Process intensification with membranes

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In the field of process engineering, the term “process intensification” includes measures to improve the efficiency of a process drastically. The improvements may include, for example, an increase in the space-time yields of a system, a significantly higher energy and/or raw material utilization or relate to a new product or new product qualities. A process intensification may involve different concepts and measures, which are explained in the introductory part of the following article. Based on the specific properties of the membrane process is shown later that with the use of membranes a process intensification was associated mostly. Frequently thus could also be created new products and/or product qualities.

1. Introduction

For several years, one trend within process engineering and chemical engineering has been described with the concept “Process intensification (PI)”. The concept was introduced during the seventies in connection with chemical processes /1/. In the eighties, a working direction under the concept was developed within process engineering through the work of C. Ramshaw /2/. C. Ramshaw has intensified the heat exchange and mass transfer for gas to liquid mass transfer processes by means of centrifugal acceleration in rotary contact apparatuses, which is several times higher compared with gravitational acceleration, and has introduced the “High-g Technology” based on it. With the development of microprocess engineering in the nineties, the area of “process intensification” was further stimulated and looked at with a broader point of view.

According to contemporary understanding, process intensification can be associated with

- an increase of space-time yields in a system,
- an improved use of energy and raw materials,
- a drastic lowering of production costs (investment costs and/or operating costs),
- an improvement of environmental protection (reduction of exhaust air, sewage and waste streams),
- an increase of the inherent process reliability and
- the generation of new or improved product quality. The difference to regular advancements of processes exists in that, on account of new approaches, significant improvements in one or several directions listed above are achieved. Such improvements can be achieved on the basis of a detailed understanding of the procedures taking place in a process and the introduction of new methods and technologies. The measures, which lead to significant improvements over conventional processes, can be divided into different categories, which are considered in more detail below.

2. Measures for process intensification

Process intensification can be achieved with different measures, which can be divided into the following categories.

2.1. Process enhancement

The process enhancements contain an essential intensification of mixing, heat and mass transfer processes. In connection with chemical or biochemical reactions coupled thereto, the space-time yield and/or selectivity can thereby be increased substantially. Through a homogenisation of the procedures in the process space, improved and/or new product qualities can also be achieved. As an example, the development of micro-reaction technology is often named in this context, which shows that blending the reactants and the heat transfer can be greatly intensified with the minimisation of reactor dimensions. The ratio of surface to volume rises with micro-structured devices to several thousand m²/m³. Heat exchange and mass transfer through the wall of a process space can thereby be substantially strengthened, so that also the full potential of a chemical reaction is exhausted. As a result of the short distances, big gradients for momentum, heat and mass transfer are also connected with it. The necessary production rates can be achieved if one operates the required number in flow ducts and/or reactors in parallel (numbering-up). If the results achieved in the laboratory are not achieved with the large-scale system, the risk that is connected with a usual scaling-up does not exist with the concept of “numbering-up”. By contrast, measures must be taken to counteract fouling of the walls and a blockage of the small ducts. This kind of process intensification is applied advantageously, inter alia, in mixing-sensitive and/or highly exothermic or endothermic homogeneous reactions.

Process enhancement is often also posed in connection with micro-processes over an apparatus that is characterised by the absence of driven moving parts. Apparatus are operated in connection with pumps or fans. In particular, this applies if it is possible with a machine to master difficult process conditions (e.g. high pressure, high temperatures). For example, microreaction technology according to Ramshaw includes such a transition from a mass transfer apparatus to a mass transfer machine. The advantages and disadvantages of mass transfer machines, compared with apparatuses, were already treated by Brauer /3/ and Mersmann /4/ in 1986, on the basis of examples.

2.2. Process integration

Process integration consists of the simultaneous execution of several basic operations in one apparatus and/or in one machine. Originally these were carried out in sequentially-connected separate apparatuses or machines. With simultaneous execution of basic processes in an apparatus and/or a machine, the transactions overlap and mutually influence each other. With exact knowledge of the transactions, these can be specifically influenced and limitations of chemical conversion can be overcome. The transactions can be “intensified”. Examples of integrated methods are reactive distillation, reactive chromatography, as well as extruders and similar screw machines, in which several transactions happen at the same time (e.g. mixing, heating, melting, reacting and giving a shape). The integration of several process stages in one apparatus and/or in one machine is often linked with advantages, in spite of necessary compromises, as a result of the mode of operation of individual basic operations not being optimal. As advantages of such integrations, there can be mentioned: increase of yields in chemical or biochemical reactions, minimisation of operation costs and investment costs, enclosed design and low handling effort. In the pharmaceutical and
food industries, in this way product contamination can also be avoided in the safest manner.

2.3. Hybrid processes

With a hybrid process, similar effects can often be achieved like with process integration. With this, individual processes are operated in separate apparatuses, but which are joined together so that they mutually support each other during the chemical conversion. It is about an active group by which synergies are created that allow the limits of a single procedure to be exceeded. Hybrid processes for process intensification therefore contain configurations of process stages with new effects.

2.4. Reduction of process stages through new or improved procedures

An essential efficiency increase can often also be achieved by introduction of a new or optimised process. In particular, when one succeeds with reducing altogether the process steps necessary for the production of a product. Thus, e.g. a precipitation and/or crystallisation can be operated in such a manner that the required particle size and/or particle size distribution is generated directly. Costly product processing by grinding and classification can be dispensed with.

A specific influencing of elementary steps of a basic operation can often be achieved also with in-line and/or on-line process monitoring in the form of a control circuit. The precondition here is that there are sensors with which the desired control variable (e.g. the particle size) can be measured in-line and/or on-line.

2.5. Use of new auxiliary agents

Process intensification can also be achieved with existing procedures through the use of a new auxiliary agent. These include, for example, improved filtration aids and flocculants, and new extraction and absorption agents (e.g. ionic liquids). During reactions, higher space-time yields can be achieved in particular by using new and/or improved catalysts.

Many examples show that the introduction of a membrane process was often connected with process intensification for the purposes of one of the possibilities described above.

3. Identifying properties of the membrane process

In the last five decades, membrane processes have opened new possibilities in the technology for substance separation that are increasingly used today. Decisive for this development were the following advantageous properties of the membrane processes:

- high selectivity of the substance separation,
- substance separation without additives,
- physical separation principle without chemical change of components,
- possibility of substance separation in the molecular area without phase change,
- gentle separation conditions,
- simple, modular system design,
- enclosed system design,
- possibility of continuous operation.

Often, only one of these properties is decisive for the application of a membrane process. Product saving separation is used for example in the fields of medicine and biotechnology. The possibility of selective substance separation without additives is in the foreground with applications for the specific discharge of substances from a mixture or during materials recycling. With such applications it is advantageous if the substance mixture is treated at the source of the origin. Hence, one is anxious to integrate closed and continuously working reprocessing procedures into the process. The enclosed and modular system design and also the continuous operating method of membrane systems, do justice very well to the process-integrated separation stage. Membrane systems, which allow selective substance separation in the molecular domain without phase separation, are an alternative to the thermal separation processes with additives (e.g. absorption, adsorption, extraction and chromatography). All arguments speaking in favour of the use of membrane technology measures also represent measures for process intensification in a broader sense.

With the use of membrane technology, often the production of a new product quality also becomes possible. Thus, for example, sterile products were able to be produced without the negative changes of thermal sterilisation. Moreover, in the process, products are generated in which no killed cells are included. Today this method is used on a large scale for the sterilisation of beverages and other liquids. ESL milk (ESL = extended shelf life), introduced only few years ago based on microfiltration with membranes, is one example of this.

In the case of a high bio-burden and the availability of other substances in the form of colloids, very dense top layers form quickly on the membrane, which strongly hinder filtration. For the treatment of such suspensions, crossflow filtration was developed, with which the membrane is flooded by the suspension to be filtered. On account of the crossflow, a back transport of separated substances away from the membrane is achieved, due to diffusion and achieved hydrodynamic forces. There are different forms of crossflow filtration...
z = 1.2

These can be determined with the following equations:

\[ ε_{Mo} = \frac{π}{4} \approx 0.785 \]

with a square array of the capillaries in the packing and

\[ ε_{le} = \frac{π}{\sqrt{12}} \approx 0.907 \]

at the hexagonally densest packing of the capillaries. In practice, during module manufacturing with capillary membranes values are achieved in the range from 0.45 to 0.65.

4.1.2. Dialysis

The gentle separation conditions at ambient temperature are used for hemodialysis, performed in the detoxification of the blood and thus the human body. Here, the transport of the substances to be removed from the body through the membrane into the dialysate (predominantly processed water) is caused primarily by a concentration difference and the diffusion coupled thereto. For the process enhancement of this, actually slowly accruing diffusion, extremely thin membranes (thickness down to 5 μm) were developed, mostly in the form of hollow fibres. The membranes can be produced with a spinning process in large quantities at a reasonable price. The substance transport could still be optimised by the fact that one has succeeded to design the membrane surface necessary for the treatment (approx. 1 m²) in a relatively small volume. This is possible because the membranes are produced with an inner diameter in the range of approx. 200 μm. The necessary throughput is achieved by the fact that the capillaries in the membrane module are connected in parallel and operated in the required number (numbering-up). For a dialysis module, if one uses the capillary dimensions listed above and a packet density of ε_{Mo} = 0.5 as a basis, based on Fig. 1 it can be seen that one achieves, with respect to the capillary inner diameter, a specific membrane surface of approx. 7000 m²/m³. Similar orders of magnitude are aimed for with fibre membranes, also with gas separation. With other technical applications of capillary membranes, like for example water filtration or the gassing and degassing of liquids, specific membrane surfaces of 1000 to 2000 m²/m³ in a membrane module are absolutely usual.

4.1.3. Membrane contactors

For the gassing and degassing of liquids, membrane modules are used as membrane contactors. Contactors are used if a mass transfer should be achieved across the phase boundaries between two phases. For hydrophobic microporous membranes, the interfacial forces in connection with the low pore diameters prevent the penetration of a liquid into the pore structure up to a certain pressure, so that both phases are directly in contact via the pores in the membrane surface. To this end, membranes with a surface porosity of 75 to 93% are used, with simultaneously a maximum pore diameter in the range of 0.1 to 1 μm. The mass transfer is determined primarily by the laws of diffusion. Membrane contactors are used for absorptive gas separation, for bubble-free gassing of liquids, as well as for extractive and distillative substance separation. They allow a flow guide in direct current and counter-current and allow the throughput of the discharging and absorbing phase to be varied in a wide range.

In Fig. 2, the mass transfer surface with respect to the gas throughput of different contact apparatuses is applied as a function of the specific energy input resulting from the pressure drop /S/. One detects that with conventional contact apparatuses, in contrast to a membrane contactor, a high specific mass transfer surface is also always connected with an increased energy input. With a
membrane contactor, on the other hand, a large specific exchange surface is also guaranteed with a low volume flow and hence also with low energy input. This one is used for benefit, inter alia, for extra-corporeal blood oxygenation with membrane oxygenators. They have extensively replaced the earlier usual bubble oxygenators. Membrane oxygenators are routinely used today during surgery in connection with heart-lung machines and take over the task to supply blood with oxygen and to remove the carbon dioxide at the same time.

Another example of the application of membrane contactors is air humidification in air conditioning systems. With an appropriate membrane selection, micro-organisms are retained by the membrane and only water vapour is transferred to the air.

Membrane contactors are used as a matter of routine today, also for degassing water in combination with ultra-pure water treatment. With them, vacuum degassing or degassing with a stripping gas can be implemented /6/.

It can be seen from Fig. 2 that at high gas throughputs, the exchange surface area related to the gas throughput decreases and the specific energy input increases as a result of the rising pressure drop. Hence, membrane contactors have not yet asserted themselves with large gas throughputs.

4.1.4. “Numbering-up” principle

With all membrane applications, the principle of numbering-up is consistently applied. It is enough for the case of capillary membranes and tubular membranes to examine the transactions in a capillary and/or a tube of the length later to be installed. Then the results can be transferred to large-scale systems through numbering-up (parallel connection of many membrane capillaries and/or tubes to a membrane module and of several membrane modules in a module block). With very big systems, the principle will be consistently accomplished by interconnecting several module blocks in parallel with the necessary systems capacity in each case.

Nevertheless, in conjunction with membrane technology, the disadvantages of microstructured apparatuses and “numbering-ups” also become clear. A uniform inflow to a great number of membrane units and/or a great membrane surfaces over long periods of time without periodic cleaning is usually not possible to achieve. With periodic membrane backflushing, exposure of the membrane surface area cannot be guaranteed with a simultaneous overflowing of the membrane. Moreover, the slowly occurring processes of membrane fouling are to be taken into account. Given that these events do not occur uniformly but have a greater effect in some places through slight differences in the flow guidance, the non-uniformities of the ongoing processes are thereby still intensi-
4.1.5. Process intensification through moving installations or moving membranes

A membrane module has no movable parts and can therefore be assigned to the apparatuses. In addition, membrane units have also been developed with which mass transfer is intensified through moving installations or moving membranes. In this case, membranes from ceramics are preferably used, often in the form of membrane disks. Particularly favourable conditions arise when, in the process, a shear gap over the membrane is realised. These membrane units have movable parts with their own driving mechanism and, hence, can be called mass transfer machines. According to their construction type, the following categories can be distinguished:

- the membrane is rigid and is overflowed on account of moved installations;
- the membrane moves, and is thereby overflowed and
- the overflow is implemented by rigid and moving membranes.

As advantages of these systems compared with systems with membrane modules, there can be mentioned:

- a reduced specific energy demand since the energy being entered into the system principally serves to reinforce the mass transfer transactions into the membrane and to decrease fouling. Energy dissipation in pumps, pipes and valves, which occurs in the membrane modules, is avoided.
- Membrane machines with moving parts can be operated with higher viscosity media compared with membrane modules, such as for example highly concentrated suspensions. A higher permeate yield is thereby also often possible. This applies particularly to suspensions with structurally viscous or thixotropic flow behaviour.
- Advantageous with filtration processes with moving parts is also that the flow conditions on the membrane influence the trans-membrane pressure difference to a lesser extent than with membrane modules. With membrane modules, the shear rates on the membrane rise with increasing throughflow speed and at the same time the pressure drop in the module increases, so that the pressure difference of the filtration across the module length changes significantly.

4.2. Process integration with membranes

4.2.1. Membrane reactors

Examples of process intensification through process integration are the membrane reactors and/or bioreactors. As a rule, the membrane is arranged with them in the reaction chamber. With chemical and biochemical processes, this opens the possibility to separate intermediate products and/or by-products of the reaction selectively from the reaction mixture. This direct use of the membrane properties in reactors is still used relatively little up to now in the petrochemical industry, but is the object of numerous research projects. Because many reactions are operated in a spatially confined reaction chamber at high temperatures, selectively active membranes very resistant to temperature are mostly required. On the other hand, many biochemical reactions can be coupled with the existing polymer membranes, which is why bio-membrane reactors are already used on an industrial scale in many ways. Chemical and/or biochemical reactions can be operated under optimum conditions through a continuous separation of value-added products and/or inhibitory substances from the reactive substance mixture. The reaction equilibrium can thus be shifted towards the product side and possible subsequent reactions can be suppressed. Thus, it is often possible to increase the turnover and space/time yields substantially. One example for this is the separation of water in polycondensation reactions by means of the pervaporation.

4.2.2. Membrane bioreactors for wastewater treatment

Something that has prevailed on an industrial scale are membrane bioreactors with submerged membrane units in the activated sludge basin of a biological purification stage for aerobic wastewater treatment. The membranes are overflowed through the circulation in the basin as a result of the gassing with air. The membrane units form a membrane bio-reactor (MBR) together with the basin. Membrane units with capillary membranes and with flat membranes are offered. A comparison of the two systems is made in /8/. The filtrate is sucked off from the open basin on the filtrate side by creating a negative pressure < 0.5 bar. The first municipal sewage treatment plant of this kind was put into operation in 1989 in Japan. In /10/ operational results of such facilities are reported. The permanent or cyclic air supply that is also connected with circulation in the basin allows a stable operation of the systems in conjunction with cyclic backflushing. As a rule, they are operated with specific filtrate flows < 40 l/m²·h. The specific energy input is given as 0.05 to 0.15 kWh/m³ filtrate.

Through this process, integration advantages arise on account of the savings of secondary settling tanks and a higher biomass content, whereby the space-time yield is also increased. The filtrate of such systems mostly fulfils the requirements that are placed on the inlet to an RO system. Hence, an RO system can be connected directly for further water treatment. Such an application for closure of a water circuit is reported in /11/.

4.2.3. Electro deionization

Another example of successful process integration with membranes is Electro deionization (EDI), which is widely used in industrial processes for ultrapure water preparation. It combines electric dialysis with ion exchangers in such a manner that the exchanger resins are continuously regenerated, allowing continuous deionization. The regeneration of the contaminated resins with salt and/or acid and alkaline solution, which is necessary with ion exchanger columns, is omitted. Different methods were developed that are described in detail by Duscher /12/.

4.2.4. Membrane precipitation

With crystallization and precipitation processes, the objective is to guide the process so that the product is generated in the desired particle size distribution and morphology. The aim can be frequently achieved in continuous stirred-tank reactors on a laborato-

Fig. 4: Particle produced from calcium carbonate with a membrane process that has been developed in TU Kaiserslautern

In other cases, membranes are used in reactors, e.g. as the carrier of a catalyst, so that in addition to the selective substance separation, an accelerated material transformation is achieved. The various possibilities of the use of membranes in membrane reactors were indicated by Westermann et al. /8/
ry scale, but the problem is to transfer the process, which is significantly influenced by micro-mixing, to continuous stirred-tank reactors on a production scale. Elaborate post-processing steps, such as crushing and screening, are required when the described objective is not fulfilled. The effort increases significantly when particle systems are to be generated in the range of a few micrometres or even nanometres.

In TU Kaiserslautern, a new precipitation method was developed where precipitation takes place in capillary membranes /13/. The method was applied to precipitate calcium carbonate from a calcium hydroxide solution with carbon dioxide. In the process, the gaseous component diffuses through a membrane into the boundary layer flow, so that super-saturation and particle formation take place in it. On account of hydrodynamic lift and the increasing size of the particle, this moves away from the membrane, and thus out of the reaction zone, so that it can grow further. Since it is a highly hydrophobic porous membrane, the diffusion resistance of the membrane is negligibly small. For the case of calcium carbonate precipitation, it was proved that the reaction takes place in the laminar substrate of the flow, i.e. that the concentration boundary layer for CO₂ is smaller than the flow boundary layer. Furthermore the significant influence in this case of hydrodynamic lift (lift force) was shown.

Experimental studies show that it is possible to generate particles in the < 1 μm size range in high numbers with the process. Also novel porous spherical particles could be generated from calcium carbonate (Fig. 4).

4.3. Hybrid processes

For a long time it has been known that in many cases membrane processes are used especially advantageously in combination with other (conventional) separation processes (hybrid processes). Such processes can serve to increase the effectiveness of chemical conversion substantially.

As an example of a hybrid process, the purification of suspensions with colloid ingredients (e.g. vinegar, oil, beer, wine) with membranes should be mentioned, in which cross-flow microfiltration is combined with a centrifuge (Fig. 5). Concentration of the turbid matter takes place through the separator and the fine filtration and sterilisation filtration is carried out with the crossflow microfiltration in a continuously operated process. It often replaces a multistage discontinuous purification process, as is illustrated as an example in Fig. 6 and 7. With the process in Fig. 6, pasteurisation (thermal process stage) is connected downstream of the purification process for the increase of the shelf-life of the product. A new product quality could already be achieved by the substitution of pasteurisation in Fig. 5 with Dead-End filtration with membranes in the form of cartridge filters, according to Fig. 7. In addition, to guarantee a high service life of the filter cartridge, the use of upstream deep filter cartridges is recommended. The substitution of filter aids and/or sheet filters and cartridge filters that have a relatively short service life with relatively durable membrane modules is one reason that the process according to Fig. 5 can be operated economically, in spite of increased energy requirements. The combination is interesting for large and small operations if, at the same time, attention is paid to a high utilisation extent of the system. On account of the operating method, an automatic operation is easily possible, so that a relatively small system can be implemented with a high utilisation extent.
4.3.2. Combination of reactors with membrane stages

The direct coupling of a reaction with a separation stage on the basis of membranes, described in 4.2.1, can also be implemented in the form of a hybrid process. Here, the chemical reactor is spatially separated from the membrane stage, but they are operated coupled. This combination is used widely in biotechnology.

4.3.3. Hybrid processes with membranes in the field of Fluid Process Engineering

New approaches for hybrid processes with membranes in the field of Fluid Process Engineering are described by T. Cellar et al. /14/. They describe, inter alia, the coupling of the rectification with vaporization or vapor permeation for overcoming the azetropic point. One main application area of such combinations is the dehydration of bio-ethanol and other solvents. Furthermore, the reactive distillation and its combination with membrane processes are addressed. Such a combination offers the possibility to selectively improve the yield and the conversion in the reaction and simultaneously to influence favourably the distillative separation by the use of membrane separation. Other variations for the combination of membrane processes and the rectification into one hybrid process are described in /15, 16/. In vapour permeation, the membrane surface, in contrast to pervaporation, is directly subjected to the vaporous mixture. Here, process integration would also be suitable, i.e. the integration of the membrane surfaces into the head of the rectification column so that both processes operate in one apparatus.

In /17/, the coupling of a reactor is described with a pervaporation stage for the preparation of acetals in the form of a hybrid process. Through the coupling, a significant increase in conversion and a concomitant significant energy saving could be achieved.

4.4. Reduction of process steps with dynamically operated membrane processes

Some of the examples listed above show that a clear reduction of process steps is connected with the described measures. Dynamically operated membrane processes are continuously operated and, hence, can be integrated simply into the corresponding processes. For instance, the advantages of crossflow microfiltration have been used since the early 90s of the last century for industrial vinegar production /18/. Before, vinegar was fined with bentonite and clarified with precoat filters and other depth filters. Today, vinegar is mostly produced semicontinuously, primarily from ethanol by submerged fermentation over a period of about 30 hours and discharged directly from the digester via crossflow filtration in the desired quality, in the form of a hybrid process.

4.5. Use of novel auxiliary agents

Process intensification can be also achieved by novel and/or improved auxiliary agents. These include for example optimised catalysts and/or bio-catalysts (enzymes). Enzymes unfold their activity even in the low concentration range. Low application concentrations make their recovery problematic after substance conversion. Therefore, in the food industry, for example, they are no longer recovered in some cases, and are used as so-called “lost enzymes”. However, the costs are increased through the constant “enzyme consumption”. The enzyme and its attendant materials may also be considered as a disruptive component and an impurity in the product. With enzyme immobilization, the use of valuable enzymes and higher enzyme concentrations becomes economically justifiable and the advantages of continuously operated flow systems become applicable. Such systems are implemented, for example, with capillary membranes for ultrafiltration, so that the enzyme is immobilized inside the capillary membranes that represent a barrier for the enzyme. The membranes are permeable to the starting materials and products and are placed in the reactor or in a perfused membrane module associated with it. In /19/, one of the first industrial scale applications of such a system for the production of amino acids is described.

Besides this “physical immobilization”, enzymes are also bound directly to the internal or external surface of a carrier membrane and are immobilized with it.

In many cases, the economical use of enzymes in biochemical conversions only became possible with an appropriate membrane use, since only in this way is an economical, sufficiently long lifetime of the enzymes achieved.

Membranes, preferably made of ceramic, are accordingly also suitable with chemical reactions as a carrier for catalysts. In other cases optimised catalysts can be used in the form of nanoparticles or macromolecules with an accordingly high specific surface, which can then be recovered continuously or batchwise after the reaction with a membrane process for repeated use. Such membrane applications are numerous and are operated successfully in the petrochemical industry.

5. Summary

As explained, the “process intensification” concept identifies the endeavours to clearly improve chemical conversion in chemical engineering processes. It was shown that such clear improvements were often achieved with the use of membranes. On account of rising requirements, as well as rising energy and raw material prices, the objectives linked with “process intensification” still remain topical. Accordingly, the membrane applications will increase furthermore. However, the task definitions appearing in connection with process intensification are complex. Some require a membrane or membrane module development adapted to the task. In such cases, it needs to be considered whether the opportunities offered with it justify the often protracted development work. The fact that such opportunities exist is pointed out, for example, by a contribution in the an issue of the Journal “Chemie Ingenieur Technik” /20/, which reports about clear improvements in the depletion of LPG gas from natural gas by means of zeolite membranes.

On account of the sometimes numerous coupled elementary processes, such improvements can be detected in many cases only on the basis of a “comprehensive” consideration of all processes that are coupled only to each other. Often this is possible only with the help of mathematical modelling and simulation of the processes.

Literature:
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