



Heterogeneous reactive extraction for an intensified alcohol production process

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ABSTRACT

The heterogeneously catalysed hydration of olefins with ion exchange resins in randomly packed trickle bed and flooded bed reactors is a widely used process for the production of sec. alcohols, e.g. isopropyl alcohol (IPA). Typically, such processes are operated at temperatures ranging from 130 °C to 190 °C and pressures between 6 MPa and 10 MPa. Therefore, alcohol and water are in liquid state and the olefin is in liquid or supercritical state, respectively. The alcohol is formed in the water swollen gel phase of the macroporous ion exchanger and may be extracted by means of an olefin rich organic phase which is immiscible with the aqueous phase surrounding the catalyst beads. In presently operated industrial processes the importance of this simultaneous extraction is not fully considered. By the continuous removal of alcohol from the catalyst phase the driving forces for the reaction can be maintained on a high level and the selectivity for alcohol production can be improved. This work proposes a new reactor concept where the reactor is equipped with a structured catalytic packing for enhanced mass transfer performance. The new reactor then operates as a heterogeneous reactive extraction column offering similar advantages like reactive distillation processes. Furthermore, the modified reactor concept leads to a less energy demanding product purification sequence significantly lowering the operative costs for the process. As a result, the analysis of processes as a whole can be a promising approach to process intensification especially when modifications to one process unit affect other units.

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1. Introduction

The first plant applied on a large scale for the direct hydration of propene with strong acidic ion exchange resins was started in 1972 at the Meerbeck site of Deutsche Texaco AG, FRG. The reactor was designed as co-currently operating trickle bed subdivided into multiple trays with intersectional injection of cooling water (Fig. 1). The molar feed ratio of water to propene is about 12.5–15:1 and the conversion of propene is at least 75% per pass (Neier and Woellner [1]). Thus, the organic phase is almost consumed when the reaction mixture leaves the reactor and, as a consequence, the formed IPA has to be recovered from a very dilute (approx. 5–7 mole% IPA) aqueous phase. Regarding the ion exchange resin catalysed liquid phase hydration of linear olefins various patents (Brandes et al. [2,3]; Carls et al. [4,5]; Henn et al. [6]; Neier et al. [7]) discuss several difficulties which comprise polymerisation of propene deactivating the catalyst, hot spots by polymerisation and a high pressure drop. In general, due to the highly selective sorption of water by the catalyst no polymerisation of the olefin occurs. The mentioned patents report a remarkable loss of

selectivity for IPA of about 50% when the catalyst gets dry. The trickle bed reactor as used for IPA production can show incomplete catalyst wetting (Pangarkar et al. [8]). The related results, therefore, indicate an incomplete wetting of the catalyst phase which provides direct contact of concentrated (liquefied) olefin to dry catalyst. The patent authors use a high water to propene feed ratio in order to overcome the problem of a poor wetting performance. This results in a large water recycling stream.

Another characteristic property of a randomly packed fixed bed containing wet acidic ion exchange resin beads (approx. 1 mm O.D.) and free water in the void space of the bed imposes some more undesirable effects on fluid dynamics. The free water which completely fills the void space between the catalyst beads acts as an adhesive agent on the catalyst forming a pasty lump. Thus, there is no space for the olefin to pass the catalyst bed, and as a consequence, the olefin accumulates in front of the catalyst bed leading to a rising pressure drop (Fig. 2). As the pressure drop reaches a sufficiently high level only a few channels are formed in the bed and the accumulated olefin then rapidly flows off through these few channels. The channels in the bed will relocate when the high pressure drop is released and the described cycle restarts. Adjacent to the high pressure drop maldistribution of olefin in the bed and a small interfacial area degrade the mass transfer performance of the trickle bed reactor. The only advantage of

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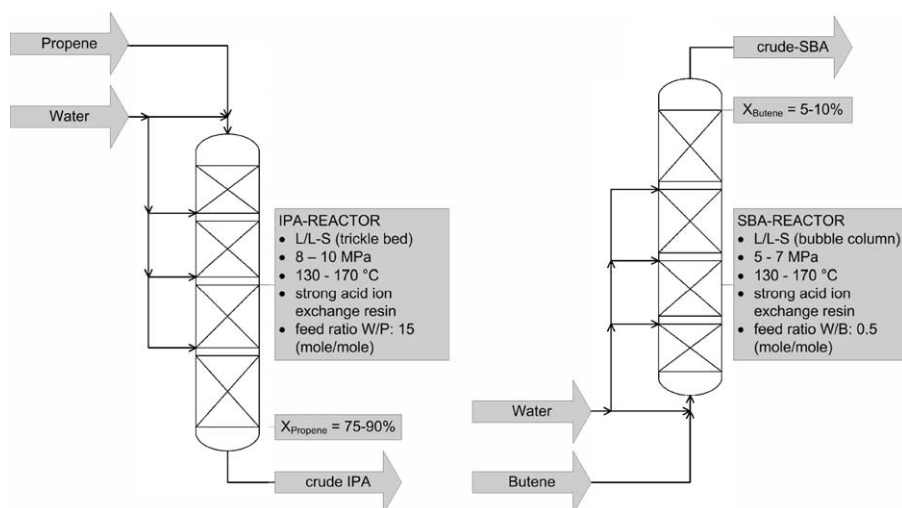


Fig. 1. Scheme of industrial multiphase reactors for the production of isopropyl alcohol (IPA) and secondary butyl alcohol (SBA).

the trickle bed reactor for the case considered here seems to be the high catalyst loading capacity. Nevertheless, for the given application the trickle bed reactor is probably the worst choice of currently available multiphase reactor types.

In 1983 Deutsche Texaco AG started a plant for the ion exchange catalysed liquid phase hydration of linear butene isomers. Here, Deutsche Texaco AG used a submerged fixed bed reactor with gas bubbling as described in Gianetto and Silveston [9] or a flooded bed reactor as described in Al-Dahhan et al. [10], respectively. Due to the co-current up flow this reactor type has an improved wetting

performance for which a significantly reduced molar feed ratio of water to butene of about 1:2 is feasible without any loss in selectivity (Fig. 1). However, the submerged ion exchange resin bed still shows the same behaviour as described in the previous paragraph. Accordingly, the difficulties of olefin maldistribution, rather small interfacial areas and transient pressure drop are not yet eliminated.

2. A new reactor concept: heterogeneous reactive extraction

In view of the mentioned deficiencies of trickle bed and flooded bed reactors for this application a new multiphase reactor concept is desirable. The main problem arising in randomly packed fixed bed multiphase reactor types is the lumping of the acidic ion exchange resin beads by water imposing high pressure drop, maldistribution of olefin and incomplete catalyst wetting. Within this new reactor concept the main objective is the generation of void space for the olefin and large interfacial surface area for a good mass transfer performance.

A possible solution can be the use of so-called open cross-flow structured catalytic packings which are commercially available and are widely used in heterogeneously catalysed reactive distillation processes (Pangarkar et al. [8]). Structured catalytic packings, e.g. Katapak[®] developed and manufactured by Sulzer Chemtech (Goetze et al. [11]), provide void space for the olefin between catalyst filled wire gauze pockets and corrugated metal sheets significantly reducing pressure drop (Fig. 3). Furthermore, large specific packing areas, good radial mixing and flexibility regarding catalyst load are typical properties of these types of packings. Moreover, structured packings extend the applicability of mechanically less resistant ion exchange resin compounds. In order to achieve good wetting of the catalyst and the packing surface, a hydrophilic construction material, e.g. stainless steel wire mesh, is beneficial.

By changing the catalyst arrangement from a randomly packed fixed bed into a structured packing it is now possible to account for the extraction of the desired product alcohol by the olefin phase. The simultaneous extraction of the formed alcohol is advantageous with respect to space time yield and selectivity. This is due to the fact that strong sorption of alcohol takes place in the catalyst phase leading to the formation of the undesired by-product ether and to the reverse reaction (Petrus et al. [12,13]).

Besides this, the organic extract phase dissolves approx. 15 times more alcohol than the coexisting aqueous phase. The alcohol might now be recovered from the organic extract phase. First, a stripper

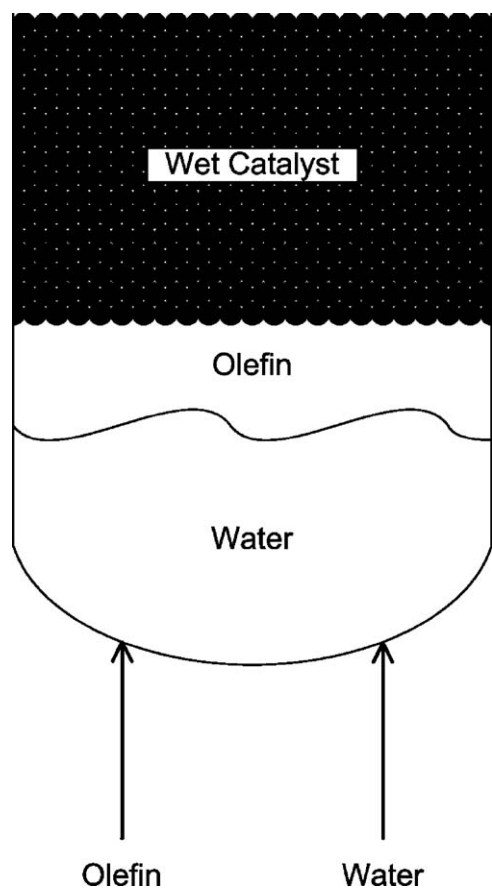


Fig. 2. Two phase region in front of a randomly packed flooded bed of ion exchange resin catalyst.

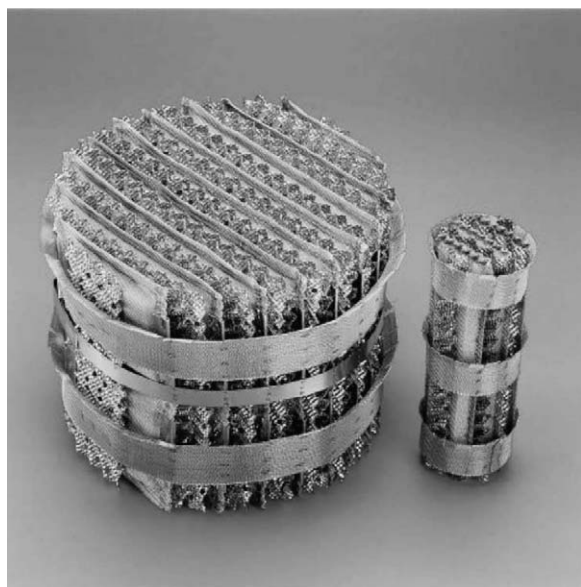


Fig. 3. Industrial and laboratory scale Katapak-SP 12. Picture taken from Goetze et al. [11].

recovers unconverted olefin and produces a bottom product mainly containing alcohol and water in a molar ratio of at least 1. A heteroazeotropic distillation unit is then used for purification of the alcohol whereas an aqueous solution containing approx. 5–7 mole% alcohol (as it is withdrawn from the trickle bed reactor) needs to be enriched before being passed to a heteroazeotropic distillation unit. Hence, the commonly used distillation column for enrichment of dilute aqueous alcohol solutions is substituted by a stripper with a significantly lowered energy demand.

3. Experimental

In preliminary experiments two similar ion exchange resins have been compared in a randomly packed trickle bed and in a structured packed bed reactor for the hydration of propene at the Sasol production site in Moers, Germany. The setups for both reactors comprising the main physical and geometrical properties are shown in Fig. 4a and b. The results presented here were obtained for the C_3 hydration system. While operating the randomly packed bed in co-current down flow the structured packing was operating counter-currently with a continuous organic phase and a disperse aqueous phase trickling along the catalyst pockets and packing surfaces. In all experiments the pressure was set to 9 MPa. Higher space time yields (STY in $\text{mole}_{IPA}/\text{ltr}_{cat}/h$) were observed for the structured catalytic packing for both catalysts and superficial mass flow velocities (G in $\text{kg}/\text{m}^2/\text{s}$) as given in Table 1. The slopes of the STY s with respect to temperature of both reactor configurations are almost the same indicating that the rate determining macroscale phenomena in both configurations are probably identical and that the improved STY s of the structured packing are probably caused by an enlarged interfacial area. However, these presumptions need to be confirmed by further experiments.

More experiments were carried out for a structured packing filled with catalyst B. Again, propene was used as the olefin for the comparison of different flow and hold-up situations. In Fig. 5a and b the reactor 7 is fed by the olefin inlet stream 1 and the water inlet stream 2. Stream 3 is the organic phase outlet and stream 4 is the aqueous phase outlet. The minor part of stream 3 served as purge stream. The recycle stream 5 is driven by pump 8 and is combined with a feed stream to the reactor inlet stream 6. Number 9 marks the position of the phase boundary layer between the organic and aqueous phase. Four different operation modes were investigated:

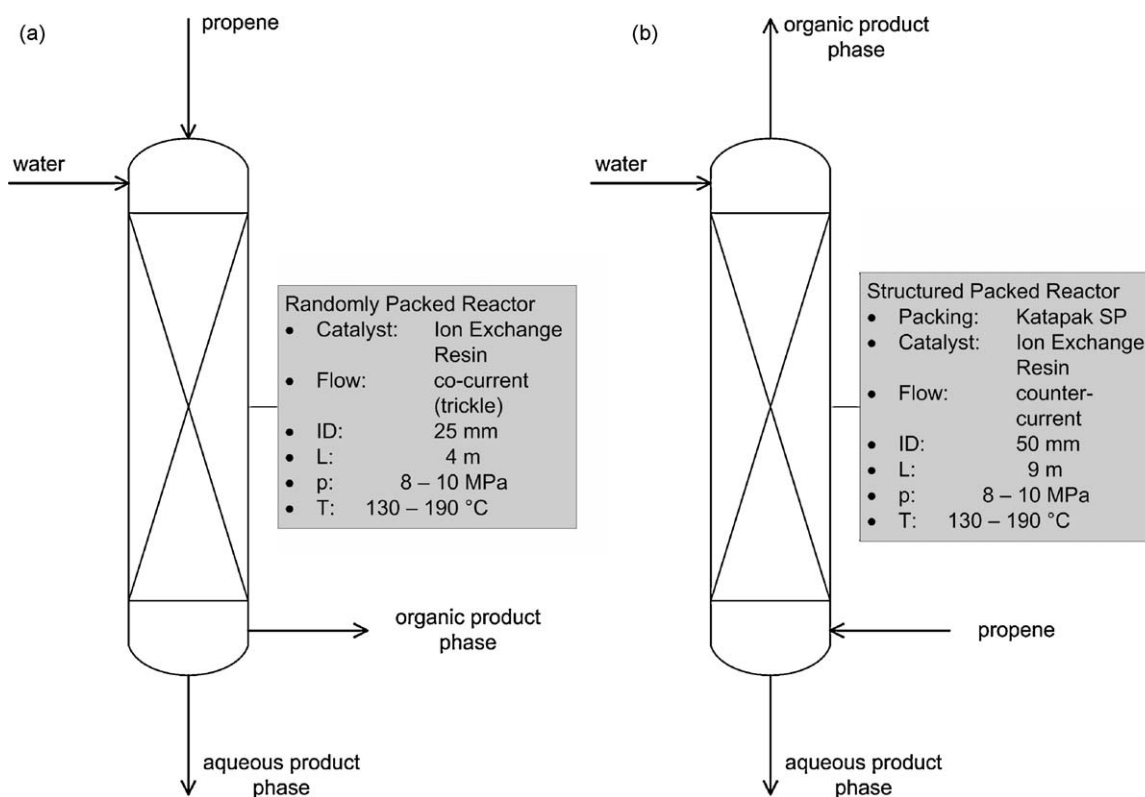


Fig. 4. Comparison of experimental high pressure reactors: (a) randomly packed reactor; (b) structured packed reactor.

Table 1

Comparison of random and structured packing for IPA production.

	Catalyst A (operated at temp. limit 160 °C)		Catalyst B (operated at 170 °C)	
	Random packing	Structured packing	Random packing	Structured packing
STY	3.34	5.37	4.79	7.96
G_{water}	1.95	0.30	1.95	0.30
G_{olefin}	0.78	0.28	0.78	0.28

(a) Propene was the stationary phase and water was the mobile phase. The phase boundary layer 9 was below the catalytic packing, see Fig. 5a. Recovery of IPA was done from the aqueous phase, stream 4. There was no recycle, stream 5 was zero.

- (b) Same conditions as described in (a), but recovery of IPA was done from the organic phase, stream 3. The major part of the aqueous phase outlet stream 4 was recycled by stream 5.
- (c) Water was the stationary phase and propene was the mobile phase. The phase boundary layer 9 was above the catalytic packing, see Fig. 5b. Recovery of IPA was done from the aqueous phase, stream 4. The major part of the organic phase outlet stream 3 was recycled by stream 5.
- (d) Same conditions as described in (c), but recovery of IPA was done from the organic phase, stream 3. There was no recycle, stream 5 was zero.

The results of these operation modes are summarized in Table 2. When propene is used as the continuous phase and water is trickling along the structured catalytic packing (modes a & b) the

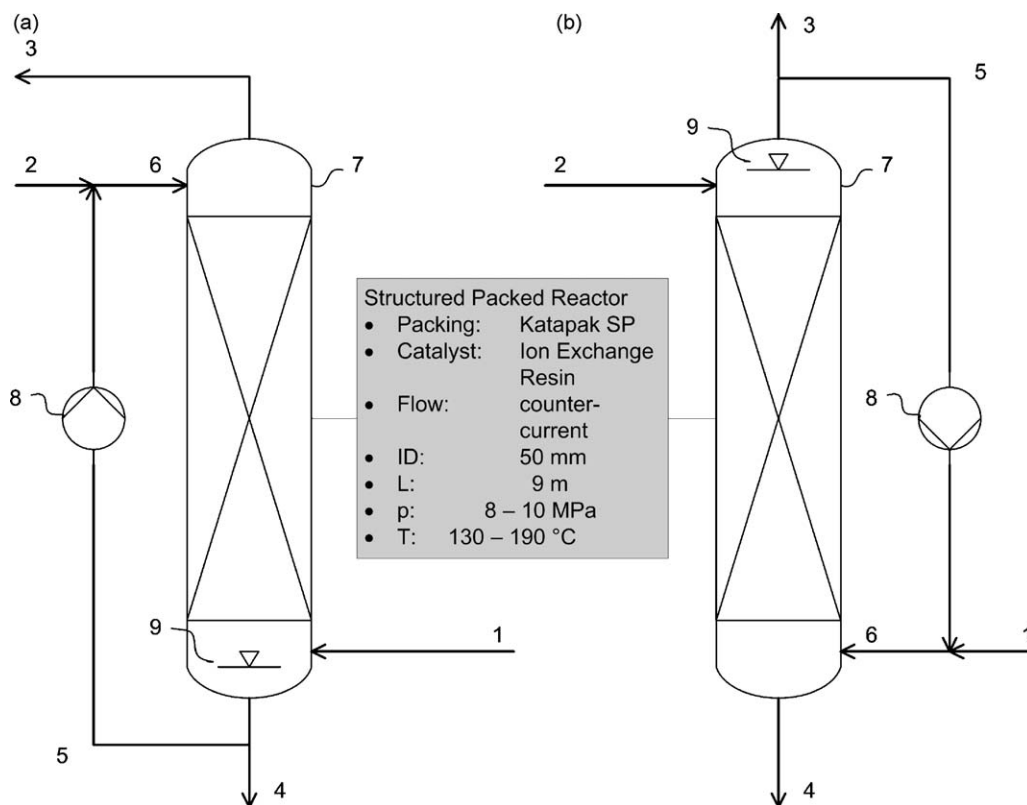


Fig. 5. Experimental high pressure reactor equipped with a catalytic structured packing (7), olefin feed (1), water feed (2), organic phase exit (3), aqueous phase exit (4), recycle (5), recycle + feed (6), recycle pump (8), and phase boundary layer (9). (a) Recycling of aqueous phase (modes a & b, c.f. Table 2). (b) Recycling of organic phase (modes c & d, c.f. Table 2).

Table 2

Comparison of operation modes of the structured packing for IPA production.

	Mode a	Mode b	Mode c	Mode d
Flow directions	Counter-current	Counter-current	Counter-current	Counter-current
Disperse phase	Aqueous	Aqueous	Organic	Organic
Catalyst [ltr.]	B	B	B	B
	0.60	0.60	0.54	0.54
Pressure P [MPa]	9	9	9	9
Temperature T [°C]	170	170	170	170
STY [mole _{IPA} /ltr. _{cat} /h]	5.48	7.96	1.62	2.89
Stream 1 [gr/hr]	Approx. 129 ^a	2010	Approx. 38 ^a	980
Stream 2 [gr/hr]	1981	Approx. 110 ^b	978	Approx. 42 ^b
Stream 3 [gr/hr]	0	2120	0	1022
Stream 4 [gr/hr]	2110	0	1016	0
Stream 5 [gr/hr]	0	2000	2000	2000

^a Fed via pressure control system.

^b Fed via level control system for phase boundary layer.

highest STYs are achieved. An increase in STY of up to 65% was obtained by changing the reactor setup from a randomly packed trickle bed into a structured packing. The lower volume-related catalyst load of the structured packed reactor may partially be compensated by an improved STY. Furthermore, by application of a structured catalytic packing which provides space for the olefin flow the problem of transient high-level pressure drop is eliminated. However, detailed information on the actual disperse phase loading in the catalyst pockets of the structured packing is still missing for the application of a reactive extraction process. Hence, experiments providing data of real fluid dynamic characteristics are necessary in order to obtain fundamental data for the design of appropriate heterogeneous reactive extraction processes. Such investigations under relevant process conditions and detailed experiments on chemical reaction and mass transfer under broader variation of process variables are planned to be carried out for future work.

4. Conclusion

A possibility for process intensification in the field of liquid phase hydration of linear olefins is presented. By heterogeneously catalysed reactive extraction remarkable enhancement of space time yield and selectivity is achievable. Since the olefin hydration is reversible, accompanied by the consecutive formation of the corresponding ether and by the well known product-inhibition by strong sorption at the active sites of the catalyst (Petrus et al. [12,13]; Velo et al. [14]), similar to reactive distillation, continuous removal of product is very beneficial. By using an open cross-flow structured packing it is now possible to properly account for the extraction of the alcohol. Besides this, the catalyst can be used more efficiently by avoiding the formation of big lumps as in the up-to-date used randomly packed fixed bed reactors.

Furthermore, the reactive extraction allows recovering of the product from a rather volatile organic phase instead of an aqueous phase as is done in state of the art processes. This improvement can significantly reduce the operative costs of the process. Hence,

when intensifying processes it is advantageous to consider the complete process rather than only improving one unit operation. For the first time, the heterogeneously catalysed reactive extraction was demonstrated to potentially improve olefin hydration remarkably. As a conclusion, process intensification can save financial and environmental resources by considerable reduction of the energy demand of this process.

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