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CONSIDER REACTIVE SEPARATIONS

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ABSTRACT

Reactive separation (RS) is the combination of a chemical (catalytic) reaction and a separation technique. For reactive distillation (RD), the reaction is combined with distillation. Rapid development of RS is the result of growing environmental demands and increasing energy costs. Several processes are performed using RD, such as esterification, etherification (fuel antiknocks), and hydrodesulphurisation. Other RS techniques also develop rapidly. However, the success has not come without some serious problems. The heterogeneous proton catalysts still do not meet the requirements of many processes. The column internals with a built-in catalyst are rather sparse and expensive and their characteristics are not studied well enough. Therefore intensive studies are still being performed. This study presents a brief summary of the processes realisable with the usage of reactive distillation, catalysts, and column internals. Some interesting research results and application examples are also quoted.

Keywords: reactive distillation, structure catalytic packing, esterification, etherification

INTRODUCTION

Reactive separations (RS) are a family of processes that combine chemical reaction with a separation technique in a single process unit. Historically, the first process within RS was reactive distillation (RD).

The concept of RD was founded in the 1920's and the first applications are dated back to these years [1, 2]. The early beginning was fatty acid esterification performed in a distillation tray column that used sulphuric acid as the catalyst. During the next half of the century, there was almost no information about new researches and applications. However, during the last twenty years reactive distillation has become very popular as the result of the growing market for ether fuel compounds, severe environmental restrictions and increasing energetic costs.

Reactive distillation is the combination of the catalytic chemical reaction (homogeneously or heterogeneously catalysed) with distillation, realized inside a single apparatus – reactive distillation column. The advantages of RD include a huge simplification of the product recovery equipment, reduced environmental pollution and possibility to reach higher conversion and selectivity. An RD-based methyl acetate plant built by Eastman Chemical Company was the caesura in the RD development. The single RD column replaced there a chemical reactor and nine distillation columns thus reducing five times both the investment costs and energy consumption when comparing with a classic technology [3]. This outstanding result stimulated rapid development of RD and other RS techniques.

Studies have been carried out to model various RS processes and to get information about the process behaviour itself [4, 5]. The implementation of heterogeneous catalysis in reactive distillation columns (usually the term catalytic distillation ((CD) is used there) led to further process improvements, but also to a far greater complexity due to the presence of a third solid phase [6, 7]. All in all, the gas-liquid mass transfer in the case of RD is commonly taken into account while the chemical reaction is usually modelled as a pseudo-homogeneous one due to the rather slow kinetics. For other RS processes, another mass transfer mechanisms may be considered, e.g. liquid-liquid mass transfer for reactive extraction.

Apart from RD, few other RS develop rapidly. The difference lies usually in another separation technique. At present, we can mention several related RS processes. In reactive extraction, the liquid-liquid extraction is used coupled with chemical reaction. Reactive stripping may be applied to processes where one reactant, most often a reaction product, is much more volatile than the others. Usually, an inert gas is supplied to the column to remove the volatile species thus shifting the chemical equilibrium toward the desired direction. Some hybrid processes are investigated as well, like reactive distillation coupled with membrane separation.

The selection of suitable column internals is a very important problem [3]. Currently, structured column packings, the so-called structured reactive (or catalytic) packings, play still a more important role [3, 8]. The structured catalytic packings contain solid catalyst (usually in the form of very small grains, even smaller than 1 mm). The grains are placed inside containers (bags, envelopes) made from fine wire gauze and built in the packing structure. Different types of catalytic packings have been designed to solve the problem of counter-current gas-liquid flow with simultaneous heterogeneous catalysis [9-14]. Mass transfer and hydrodynamic packing characteristics have been found to be of significant importance for the process behaviour [15]. The best-known structured catalytic packings are bale packings, KATAPAK-S and MULTIPAK.

In spite of the above-mentioned meaningful advantages there are several obstacles limiting the RS development. While the RS modelling is developing very fast (e.g. Taylor and Krishna [8] cite over 150 references dealing with various modelling aspects), the number of experimental studies is rather limited. The transfer and flow properties of the column internals applied are crucial for

a proper modelling and design of the RS plants. However, the reliable description of them is still lacking. Another important problem, the kinetics of the chemical reactions carried out using RS, appears in the literature rather seldom. Although a large European research project INTINT [16] (realized between 2000-2003 with participation of the authors of this study) slightly improved the situation, a huge work has still to be done. The complex design and modelling of RS, a cumbersome scale-up and lack of reliable experimental data on the kinetics, transfer and flow behaviour are the main items limiting the development of the technologies.

The study is not intended to deal with RS modelling. Our aim is to present shortly the possible field of RS applications: industrial processes, catalysts, plant arrangements, and column internals. In our opinion the success of RS is evident; however, we would like to present some serious obstacles that RS meet during its development. Among the RS processes, RD seems to be the best studied one and several applications of it could be found in the industry. Thus, we focused our study on the reactive distillation issues mainly.

REACTIONS AND CATALYSIS

RS are especially applicable to slow, reversible reactions taking place in the liquid phase. Therefore the majority of the RS/RD applications are esterification and etherification processes. During the RD technology development, the turning point was the industrial installation for the methyl acetate synthesis (Eastman Chem. Co.), which reduced both the energetic and investment costs by a factor of five. Nowadays, few other esters, for instance those of higher organic acids as, are manufactured using the RD technique [3]. Several anti-knock fuel additives (MTBE, ETBE, TAME, dimethyl ether) can also be efficiently produced using RD [17].

A majority of the reactions described above, especially esterification and etherification, are proton catalysed. The solid protonic catalysts are the critical point of the RD technology. Whereas there are several homogeneous possibilities, especially those utilizing sulphuric acid, heterogeneous protonic catalysts are rather scarce. Acidic sulphonic resins (ionites) like Amberlyst, Lewatit or Nafion are the solid protonic catalysts commonly used in many RD applications. Amberlyst and Lewatit are based on a styrene matrix with built-in sulphonic groups. The ionites are rather cheap and commonly used. The main drawback is an allowable temperature of about 120°C; the others are the activity and durability of the catalyst, being rather far from the demands. Nafion is another resin based on PTFE (Teflon) and thus convenient for applications up to 200°C.

The common disadvantage of the ionites is their low activity. Usually, the RD processes are slow and the amount of a catalyst built into column internals is insufficient to reach the required conversion. Thus studies are being continued to find new catalytic options.

Immobilisation of heteropolyacids is likely to fail as the acids become immediately diluted in almost all the liquids, and even gases, to cause rapid degra-

dation of the catalyst. There is no information about application of solid superacids to the processes in the RD area. Reference [18] reports on other catalysts such as acidic zeolites, ZrO_2 , and modified K_2CO_3 . An interesting option seems to be porous silica with built-in sulphonic groups, resembling the ionites, though based on a silica matrix of elevated temperature resistance [19].

Another reaction that may be realised using RD is transesterification, a very promising one for biodiesel process based on vegetable oils. The so-called cross-wise transesterification of plant oil can be realized using reactive stripping [20]. The nitrogen stream removes the most volatile product, glycerol triacetate, thus shifting the equilibrium toward methyl or ethyl esters of fatty acids. These reactions are also proton catalysed.

The hydrodesulphurisation of petroleum fractions, traditionally carried out in trickle-bed reactors, can also be successfully performed using reactive stripping plants leading to a serious simplification of industrial set-up [21].

CATALYTIC COLUMN INTERNALS

One particular problem is the selection of catalytic column internals. The catalytic, or reactive, packing has to assure all the features specific to classic, non-reactive column internals applied to distillation or absorption. The most important are: mass transfer coefficients, allowable column loading, specific surface – which should be as high as possible, and flow resistance – the lower the better. However, in addition, a significant part of reactive packing has to be occupied by catalyst (usually catalytic grains). This fact strongly influences the column characteristics. A void volume is decreased, flow resistance is higher, and possible loading – lower as compared to that of classic packings. The main additional challenges are to assure excellent contact between catalyst and the flowing liquid phase and possibly low axial dispersion. However, a crucial problem is an appropriate relation between reaction rate (catalyst amount) and mass transfer rate. In practice, due to poor catalyst activity, the catalyst amount has to be large. Typically, tray columns, dumped packings or structured packings are being used at present.

Tray columns

Tray columns represent the most traditional solution, but they are still in use [3, 8]. They are heavy and expensive, high in comparison with other designs, and the flow resistance is large. However, they enable to adjust the catalyst amount within a wide range and the exchange of the de-activated catalyst is easy. Tray columns are especially comfortable for side reactors, additional heating or cooling.

The catalyst can be poured directly into the tray bottom; this however can lead to a mechanical degradation or washing out by the flowing liquid. Usually, the catalyst is placed inside the containers made of a wire mesh or perforated steel sheet, shaped as cylinders or flat envelopes. The containers can also be placed in downcomers.

Dumped packings

Dumped packings are rather cheap and easily replaceable, but flow resistance is high and the mass transfer is moderate. A layer of catalytic grains can be placed between two layers of classic dumped packing (e.g. Raschig rings). However, the column load is strongly restricted and the pressure drop is increased. The packing elements (e.g. rings) can be made directly from the catalytic material. However, the mass transfer area between liquid and catalyst is usually too small. Moreover, the material mechanical resistance can be inadequate. A better solution seems to place catalytic grains inside the container, e.g. cylindrical one, made from wire gauze. An interesting design is a wire mesh envelope filled with grains and placed inside a Raschig ring.

Structured catalytic packings

The structured catalytic packings play an even more important role. They display a good mass transfer rate, low pressure drop and a good contact between catalyst and the flowing liquid. They can be rated as the most efficient from the process point of view. While a tray column can be compared with a cascade of tank reactors, the column filled with structured packing resembles a tubular reactor, obviously being more advantageous. However, structured packings are expensive and the catalyst exchange is almost impossible. Due to geometrical reasons, the amount of catalyst built in the packing structure cannot be changed over a wide range. This can often lead to an undesirable complication of the column configuration. In spite of this, structured catalytic packings play an even more important role. It should be mentioned that the knowledge of the packing characteristics, including mainly hydrodynamics (flow resistance, liquid hold-up, axial dispersion) and mass transfer is crucial but still unsatisfactory.

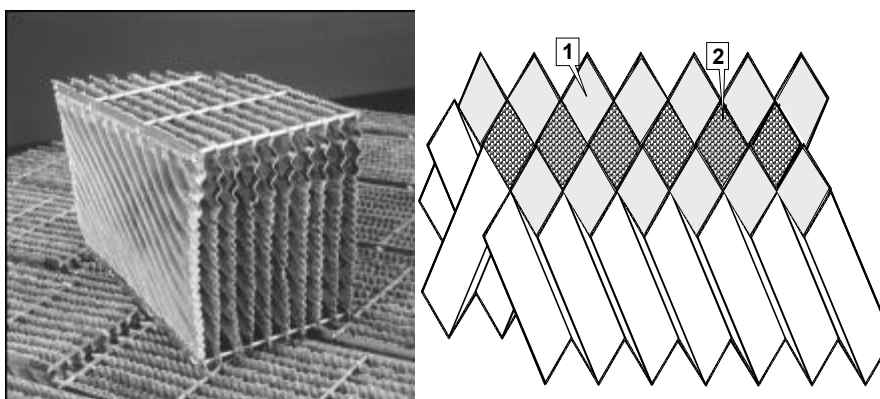


Fig. 1. KATAPAK-S (Sulzer): 1 – channels open for gas (empty ones), 2 – channels open for liquid (filled with catalytic grains).

Perhaps the best known structured catalytic packing is KATAPAK-S made by Sulzer Chemtech [13, 14] (Fig. 1). Wire gauze corrugated sheets are stacked in such a way that the corrugations cross themselves. Thus a number of triangular channels are formed from which half is filled with catalyst and open for the liquid flow only, while the others are empty and open for the gas flow (in fact, certain amount of liquid flows there as well). The contact between the liquid phase and the catalyst, flow resistance, mass transfer and axial dispersion are advantageous. However, the amount of the catalyst is rigorously fixed to slightly less than 50% of the packing volume and its exchange is impossible. A similar solution is offered by KATAMAX (Koch Co.) [3].

The second design is MULTIPAK of Montz [12, 15, 17] (Fig. 2). Corrugated gauze sheets are stacked there alternately with flat gauze envelopes filled with catalyst. The amount of catalyst can be changed over a wider range than that in KATAPAK-S. However, its exchange is almost impossible as well. The allowable column loading is usually lower as compared to that of KATAPAK-S, and the flow resistance is higher; the flow through the packing is slightly less stable. However, the specific surface is usually higher than that of KATAPAK-S. A design slightly similar to MULTIPAK is KATAPAK-SP (Sulzer) composed of gauze envelopes and corrugated steel sheets originating from MELLAPAK.

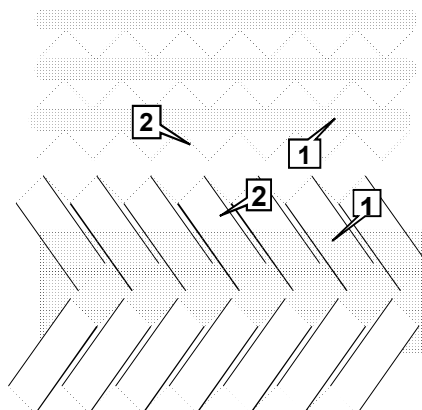


Fig. 2. MULTIPAK (Montz): 1 – wire gauze envelopes filled with catalyst, 2 – wire gauze corrugated sheets.

Another example is the bale packing licensed by Chemical Research and Licensing [3]. Lens-shaped bags filled with catalyst are closed in two sheets of fibreglass cloth and rolled with a thick wire mesh forming a bale. The bales, 40-50 mm in diameter and 300 mm long, are stacked vertically in the column.

Recently, monoliths have been studied intensely as an alternative catalytic column packing [22]. Monoliths of low channel density, e.g. 25 cpsi (channels per square inch), with a catalyst deposited on the channel walls, can be applied for cocurrent and countercurrent gas and liquid flow.

RESEARCH AND APPLICATION EXAMPLES

During the last years, we participated in a large experimental programme on structured catalytic packings, mainly connected with the European Research Project INTINT [16]. The studies included mass transfer, flow resistance, flooding limit, liquid hold-up, axial dispersion, rate-based modelling and reactive experiments. Two variants of KATAPAK-S and three variants of MULTIPAK have been investigated. A large database created (over 2000 experimental points) enabled to explain the flow and transfer phenomena of the structured catalytic column internals. Rate-based models created were validated based on reactive RD experiments. Some of the most interesting results, both experimental and theoretical ones, as well as an example of literature application, are presented in this section.

Flow resistance

Besides others, extensive hydrodynamic studies were performed on five reactive packings listed in Table 1. The experiments included pressure drop over the dry packings (single-phase gas flow) and over the irrigated ones (two-phase gas and liquid flow).

Table 1. Parameters of the packings studied: specific surface a and void fraction ε .

Packing	a/m^{-1}	ε
KATAPAK-S-250	128	0.62
KATAPAK-S-500	265	0.61
MULTIPAK 0	320	0.65
MULTIPAK 1	369	0.56
MULTIPAK 2	318	0.57

During gas-phase flow experiments [15], an interesting phenomenon was noticed for MULTIPAK types 0 and 1 (Table 1). The pressure drop for the completely dry packing was higher than that for the prewetted packing (and even higher than the pressure drop for low liquid loads during the two-phase flow) (Fig. 3). This could be caused by a thin layer of liquid present at the surface of wire gauze. The liquid film smoothes the coarse wire gauze surface; the large amount of liquid in the catalyst pockets forms the reservoir protecting the film against drying. The plots of the friction factor for the dry and prewetted packings versus Reynolds number resemble those for coarse and smooth tubes, respectively. It should be emphasised that for other catalytic packings (KATAPAK-S and MULTIPAK 2) the phenomenon did not appear.

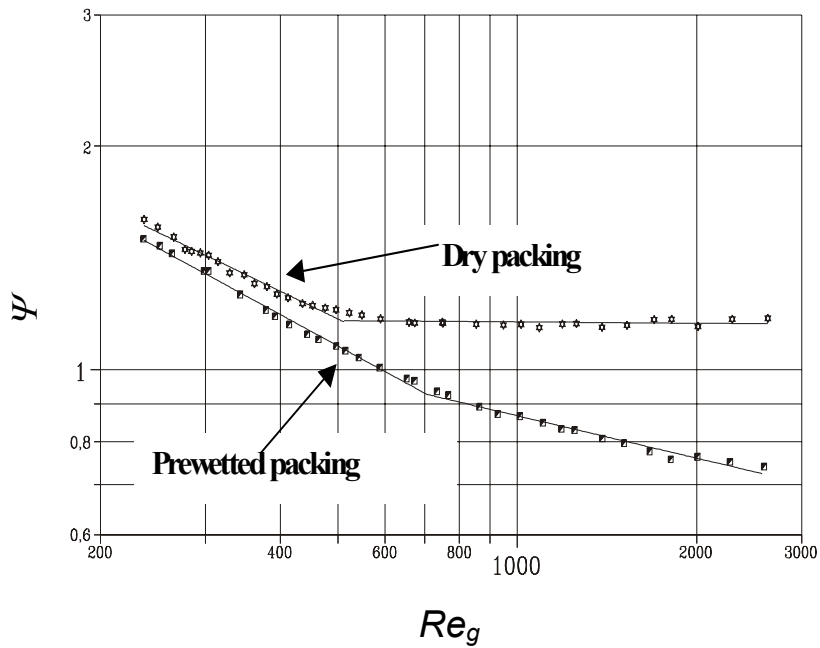


Fig. 3. Flow resistance for dry reactive packing MULTIPAK 0 in terms of friction factor vs. gas Reynolds number [15].

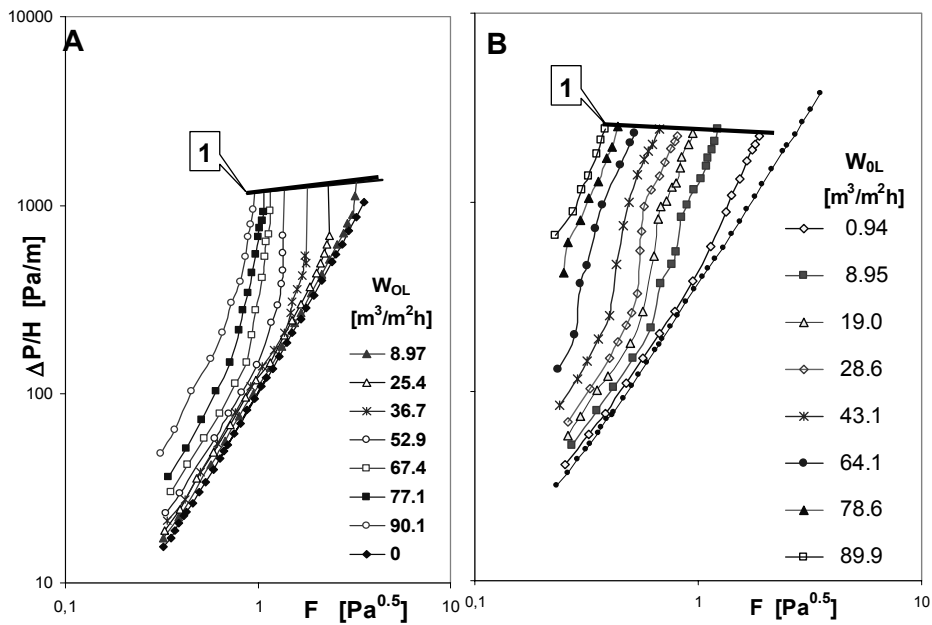


Fig. 4. Pressure drop for irrigated packings: A – KATAPAK-S-500 and B – MULTIPAK 2. Line 1 – flooding.

The pressure drop for irrigated packings KATAPAK-S-500 and MULTIPAK 2 is exemplified in Figure 4. The thick solid line represents flooding. It should be stressed that KATAPAK-S works more stable as compared to MULTIPAK. The channels of MULTIPAK are small causing local floodings at relatively low loadings. Critical points are contacts of the packing layers. In Fig. 4B the inflexions on the curves show the beginning of this region.

Liquid hold-up

Dynamic liquid hold-up is an important operation parameter for RD columns. It is commonly understood as the liquid currently flowing down the column during the operation. The common experimental method is to cut off the liquid feed and to measure the amount of liquid that freely flows down from the packing; this is the so-called free-draining hold-up. Usually, the free-draining time amounts to 30-60 minutes.

A rigorous study of liquid dynamic hold-up for the MULTIPAK and KATAPAK-S packings was presented by Jaroszyński et al. [23]. The hold-up was measured using free-draining experiments and the tracer response technique. During free-draining experiments, extremely long draining times were applied up to 72 hours. Next, the hold-up value extrapolated to the infinite time was assumed as the true dynamic component of liquid hold-up. Moreover, static hold-up experiments were performed using times up to 504 hours. The total hold-up, that means, the sum of the dynamic and static components, was derived. The authors would now present the results not published so far. The total hold-up derived from the free-draining experiments described above was in an excellent agreement with the hold-up derived from tracer experiments, usually called the "dynamic liquid hold-up". The result shows that the flow phenomena in reactive packings are somewhat surprising as the static liquid hold-up (as commonly understood) in fact flows down the column during operation.

Tame synthesis using a half-industrial RD column

Another study dealt with the synthesis of tert-amyl methyl ether (TAME) [17], an important fuel antiknock additive. The sketch of the test column equipped with pre-reactor is presented in Figure 5d together with the assumed reaction system (Fig. 5e). The experiments were performed using a 200-mm ID, 4-meter high half-industrial column [17]. The light gasoline fraction from the fluid catalytic cracking (FCC) unit containing certain amount of isoamylenes was used as a feed. Consequently, the industrial hydrocarbon fraction included approximately one hundred chemical compounds, which were lumped into 11 representative compounds.

The rate-based modelling was performed using the PROFILE programme package created within the INTINT EU project [16]. The derived modelling concentration and temperature profiles are compared with the experiments in Figure 5a-c. Taking into account the scale of the experiments and the inevitable simplifications the discrepancies between modelling and the experiments are not substantial.

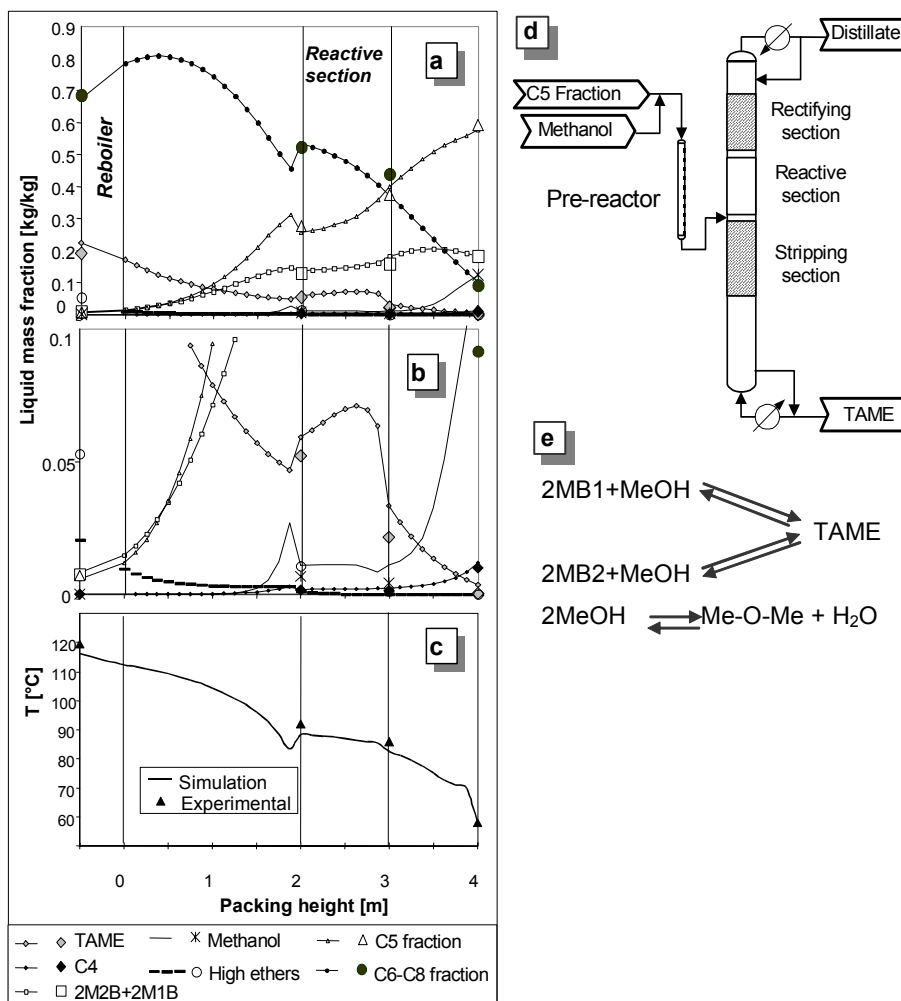


Fig. 5. Concentration and temperature profiles for TAME experiment. Simulations (lines with small symbols) and experiments (large symbols): a – full concentration range, b – low concentration range, c – temperature, d – experimental set-up, e – reactive system assumed. MB1(2) – 2-methyl-1(2)-butene; MeOH – methanol; Me-O-Me – dimethyl ether.

Hydrodesulphurisation of the petroleum fraction

Hydrodesulphurisation of the petroleum fractions derived from primary distillation is usually performed in trickle-bed reactors. The scale of the process is one of the largest in the chemical industry. For example, the fraction called the light gas oil (boiling range 245-345°C, components C10-C20) reacts with hydrogen in co-current trickle-bed operation to remove sulphur as hydrogen sulphide. Typically, a CoMo catalyst is applied deposited on porous alumina grains. To avoid excessive pressure drop in the trickle-bed reactor, the grains should be ra-

ther large, e.g. 5 mm in diameter. However, significant resistance of liquid phase diffusion in porous particle is there accompanied by fast catalytic reaction. Thus the Thiele modulus is usually large and the efficiency factor may be very low. The demands for reactor pressure drop and effective catalyst use are opposite as the first one requires large catalyst grains while the second – very small.

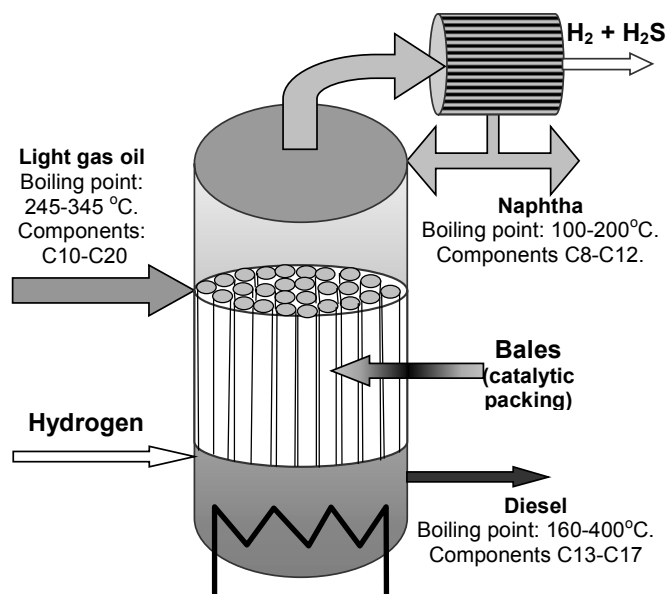


Fig. 6. Scheme of hydrodesulphurisation of the petroleum fraction using reactive stripping technology.

Vargas-Villamil et al. [21] proposed hydrodesulphurisation of the light gas oil performed in an RD column working in the reactive stripping mode (Fig. 6). The column is packed with catalytic bales (see section 3.3) that contain very small grains of the CoMo/Al₂O₃. A stream of hydrogen is supplied to the column bottom to remove the sulphur from the petroleum compounds. In addition to the hydrodesulphurisation reaction, the distillation takes place in the column, the light gas oil being separated into naphtha and diesel fractions with strongly reduced sulphur content. The process described above was performed in Mexico on semi-industrial scale and the results were claimed to be excellent [21].

FINAL CONCLUSIONS

Reactive separations are up-to-date and promising chemical technologies with special attention paid to the catalytic distillation. The processes can be successfully applied in several chemical technologies. Their advantages are well known, especially for the catalytic distillation: an elimination of the azeotrope separation, enormous savings in the energy consumption (up to five times lower when comparing to traditional technologies) and investment costs (also cut by

a factor of five). The technologies are environment friendly, the use of additional chemicals is significantly, or even totally, reduced.

However, the evident success has not occurred without some obstacles. There are only few, rather expensive, catalytic packings on the market. The design of the process is cumbersome. As a matter of fact, it requires advanced modelling. The problem of scale-up is very complex. But the crucial point seems to be catalysts. The sulphonic resins are cheap, but their activity is low and the admissible temperature range is strongly limited. Usually, additional reactors have to be used to reach a pre-determined conversion. The selectivity is an additional challenge. Catalytic distillation is one of very few processes where the critical point is placed within catalysis due to a large progress in chemical engineering. A serious development of catalysis is now required to fully explore the benefits of reactive distillation.

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