High Performance Gas-Liquid Reaction Technology

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Abstract

High performance of reactors is often related to high throughput or high product quality. Scale-up ability, flexibility in operating parameters, product equivalence and new reactor concepts are other factors to be considered. Mass transfer in loop reactors is discussed and compared with other gas/liquid contacting systems. Guidelines for reactor selection are given.
In the chemical and food industry the importance of achieving product equivalence in different sizes of reactors is an increasing requirement. Solutions to meet these requirements are discussed.
With practical examples from industrial applications it is shown that other concepts may improve the performance of a reactor. A reaction concept for oxidations, the flexibility to work with variable working volumes and a concept for continuous hydrogenation are presented.
Future trends in gas-liquid reaction technology are outlined.

Introduction

Gas-liquid reactions are widely used in the process industries for the manufacture of organic intermediates. Many of these chemical reactions are carried out in the presence of homogeneous or heterogeneous catalysts. Typical examples are alkylations, alkoxylations, aminations, carbonylations, hydrogenations and oxydations. Many different types of reactor systems are available for these reactions and have been described in literature. Most of these systems are commercially used. However, the initial development of a chemical reaction is often done in a rather simple laboratory autoclave, latterly more often in more sophisticated laboratory stirred vessel systems. As soon as the chemistry is investigated and optimized, the process and chemical engineers are faced with the problem of selecting a practical and economic reaction system. The chemical engineer's role is to use the results from the chemist in selecting a reaction system with a high performance. By performance, we mean the ability of this system to do the reaction well. This performance may be expressed in the ability to:

- reproduce the chemist's laboratory process on an industrial scale
- achieve a high selectivity and yield
- reach a high capacity and throughput
- demonstrate an excellent reproducibility
- allow flexibility with respect to production parameters (turn down ratio, variation of grades, etc.)
- perform the reaction in a safe way
- fulfill the requirements of environmental regulations

The objective of this paper is to cover some of the aspects that are important in the selection procedure and to discuss some solutions with practical examples.

Reaction Kinetics and Mass Transfer

Some chemical reactions may be done at conditions where the mass transfer from the gas to the liquid is not limiting at all and where only the conversion rate will dictate the type and size of the reactor system. As a matter of fact, most chemists will firstly choose such conditions in their laboratory autoclaves that the effects of mass transfer will be excluded. For developing a new chemistry and to investigate the kinetics, the chemist may choose

- low substrate concentrations
- high stirring speeds
- low temperatures
- high pressures
- low catalyst concentrations

Only after finding the kinetics, will he start to change parameters in order to improve the economics of the process. This is often the moment, where it is found that the reaction becomes mass transfer controlled. Changing the reaction parameters will probably result in problems such as, undesired side reactions, difficulty in controlling the temperature or catalyst deactivation effects. However, it is important to find the conditions where mass transfer starts to play a role, because mass transfer could be a limiting factor on the larger scale reactors.

Where the chemical reaction is solely controlled by the kinetics, the scale-up to industrial size reactors should not be too difficult and the type and size of reactor is mainly dictated by the desired capacity.

The aspects of scaling-up stirred vessels and Loop reactors has very recently been reported by L.L.van Dierendonck, et al. From this paper, it may be concluded that the scale-up of stirred vessels can be very complex and difficult. The scale-up of loop reactors however, seems to be much easier and more reliable.

Loop Reactor

The Loop Reactor (Fig.l) consists of a reaction autoclave, a circulation pump, a heat exchanger and a venturi type ejector (Fig.2). This system thus requires the same number of elements as a stirred vessel system, but is arranged in a completely different way.

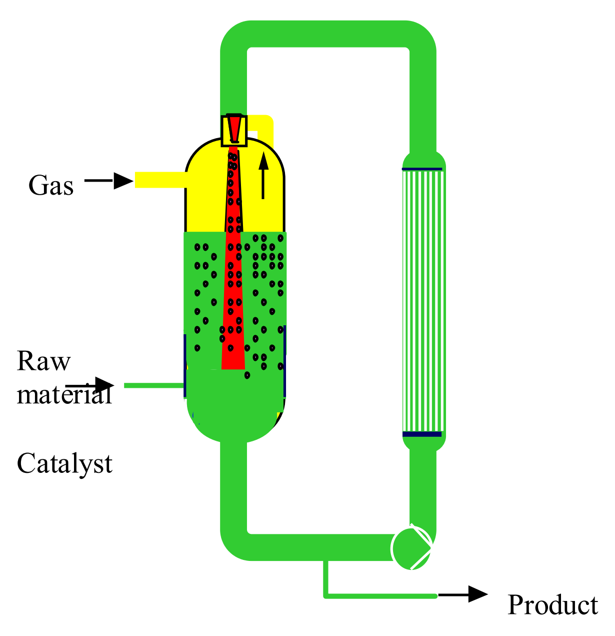

Figure 1 – Loop Reactor

- The reaction vessel of a Loop Reactor does not need baffles and is normally built with a larger L/D than the stirred vessel and is thus lower in cost, especially for high-pressure reactions.

- The external heat exchanger (instead of coils or internal exchangers) can be built as large as needed and is not limited by the reactor's working volume. The full heat exchanger area is available, also if the reactor is operated with reduced working volumes.

- The circulation pump (instead of an agitator) allows high power input per m^3 working volume in those cases where high mass transfer rates have to be achieved. The maximum power input of stirred vessels is often a limiting factor, especially for large reactors. New pump designs are now available with mechanical seals that can be operated at pressures of up to 200 bar g. A unique impeller and a special hydrodynamic pump house profile allow pumping of liquids with a high solid content and high gas loads, without the aid of an inducer and thus avoiding abrasion problems where heterogeneous catalysts are used.

- The down flow Jet Mixer (instead of a sparger or other gas distribution system) is a high performance gassing tool. The ability to finely disperse very small gas bubbles to the liquid with a gas-liquid ratio between 0.5 and 2.0, or even more, makes this an ideal tool for gas-liquid reactions.

The hydrodynamics and the mass transfer characteristics of a Loop Reactor have been investigated and reported by several authors. (Henzler (1981/1982/1983), Zahradnik et al. (1982/1991), Dutta et al. (1987), van Dierendonck et al. (1988), Cramers et al. (1992/1993) and Havelka (1997)).

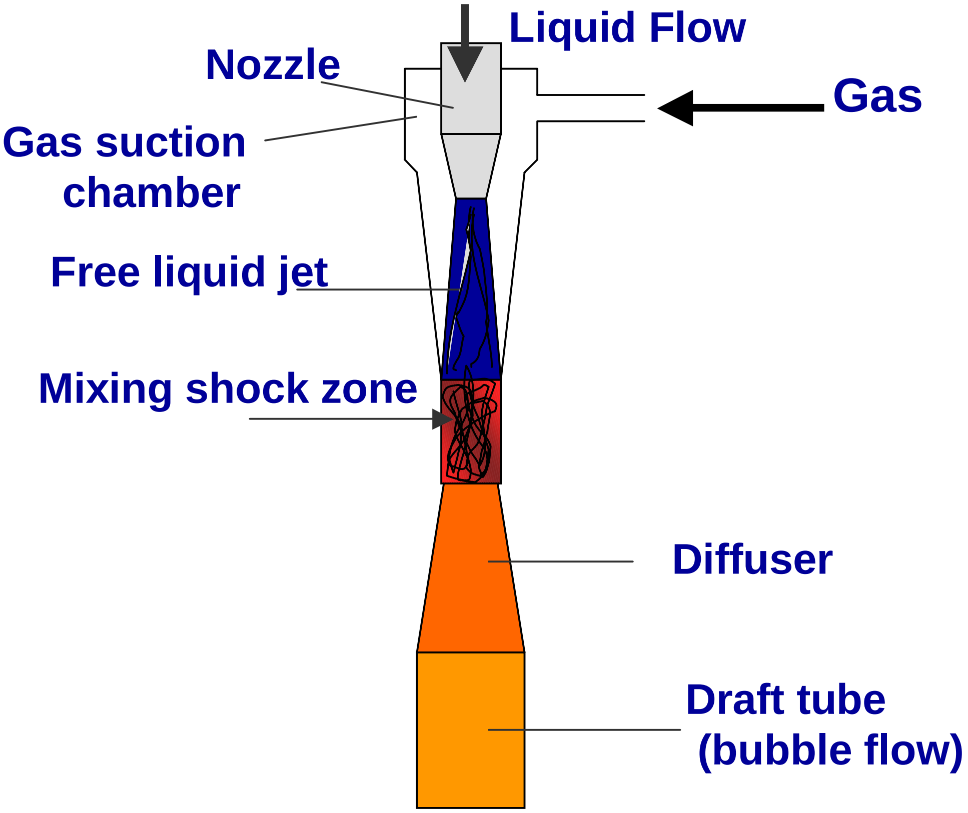

Figure 2 – Venturi Ejector

The effect of the Jet Mixer is not only resulting in a high gas fraction in the vessel, but is also offering a high mass transfer rate within the Jet Mixer itself. (Table 1.)

Table 1. Comparison of different gas-liquid reaction contact systems

Contact System	Bubble size (mm)	Energy dissipation (W/kg)	Mass transfer coefficient K_La (s'^{1})
Bubble Column	3-4	1	0.04 - 0.06
Stirred Vessel	2-3	3	0.1-0.15
Loop Reactor	1-2	5-15	0.3 - 0.45
Jet Mixer	0.1-0.4	500 - 3000	4-6
Impact Zone	<0.1	5000 - 30000	10- 15

All data for a water/air coalescing system (ambient/atmospheric)

The Mass transfer characteristics of a Jet Mixer have been reported and the typical relation of the mass transfer coefficient to the gas-liquid ratio is shown in Fig.3.
It is showing an optimal K_La at a gas-liquid ratio between 0.5 and 2.0.

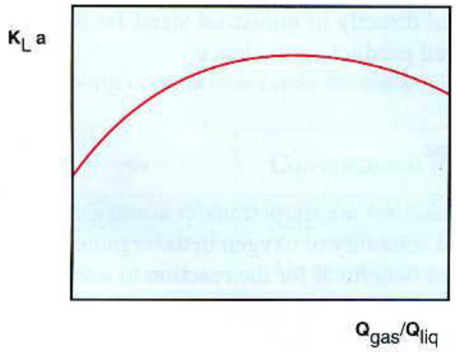

Fig. 3

The Mass transfer characteristics of the reaction vessel are typically proportional to the gas-liquid ratio and are shown in Fig.4.

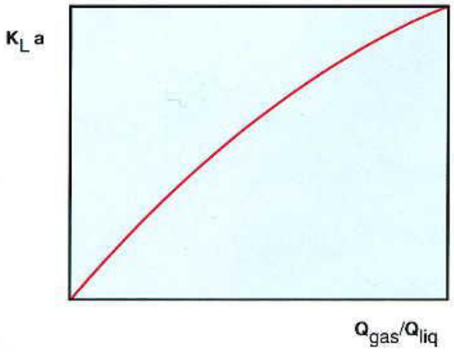

Fig. 4

The overall mass transfer of a Loop Reactor is thus a combination of both as shown in Fig.5.

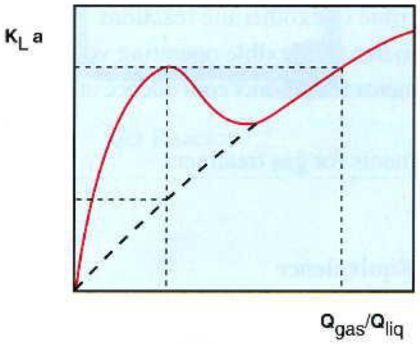

Fig. 5

From this graph it may be concluded that high K_La values can be obtained at reasonably low gas-liquid ratios, because of the high contribution in mass transfer of the Jet Mixer. It also shows that a major part of the reaction will take place in the Jet Mixer, but that still a substantial part of the reaction will take place in the vessel itself. Newer design of Loop Reactors can achieve higher gassing rates to the vessel by removal of the collision plate and by applying pumps that are able to circulate liquids with a high gas load. This will promote the mass transfer in the vessel.

It should also be mentioned here, that the Loop Reactor is generating two circulation systems. A liquid circulation, by the circulation pump, through the heat exchanger and the Jet Mixer. Secondly a gas circulation generated by the self-priming effect of the Jet Mixer. Non reacted gas will separate from the liquid and be collected in the headspace of the vessel and can be sucked in again by the Jet Mixer. This internal gas circulation gives a highly effective utilization of the gas, but also offers additional process options as will be shown later.
One may therefore conclude that the Loop Reactor is an interesting alternative to the stirred vessel if one or more of the following conditions are found:

- reactions at higher pressures
- mass transfer controlled reactions

- endothermic or exothermic reactions
- requirements for flexible operating volumes
- requirements for product equivalence at different reactor sizes
- requirements for gas treatment

Product Equivalence

Product equivalence is the ability to achieve the same product quality, in all respects, independent of the size and the type of equipment.

In the pharmaceutical and fine chemical industry the requirements for a constant and reproducible product quality are of eminent importance. Products are used in medicines, for body care or as food additives. Facilities producing chemicals in these fields have to be fully qualified to cGMP and have to fulfill special requirements of the approval authorities. As soon as an approval procedure for a certain product has been completed, a change of process conditions or process equipment will be difficult if not impossible.

A hydrogenation facility, for example, may have several types and sizes of hydrogenators. It is therefore essential that batches produced in different reactor types or sizes have the same purity and can be reproduced in the same quality. If not, the production will always have to be performed in the same reactor.

Most hydrogenation reactions are mass transfer controlled and the selectivity and product quality will be effected. Selectivity is often influenced by the hydrogen condition on the catalyst surface. A hydrogen rich situation on this surface will often promote the selectivity.

The following conditions are preferred:

- good agitation/gassing
- high hydrogen pressure
- low reaction temperature
- low catalyst concentration
- low catalyst activity

For certain reactions the selectivity will be just the other way around and poor hydrogen conditions will be required.

If the facility is equipped with stirred vessel systems, the operating conditions and mass transfer rates of the smaller reactors have to be adapted to the limited mass transfer rate of the largest reactor, in order to achieve the required product equivalence in all reactors. This is of course possible, but the conditions selected will not be ideal and may result in lower productivity. The reaction conditions will presumably be less selective.

Loop Reactors offer high mass transfer rates resulting in a hydrogen rich situation on the catalyst surface often resulting in improved selectivity and a longer catalyst life. The performance of a Loop Reactor is independent of the size and product equivalence can be reached easily without adaptations. Moreover, it has been seen in practice, that the results from small-scale laboratory reactors can be reproduced directly in industrial sized Loop Reactors with the required product equivalence.

Oxidations

Many oxidations are mass transfer controlled because of the limited solubility of oxygen in the organic liquids used. It would be beneficial for the reaction to use pure oxygen at high pressures, however the substrates and solvents are often flammable and it would be dangerous to do so. Instead of pure oxygen most processes apply air or oxygen-enriched air. This has the disadvantage that large amounts of off-gas will leave the reactor, containing solvent vapors that have to be recovered.

The internal gas circulation of the Loop Reactor makes it possible to operate the reactor as a dead-end reactor without vent, using pure oxygen, but applying an inert and safe headspace. The headspace of the reactor is once filled with nitrogen and pure oxygen can be used without generating a dangerous headspace. (Fig. 6)

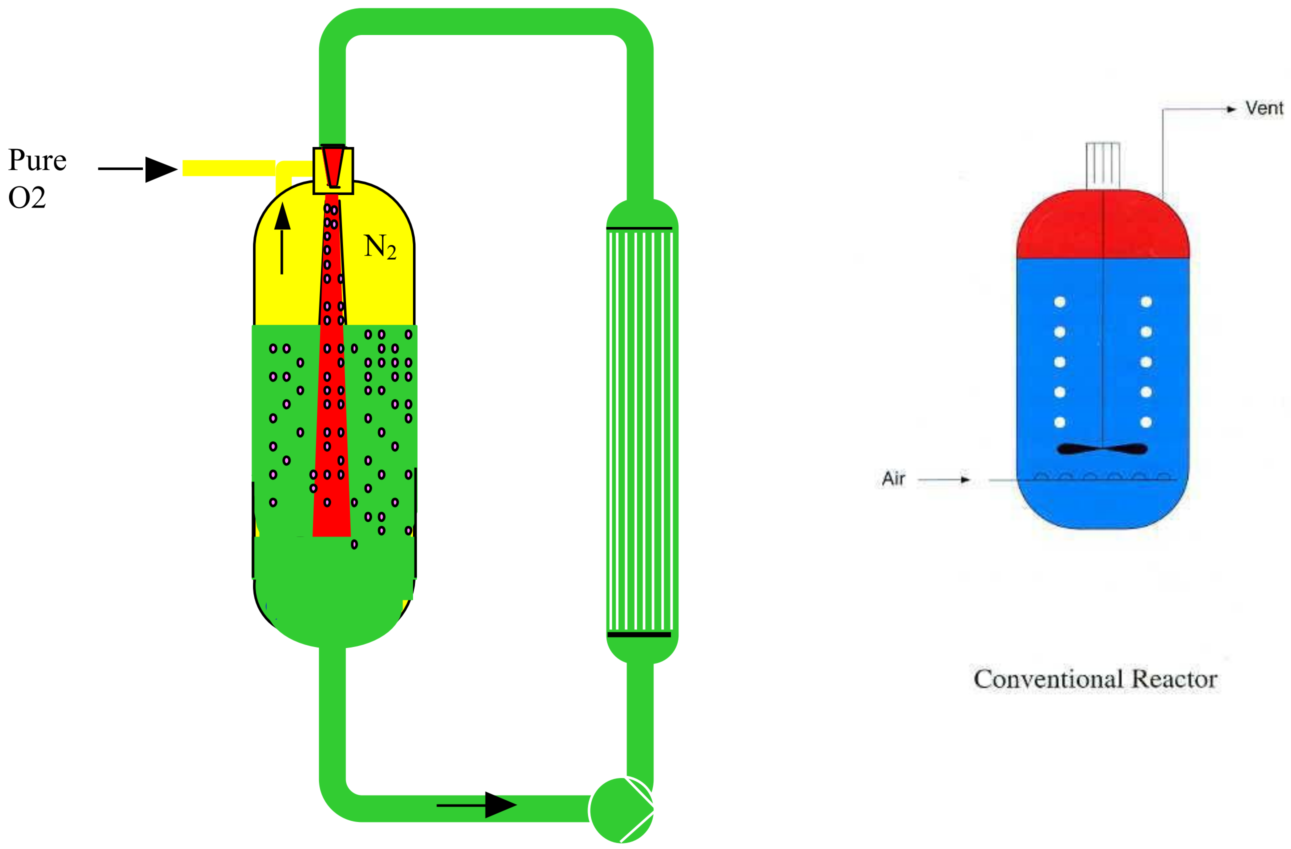

Figure 6 – Comparison of Reactor Concepts

The following comparison could be made:

	Conventional Reactor	Loop Reactor
Head space	Safe	Safe
Gas inlet	Air or oxygen-enriched air	Pure oxygen
Oxygen utilisation	Partly	Complete
Gas outlet	Nitrogen with unused oxygen	No vent
Vent treatment	Solvent recovery	No vent

Flexibility in Working Volume

A multi purpose facility for producing pharmaceutical chemicals or specialty chemicals is normally set-up with different types and sizes of reactors in order to be flexible to the required production volumes for each product.

The following parameters may effect the choice of equipment:

- type of reactions to be performed
- required temperatures and pressures
- maximum viscosity required
- maximum solid content required
- required material of construction
- minimum/maximum working volumes

Considering the fact that stirred vessels can only be operated in a narrow range of operating volume without losing mixing efficiency, heat transfer surface and mass transfer rates, it is assumed that the working volume may only be varied between 50 and 110 % of the nominal capacity.

Loop Reactors may be operated between 25 and 110% of the nominal capacity, still offering the same heat transfer area, the same mixing efficiency and almost the same mass transfer rates.

For a certain production schedule a comparison was made as shown in table 3.

Only 3 Loop Reactors are required to be able to produce batch sizes between 25 and 1760 liters, with the advantage that the small reactor will have exactly the same performance as the largest one.

In the case of stirred vessels, 6 reactors would be required and it is questionable that the largest one will perform exactly the same as the smallest one.

The above example illustrates how important the right choice of reactor type and size can be for a multi purpose facility. In reality both systems will be used. Certain reactions will not require the high efficiency of the Loop Reactor or a number of reactions have to be done at high viscosity or with a very high solid content. This would preferably be done in a stirred vessel.

Stirred Vessels		Loop Reactors	
Nominal volume in liters	Working volume in liters	Nominal volume in liters	Working volume in liters
50	25-55	100	25-110
100	50-110	400	100 - 440
200	100 - 220	1600	400 - 1760
400	200 - 440		
800	400 - 880		
1600	800 - 1760		

Table 3

Continuous Operation

As discussed before, the Jet Mixer is generating very finely dispersed gas bubbles and offers very high local mass transfer rates.
The highest energy dissipation takes place in the impact zone of the Jet Mixer, resulting in extremely fine gas bubbles and very high mass transfer coefficients. This fact has lead to the idea of the continuous operation of the Loop Reactor. The concept is shown in a simplified flow diagram (Fig. 7.)

The conversion of a Nitroaromatic compounds to the corresponding aniline, such as Dinitrotoluene to Toluenediamine, are excellent examples for reactions carried out in continuous Loop Reactors. While maintaining a rather high concentration of active catalyst in the reaction suspension, the nitro-compound is fed continuously into the impact zone of the Jet Mixer. The conversion of the nitro-compound will take place immediately and completely because of the presence of catalyst, hydrogen and the high-energy dissipation in the impact zone.

Consequently the reactor contents consist mainly of amine and water. The condenser in the gas circulation system can continuously remove this water. The product, Toluenediamine, is continuously filtered through the cross-flow filter system in the liquid circulation line and taken away from the reactor system.
For this particular reaction, the continuous Loop Reactor is competing with a fixed bed reactor, where the reaction is carried out in the gas phase at much higher pressures such as 200 to 300 bar g.

In a continuous stirred vessel system, this reaction would require a cascade of 3 stirred vessels. Further, due to the high exothermic reaction it would be necessary to use a solvent in order to dilute the solution and to reduce the heat released.

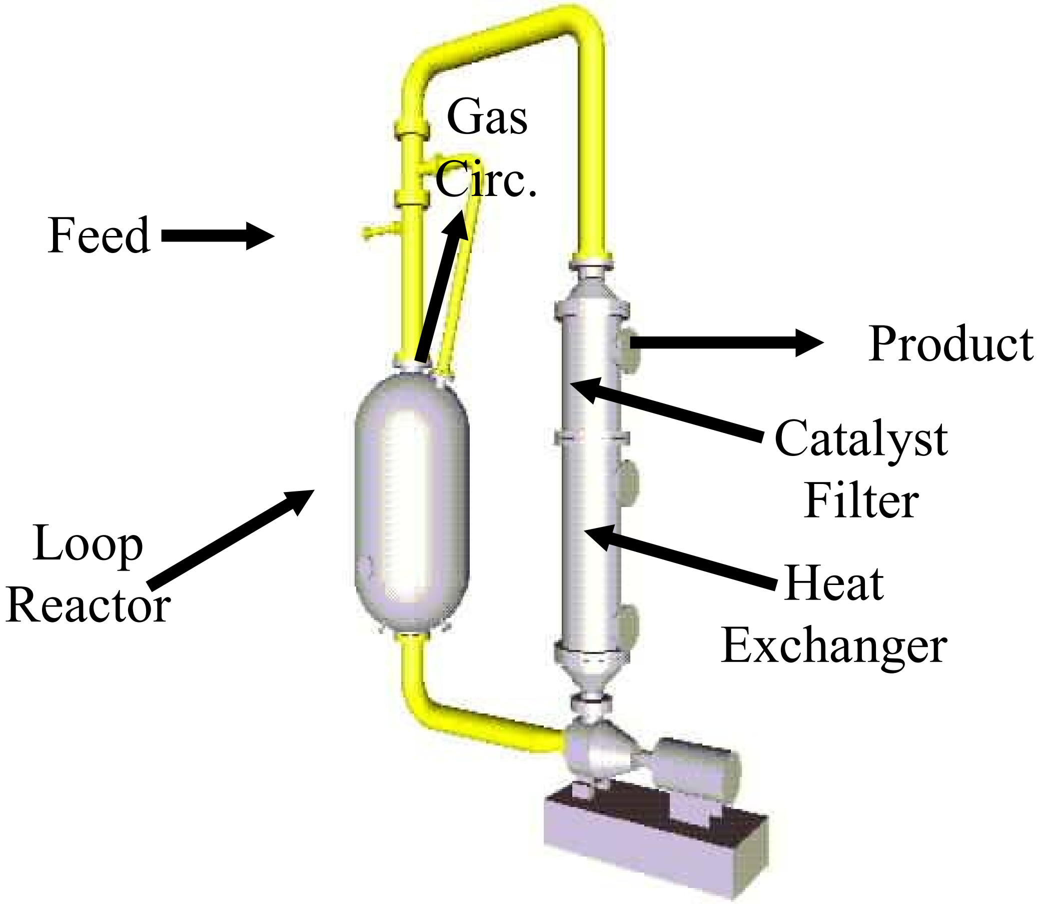

Figure 7 – Continuous Loop Reactor

	Conventional Loop Reactor	Cascade Stirred Reactor
Pressure (bar)	40	40
Temperature (°C)	120	120
Catalyst (%/ month)	5	10
Yield (%)	>98	>97
Residual Nitro (ppm)	none	<500
Solvent (%)	none	30
Capacity (tpa)	50,000	35,000
Reactor size	one 2 m^3 LR	cascade of three 3 m^3 CSTR

The high throughput and the full conversion demonstrate the high performance of the continuous Loop Reactor.

Future Trends

The Loop Reactor is now available for high working pressures of up to 200 bar g and can thus also be used for high-pressure reactions such as the discontinuous and continuous hydrogenation of fatty methyl ester to fatty alcohols over heterogeneous metal based catalyst.

The combination of monolith catalyst packings with the Jet Mixer is certainly very interesting. This will allow the performance of heterogeneous catalytic reactions without the need of catalyst filtration. The high mass transfer rates of the Jet Mixer will improve the efficiency of the monolith packing if these are placed in the Jet Mixer itself. The system would also allow the quick exchange of monolith packings with different types of catalyst for multi purpose reactors. Or the installation of two packings with different catalyst in series could be applied for subsequent reactions.

The gas circulation for removal of by-products from the gas space of the reactor will be used for new applications. Production of nitriles or esters are examples of such arrangements. The steam stripping effect of the Jet Mixer will also be used more in future.

The direct feeding of EO/PO into the Jet Mixer enables the continuous production of ethoxylates and propoxylates such as ethanolamines, PEG's, Glycolethers, ethoxylated fatty derivatives, etc.

Conclusions

- High performance is not only related to high mass transfer rates or high throughputs, but also to easy and reliable scale-up and to high flexibility with respect to operating parameters.

- The product equivalence to be achieved in different sizes of reactors is becoming more and more important not only for the pharmaceutical and fine chemical industries. This requirement can easily be fulfilled with Loop Reactors, because of the identical performance at all sizes.

- The Loop Reactor may be used more for continuous reactions utilizing the high-energy dissipation in the Jet Mixer. Combinations with monolith packings are very promising and have to be investigated.

- The Loop Reactor, originally developed for hydrogenations may be used more for other gas-liquid reactions such as alkylations, aminations, carbonylations and oxidations. This trend will continue.

- The Loop Reactor is becoming more and more a standard in reactor design for gas-liquid reactions.

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Biography

Rene F. Duveen is Technology Manager of HH Technology, International.
Previously, he was employed as Research Engineer with AKZO NOBEL (NL) and ASEA BROWN BOVERI (Switzerland) and as Technology Manager with Ing.A. MAURER S.A. and BUSS AG Basel (Switzerland), where he was responsible for the Reaction Technology Group. His experience includes research and development in laboratory and pilot plants, process design of more than 80 plants for gas-liquid reactions, such as hydrogenation, aminations, alkylations, alkoxylations, oxydations and carbonylations for the oleochemical, speciality chemical, pharmaceutical and the food industries. His background includes also project management, commisioning and start-up of more than 30 chemical plants.
He has published articles on reaction technology, heat recovery systems, viscose technology and waste water treatment technologies and has conducted seminars for many international companies.
Periodically, he has given lectures for several institutions, which run specialist courses.
Rene F. Duveen received his Chemical Engineering Degree from the Technical School of Engineering at Enschede/NL.