cylindrical shape where the top organic phase overflows through the top outlet, while the fluorous phase containing the catalyst is removed from the bottom outlet. The separator is also fitted with a gas vent and a sampling port. It operated under normal pressure as depressurisation of the reaction mixture took place before entering the separator.

2.2.3. Heat exchanger

The heat exchanger (S.S.) is a simple 1-1 tube-shell type, designed according to standard procedures [26].

2.2.4. Pressure controller

A pressure controller (Brooks Instrument) is used for down stream pressure regulation, keeping the pressure in the reactor constant independent of the gas inlet stream pressure variations.

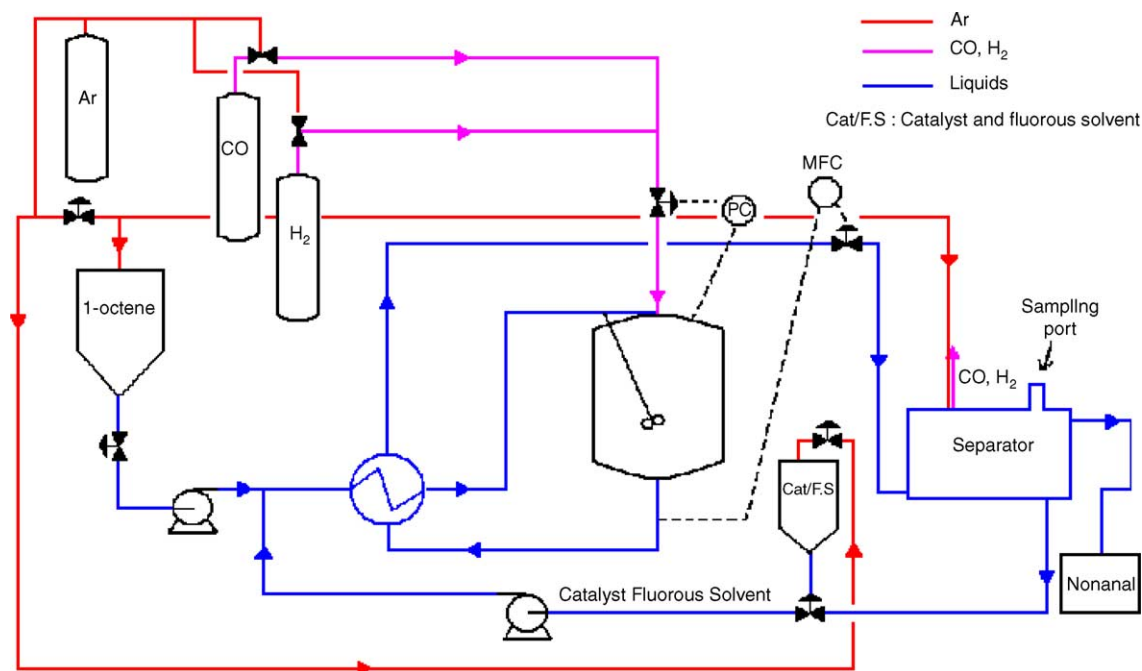


Fig. 1. Flow diagram of the continuous flow fluoruous biphasic experimental set-up.

2.3. Experimental procedure of the continuous experiments

The organic mixture composed of 1-octene, nonanal and the fluoruous solvent from the bottle or the recycling stream were mixed and preheated at the heat exchanger before entering the CSTR. Two HPLC pumps (one for the organics, the other for the fluoruous solvent) were used to deliver the

liquid streams at a constant flow rate. CO and H₂ were delivered through two mass flow controllers at a 1:1 ratio, connected to the pressure controller keeping the reactor pressure at high levels (10, 15 or 20 bar). The liquid stream leaving the reactor was cooled down at the heat exchanger in order to facilitate a faster phase separation and entered the separator through a mass flow meter and a capillary. The pressure in the separator was atmospheric and the flow of the liquid



Fig. 2. Photograph of the continuous flow fluoruous biphasic experimental set-up.

stream due to the differential pressure between the reactor and the separator was controlled by the length of the capillary. Any gases not dissolved in the liquids were exhausted through the gas vent at the separator. The reaction mixture, products and unreacted reactants, were collected at the overflow outlet while the fluoruous phase was recycled to the CSTR. In order to avoid oxidation of nonanal to nonanoic acid, two nitrogen streams were used to degas the set up before the beginning of the experiment and keep it under a nitrogen atmosphere.

In a typical separation experiment a mixture of PFMCH, 1-octene and nonanal (1:1 volume ratio of organics:fluoruous) was prepared and injected into the reactor. The system was then sealed and heated with rapid stirring (1200 rpm) to 70 °C. CO and H₂ were added slowly to the reactor to a pressure of 10 bar. The mixture in the reactor was left to equilibrate for a few minutes before the reactor outlet valve was opened and the liquid started entering the separator. At the same time the pumps started to deliver new fluoruous and organic liquids to the reactor. As soon as, the separator was filled and the organic phase started to overflow the fluoruous phase was recycled to the reactor in place of the fresh fluoruous solvent. The system was run continuously with the two phases in the separator being sampled and analysed every 30 min and for a total duration of 2.5 h. The same procedure was followed in the experimental runs with increased reactor pressure of 15 and 20 bar.

2.4. Experimental procedure of the batch experiments

5 cm³ of the organic mixture and 5 cm³ of PFMCH were syringed into a sealed graduated glass test tube (25 cm³), which was then heated at 348 K for 40 min using an oil bath. Following the heating, the test tube was put into a temperature controlled oil bath set at 300 K for another 40 min, time enough for the liquid–liquid equilibrium to be established. At the end of the experiment both phases were sampled and analysed.

2.5. Experimental conditions

Five different organic mixtures of 1-octene and nonanal were prepared simulating different conversion levels:

1. 100 mol% 1-octene; simulated conversion level 0%.
2. 60 mol% 1-octene and 40% mole *n*-nonanal; simulated conversion level 40%.
3. 40 mol% 1-octene and 60% mole *n*-nonanal; simulated conversion level 60%.
4. 20 mol% 1-octene and 80% *n*-nonanal; simulated conversion level 80%.
5. 100 mol% nonanal; simulated conversion level 100%.

Each conversion level was tested for three different reactor pressures, 10, 15 and 20 bar. For each organic mixture composition and different reactor pressure five different samples were taken simultaneously from both phases in the separator.

The samples were taken over a period of 2.5 h when the continuous system was at steady state. The results shown later are the averaged values of the analyses for these five samples.

The same conversion levels were studied under static equilibrium. Three different test tubes were used for each conversion and the results shown later are the averaged values of the three samples.

2.6. Analytical method

Gas chromatographic analyses of the organic phase mixtures were carried out in a Perkin Elmer 8410 gas chromatograph equipped with a flame ionisation detector (GC/FID, split injection of 1:100) (quantitative analysis). The column used was a J&W Scientific DB-Petro capillary column (100 m × 0.25 mm × 0.5 μm).

Gas chromatographic analyses of both phases samples from the equilibrium experiment were carried out in a Hewlett-Packard 5890 series gas chromatograph equipped with a flame ionisation detector (GC/FID, split injection 1:100) (quantitative analysis). The column used was a Supelco MDN-35 capillary column (30 m × 0.25 mm × 0.25 μm).

In order to ensure that the samples were not cross-contaminated, fluoruous layer samples were taken from the bottom of the phase while product layer samples were taken from the top of the organic phase using a different syringe for each phase.

3. Results

Horvath et al. [7] have reported that perfluoromethylcyclohexane/toluene/1-octene (40:40:20 molar ratio) form a monophasic system under typical hydroformylation conditions (100 °C, 10 bar CO/H₂, 1:1) while Foster et al. [6] have reported that 1-octene is totally miscible with perfluoromethylcyclohexane at temperatures above 60 °C under 20 bar CO/H₂ (1:1), but nonanal is visually separated even at 80 °C. Nevertheless, not many studies have been published on the partition coefficients of the substrates and the products in the fluoruous and the organic phase under the conditions of the separation process [27]. Such data are very useful for the design and optimisation of fluoruous catalysts and reagents [27]. In our case, minimising the leaching of the expensive fluoruous solvent into the organic phase would also have a positive effect on the leaching of the expensive fluoruous modified rhodium catalyst.

3.1. Efficiency of the separation principle

During the experimental runs photographs of the two phases in the separator were taken which gave useful information about the separation process. As shown in Fig. 3, the mixture entering the separator at steady state is already separated into two phases, the top organic phase and the bottom

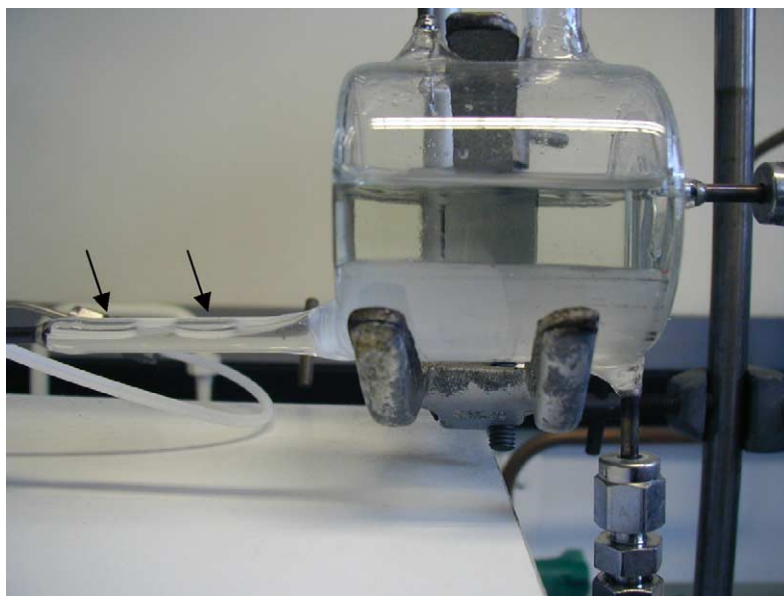


Fig. 3. Separator at steady state.

fluorous phase. Drops of organic phase appear distinct in the bulk of the fluorous phase in the transparent tube at the inlet of the separator. As soon as these drops enter the separator, they quickly ascend and are added to the organic phase, Fig. 4. Any fluorous solvent that has been dragged to the top layer, due to the motion of the drop, quickly coagulates to drops that fall back to the bottom layer, Fig. 5. In Fig. 6 the system is highly disturbed. Because of malfunction of the liquid flow control there was too high a flow of liquids and gases into the separator causing the haziness observed. Nevertheless, looking closely at the separator, at the side of the overflow and recycling outlets, the two liquid phases are well separated and the interface is almost unaffected. This

confirms that the separation is fast. It also confirms that the settler design is appropriate for the application.

3.2. Effect of the reactor pressure

Figs. 7 and 8 show the composition of the fluorous and the organic phase respectively. Each column corresponds to different conditions (different simulated conversion and different reactor pressure) with the vertical lines in between the columns grouping the conversion levels. Comparing the results for the same composition of the organic feed and for the three reactor pressures it is obvious that the reactor pressure has no effect on the separation process. This is

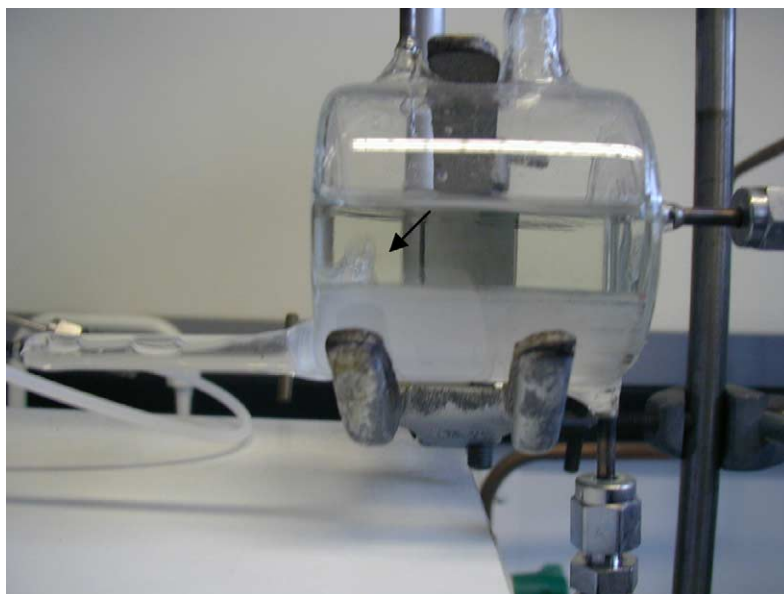


Fig. 4. Ascending of the organic phase in the separator.

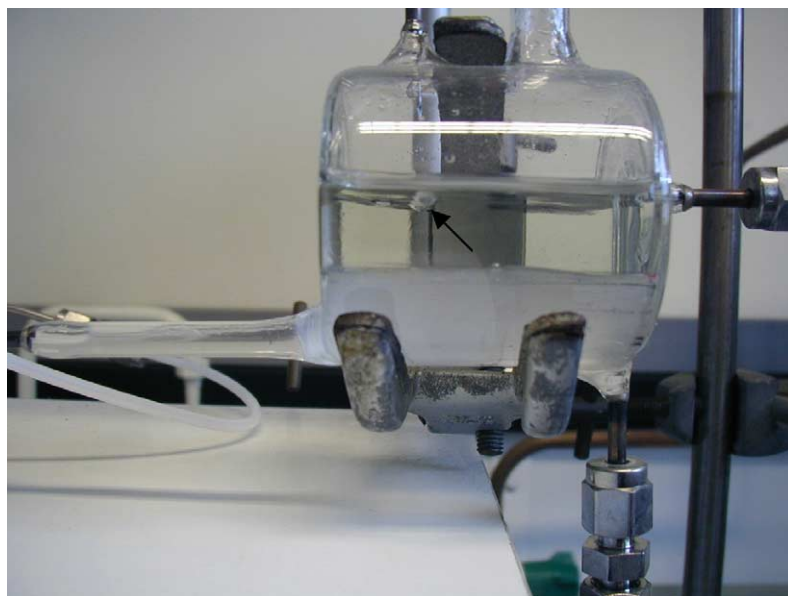


Fig. 5. Descending of the fluorine phase in the separator.

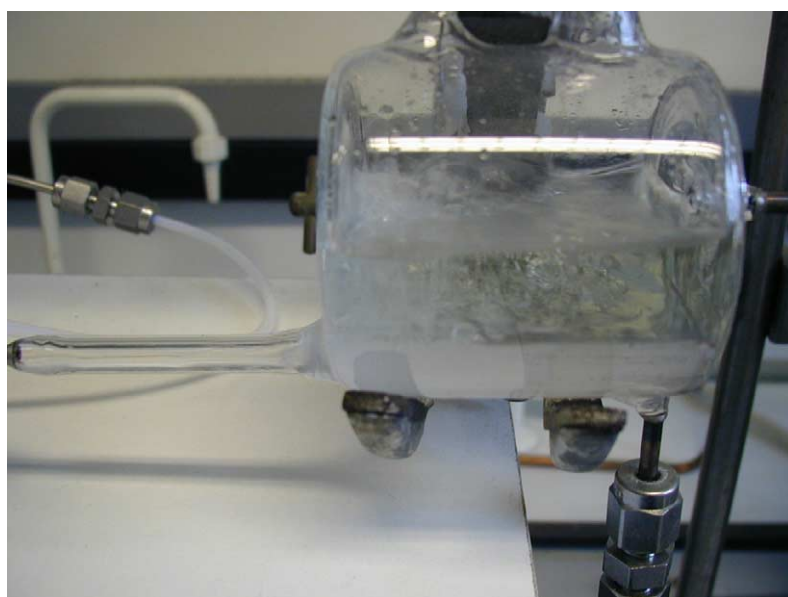


Fig. 6. Separator at high flow conditions.

expected since separation is carried out at the same temperature and pressure for all feed mixtures and reactor pressures. The small deviations in the values are due to experimental scatter in the GC analysis.

3.3. Composition of the fluorine and the organic phase

Tables 1 and 2 list the composition of the fluorine and organic phases, respectively. The values presented are the averaged values for the three reactor pressures. The composition is expressed in mol%. Examining the composition of the fluorine phase, we note that 17.3 mol% of pure 1-octene

partitions into the fluorine phase, while only 2 mol% of pure nonanal partitions into the same phase under the same conditions. As the simulated conversion increases from 40% to 60% to 80%, the total amount of the organics in the fluorine

Table 1
Composition (mol%) of the fluorine phase

	Simulated conversion level (%)				
	0	40	60	80	100
PFMCH	82.7	91.3	93.7	96.0	98.0
1-Octene	17.3	7.7	5.0	2.0	–
<i>n</i> -Nonanal	–	1.0	1.3	2	2.0

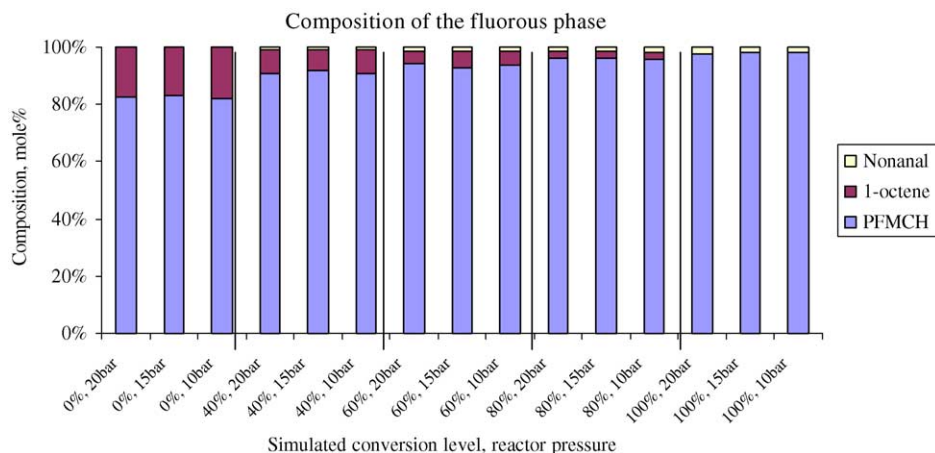


Fig. 7. Composition of the fluoruous phase, effect of the reactor pressure.

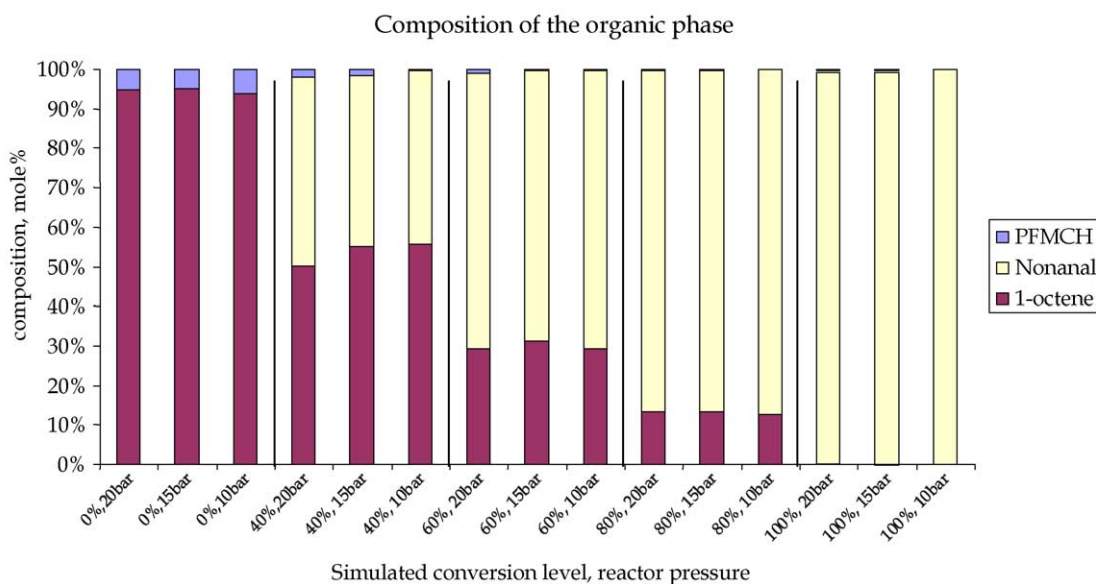


Fig. 8. Composition of the organic phase, effect of the reactor pressure.

phase decreases from 8.7 to 6.3 to 4 mol%. Consequently, the higher the conversion in the reactor, the less the retention of the organics. However, since the fluoruous phase is recycled, the quantities of the organics within it should not be considered as a loss.

Similar behaviour is observed in the organic phase composition. When pure 1-octene is fed into the system, 5.3 mol% of PFMCH is found in the organic phase, while for pure nonanal it drops to less than 1%. Again an increase in the

conversion level results in less leaching of the fluoruous solvent into the organic phase. It is important to keep this leaching to a minimum since not only would fluoruous solvent be removed continuously from the reactor, but the fluoruous solvent may also carry the expensive modified Rh catalyst out of the system. Thus, it is desirable to keep the conversion level in the reactor at a maximum. The results in Table 2 suggest that for conversions higher than 60% less than 1 mol% of PFMCH is found in the organic phase. It should be noted, though, that the accuracy of values lower than 1% is questionable due to the accuracy of the GC analysis.

3.4. Liquid–liquid equilibrium of PFMCH + 1-octene + nonanal

Tables 3 and 4 list the equilibrium composition of the fluoruous and the organic phase respectively. Comparing the

Table 2
Composition (mol%) of the organic phase

	Simulated conversion level (%)				
	0	40	60	80	100
PFMCH	5.3	1.3	0.5	0.3	0.2
1-Octene	95.7	53.7	30.0	13.3	–
<i>n</i> -Nonanal	–	45.0	69.5	86.4	99.8

Table 3
Composition (mol%) of the fluorous phase equilibrium studies

	Simulated conversion level (%)				
	0	40	60	80	100
PFMCH	82.5	89.5	93.0	95.2	98.1
1-Octene	17.5	9.1	5.5	3.2	–
<i>n</i> -Nonanal	–	1.3	1.5	1.6	1.9

Table 4
Composition (mol%) of the organic phase equilibrium studies

	Simulated conversion level (%)				
	0	40	60	80	100
PFMCH	11.2	5.5	4.1	3.3	2.8
1-Octene	88.8	58.6	40.2	22.1	–
<i>n</i> -Nonanal	–	35.9	55.8	74.6	97.2

results of the continuous runs with the equilibrium values, we see that the composition of the fluorous phase is in good agreement with the equilibrium experiments. Thus, equilibrium conditions were achieved in the separator. Nevertheless, the composition of the organic phase in the continuous runs seemed to contain less fluorous solvent than the equilibrium values. This is not as paradoxical as it might seem. The separator, in contrast to the test tube, is an open system with large quantities of CO and H₂ flowing through both liquid phases. Moreover, a constant N₂ stream flows over the top organic phase causing to some extent vaporisation of its components. As PFMCH is much more volatile than 1-octene or nonanal it evaporates more, resulting in concentrations lower than the equilibrium values. An optimised system should take this vaporisation into account. It should recover the fluorous vapours and reuse the expensive fluorous solvent.

The results listed in Tables 3 and 4 can be used to form the phase diagram for the PFMCH + 1-octene + nonanal ternary mixture at 300 K, Fig. 9. The system exhibits type II phase behaviour, having two pairs of partially miscible solvents (PFMCH + 1-octene and PFMCH + nonanal) and one pair of complete miscible solvents (1-octene + nonanal), over the temperature investigated. The equilibrium values are those represented by open squares, while

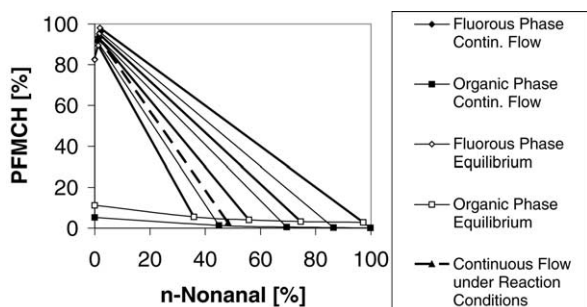


Fig. 9. Right triangle three-component phase diagram for the system PFMCH + 1-octene + nonanal, at 300 K and atmospheric pressure.

Table 5
Composition (mol%) of organic and fluorous phase under reaction conditions in the presence of homogeneous Rh catalyst

	Organic phase (top)	Fluorous phase (bottom)
PFMCH	2.87	93.55
1-Octene	48.87	5.17
<i>n</i> -Nonanal	48.26	1.29

the points represented by filled squares are the composition of the fluorous and the organic phase from the continuous runs.

Furthermore results from a continuous flow system under reactive conditions, Table 5, show that the separation of the two phases is not influenced by the presence of the Rh hydroformylation catalyst, prepared with the addition of the rhodium complex, [Rh(acac)(CO)₂], and the fluorous modified ligand, P(C₆H₄-4-C₆F₁₃), (Rh:P = 1:5) [6]. The corresponding points (triangles) in Fig. 9 do not deviate from those of the continuous flow non-reactive system in the absence of a catalyst. Future experiments should also clarify the question of rhodium distribution between the two phases and we hope that we will be able to report these in a future communication.

4. Conclusions

We have demonstrated for the first time the successful operation of a pressurised continuous flow reaction system that enables catalyst separation and recycling.

- The initial tests in the absence of chemical reaction verified the efficient separation of the system. The two well-distinct phases settle quickly in the separator. The organic phase ascends through the fluorous phase creating a top organic-rich phase while the fluorous phase descends through the organic phase creating a bottom fluorous-rich phase.
- The partition of nonanal in the fluorous phase and of perfluoromethylcyclohexane in the organic phase is kept at low levels provided that the conversion is high (60%). With reference to the simulated conversion levels, the higher the conversion, the less the leaching of the expensive fluorous solvent into the product organic phase.
- The reactor pressure has no effect on the efficiency of separation.
- The composition of both phases in the separator reaches the equilibrium values. This composition remains unaffected by the presence of a Rh hydroformylation homogeneous catalyst. However, a method should be developed to recover the fluorous solvent from the exhaust gas stream.
- The continuous system that has been developed in this work can be used for the long term testing of hydroformylation in a fluorous biphasic system.

Acknowledgements

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