EUROPEAN ROADMAP OF PROCESS INTENSIFICATION

- TECHNOLOGY REPORT -

TECHNOLOGY:
Process Intensification / Optimisation using the Advanced Buss Loop Reactor Technology

TECHNOLOGY CODE: 3.2.1

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Table of contents

1. Technology

Process Intensification has recently received widespread attention because of its ability to achieve significant reduction in capital costs as well as its ability to convert more of the material fed into the desired products. Furthermore, many of the safety, health and environmental concerns can benefit from the inventory reduction, improved containment, enhanced selectivity, and increased heat and mass transfer rates achieved by using **Process Intensification Technologies**

The key to Process Intensification's success is that it is a business-driven approach, and that it involves matching the plant to the fundamental requirements of the chemical process. In addition, Process Intensification is no longer just the realm of high volume chemicals production, but can be equally applicable to small volume specialty production.

If one looks for general trends of how **Hydrogenation Technology** is changing during the last years one sees that:

- more attention is given to optimisation in the process development stage, between research and industrial scale production
- a move to more efficient (i.e. better product quality) and hence **high performance hydrogenation plants (Process Intensification)**
- minimisation of catalyst load and catalyst consumption in the process due to the pressure of other competing companies
- minimisation of reaction pressure and hence less hydrogen usage/losses
- still greater concern for safety and environment
- operational costs become more relevant than the initial investment cost as such (Return of Investment).

All the above mentioned factors are influenced by the **Reactor Technology** chosen and hence will also affect initial investment cost and operational cost of the process as a whole. **Buss ChemTech's Advanced Buss Loop Reactor(ABLR) Technology** (as shown in Fig. 1), made up of a reaction vessel with a high performance gas-liquid ejector to achieve High Mass transfer rates, has been around for a number of years. It provides a significant degree of intensification for heat- and mass transfer, and has been successfully applied to a range of processes including hydrogenation, oxidation, phosgenation, alkoxylation, amination and sulphonation.

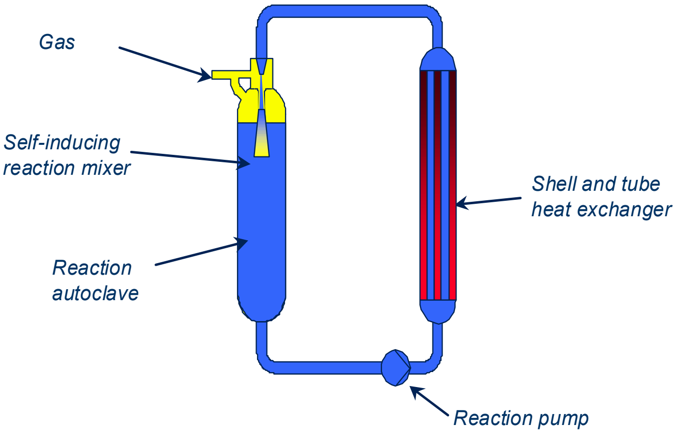
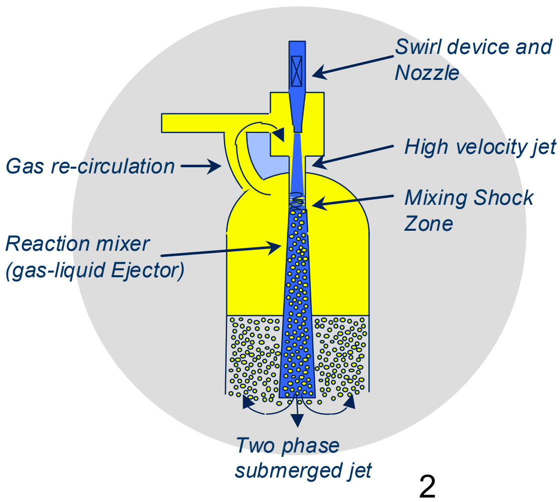


Fig. 1: ABLR

1.1 Description of technology / working principle

The Advanced Buss Loop Reactor consists of a reaction autoclave, a circulation pump, a heat exchanger and a reaction mixer (gas-liquid ejector). This system requires the same number of elements as a stirred vessel system but is arranged in a completely different way.

- The Ventury type **Reaction Mixer** (instead of a sparger or other gas distribution system) is a high performance-gassing tool. A gas-liquid ejector consists of four main sections. The pumped liquid flow passes through a nozzle that provides a high velocity jet of fluid to create suction of the gas in the gas suction chamber and entrain gas into the ejector. In the following mixing tube the liquid jet attaches itself to the mixing tube wall resulting in a rapid dissipation of kinetic energy.



This creates intensive mixing shock zone where the high turbulence produces a fine dispersion of bubbles. The ability to generate and finely disperse very small gas bubbles to the liquid (30 to 70 µm) with a gas-liquid ratio between 0.5 and 2.0, or even more, makes this an ideal tool as primary dispersion device for gas-liquid reactors. The two-phase mixture created in the reaction mixer is then injected into the fluid of the reaction vessel.

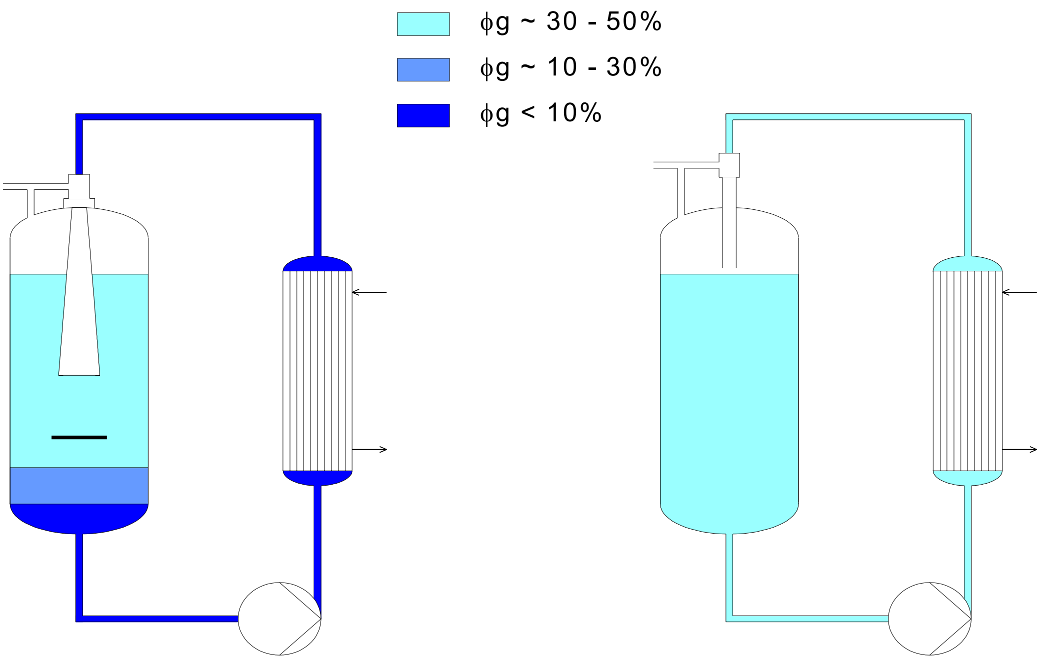
- The **Reaction Vessel** of an ABLR does not need baffles. It is normally built with a larger L/D ratio than the stirred vessel and is thus lower in costs, especially for high-pressure reactions. The two-phase mixture that "jets" into the reaction autoclave causes an intensive secondary mixing and a very high mass transfer rate due to the small bubbles, which were created in the reaction mixer. The average bubble sizes in the reaction autoclave are in the range between 0.2 and 0.7 mm (larger than the primary bubbles due to coalescence phenomenon).
- The **external Heat Exchanger** (instead of coils or internal exchangers) can be built as large as required and is not limited by the reactor's working volume. The full heat exchanger area is available, even if the reactor is operated with reduced working volumes (e.g. semi-batch operation).
- The **Circulation Pump** (instead of an agitator) allows high power input per working volume (kW/m³) in those cases where high mass transfer rates have to be achieved. New pump designs are now available which allows pumping of liquids with high solid (catalyst) contents up to 8 wt % and high gas loads up to 30 vol %.

1.2 Types and "versions"

(Describe the most important forms/versions of technology under consideration, including their characteristic features, differences and similarities)

Two basic types of Buss Loop Reactors can be distinguished:

The "classical" Buss Loop Reactor (BLR) and the Advanced Buss Loop Reactor (ABLR).



In the "classical" Buss Loop Reactor (build in the last 50 years), the gas was separated from the liquid in the reaction vessel and brought back to the head space, before entering the circulation pump.

In the Advanced Buss Loop Reactor, the gas bubbles are pumped around the loop by a special pump which is able to handle gas loads up to 30 %-vol. By this measure the active reaction volume and hence the overall performance has been increased significantly compared to the "classical" BLR.

1.3 Potency for Process Intensification: possible benefits

(In Table 1 describe the most important documented and expected benefits offered by the technology under consideration, focusing primarily on energy; CO_2 emission and costs, providing quantitative data, wherever possible. Add other benefits, if needed).

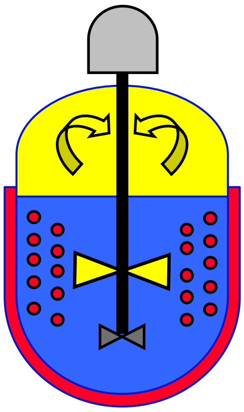
Table 1: Documented and expected benefits resulting from technology application

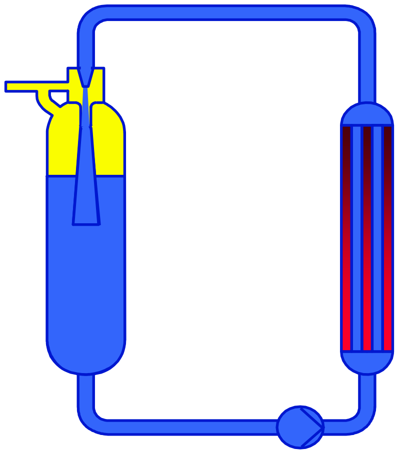
Benefit	Magnitude	Remarks
Better overall performance		Highest mass transfer rates and unconstrained heat transfer area proven in industrial plants
Significant savings in catalyst cost		• The percentage of slurry phase catalyst added to the reactants is less than in a STR, and this still gives a shorter reaction time and better yield. In some cases, the reduction is 50 to 70 %. This means that the capital tied up in catalyst stocks can be correspondingly reduced and will generate major savings in operational costs. • Catalyst lifetime can be increased when reaction time is shortened, reaction conditions are milder and byproduct formation is reduced. This results in a further reduced consumption. • Furthermore, lowering the quantity of catalyst present also reduces losses during handling and filtration which tend to be a fixed percentage of the total present. • Lower catalyst concentrations also mean that catalyst filters can be smaller and therefore less expensive.
No scale-up problems on an industrial scale and guaranteed process and performance:		The initial development of a chemical reaction is often done in a laboratory autoclave. It is important not to underestimate kinetic effects when it comes to the step from laboratory autoclave to industrial scale. The best and most reliable results are normally obtained in one of two BUSS pilot plant scale loop reactors (15 or 50 litre) which allow to achieve the highest selectivity and yield, to reach a high capacity and throughput, demonstrate an excellent reproducibility and allows flexibility with respect to production parameters (turn down ratio, variation of grades, etc.). The results thus obtained can easily be scaled up to any size of industrial reactor (up to scale-up factor 500 to 1 or more). In the case of a stirred tank autoclave, scale up is more difficult due to changes in mixing pattern and area to volume ratios between a pilot plant scale and a production scale vessel. Mixing intensity cannot be scaled up so readily as temperature and concentration gradients arise which often lead to longer reaction times and lower yields.
Reduction of reaction pressure due to the superior mass transfer rate		This consequently allows reduction of the initial investment cost of the reaction section and gas supply system
Excellent cleaning features		The autoclave of the BUSS Loop® Reactor has no internals besides from the ejector, which is located in the top of the autoclave. There are no cooling coils and/or plates, sparging tubes or baffles and no agitators, which are dipped in the reaction fluids and which are difficult to clean. The whole reactor can be completely drained, so that product losses are low when a product change is made and solvent washing (when required) is relatively quick and easy. That's why loop reactors are also particularly suitable for multi-purpose plants and increase the operational availability and flexibility.

2. Applications

2.1 Existing technology (currently used)

Typically, the Advanced Buss Loop Reactor is compared with a Stirred Tank Reactor:





Stirred Tank Reactor (STR) with jacket/coils/plates:

α_{Heat} is 200 - 900 W/m^2/K

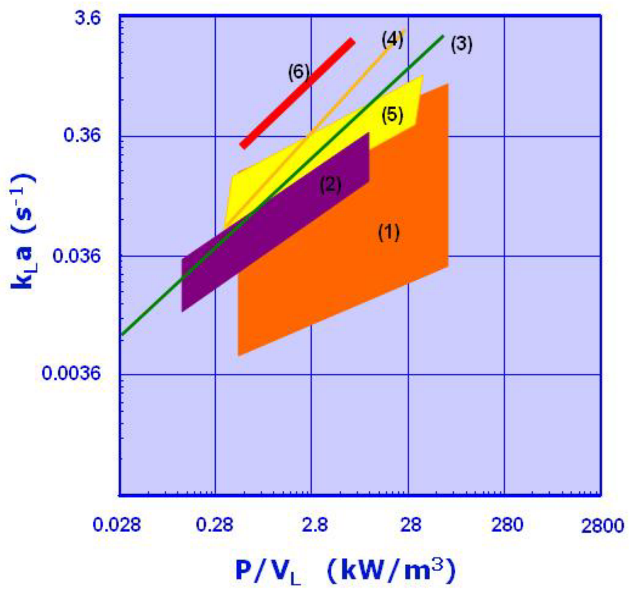
- Surface area is dependent of scale
- Surface area is dependent of reactor fill
- Surface area is < 10 m^2/ m^3

Advanced Buss Loop Reactor (ABLR) with shell & tube heat exchanger :

α_{Heat} is 900 - 1'200 W/m^2/K

- Surface area independent of scale
- Surface area independent of reactor fill
- Surface area is >> 15 m^2/ m^3

The hydrodynamics and the mass transfer characteristics of loop reactors 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. (1992/1993/2001) and Havelka (1997)) The effect of the reaction mixer not only results in a high gas fraction in the vessel, but also offers a high mass transfer rate within the reaction mixer. The reported mass transfer characteristics of loop reactors and the typical relation of the mass transfer coefficient to the power input per unit of volume is shown in Fig. 3.



1. Stirred reactor (STR) with external cooling
2. Conventional stirred vessel equipped with six bladed turbine stirrer
3. Self-aspirating stirrer in a vessel
4. Self-aspirating stirrer in combination with EKATO phasejet in autoclave
5. Buss Loop Reactor (BLR)
6. Advanced BUSS Loop® reactor (ABLR)

Fig. 3: Mass transfer rates in various reactor systems vs. power input per unit volume.

In Fig. 3 it is shown, that the newer design of the Advanced BUSS Loop® Reactor achieves higher mixing and gassing rates to the reaction vessel by using a reaction pump that is able to circulate liquids with a high gas load (up to 30 vol. %) which also enhance even more the mass transfer in the reaction vessel and external loop. In order to generate and improve mixing and/or mass transfer, the reactor equipment must direct the energy most efficiently into the fluid system. In a stirred tank reactor, the energy input clearly comes through the impeller, but this arrangement suffers from high-energy losses through frictional and other losses. The energy that remains is focused mainly upon the fluid directly in contact with the impeller. This means that while power inputs at the impeller tip may be relatively high, the majority of the fluid is unaffected and the average power input across the whole tank is low (0.1 – 0.7 W/kg).

Considering these facts one may conclude that the ABLR reactor is the most interesting alternative to the stirred vessel if one or more of the following conditions apply:

- reactions at higher pressures
- mass transfer controlled reactions
- strongly endothermic or exothermic reactions
- requirements for flexible operating volumes
- requirements for product equivalence at different reactor sizes
- requirements for gas treatment

2.2 Known commercial applications

(Is the technology broadly applied on commercial scale? In which process industry sectors is the technology most often applied: large volume chemicals – specialty chemicals & pharma – consumer products – ingredients based on agro feedstocks? What is the estimated number of existing applications? In Table 2 provide the most prominent examples of realized applications and provide their short characteristics)

Table 2. Industrial-scale applications of the Technology (existing and under realization)

Sector	**Short characteristic of application**	**Plant size [tons/batch]**	**Reported effects**
Ethoxylation	Addition of ethylene oxide to R-OH	10 – 35	- high reaction rate - low by-products - good heat removal
Organic intermediates Hydrogenation	- Double and tripple bonds - Ring hydrogenation - Hydrogenation of nitriles to amines - etc	2 – 20	- high reaction rates - high yields - low catalyst consumption
Nitro Hydrogenation	Reduction of nitro compounds to anilines by hydrogenation	2 – 10	- high reaction rate - good heat removal - enhanced safety due to semi batch operation - solvent free operation possible
Fatty Acid Hydrogenation	Unsaturated fatty acids are converted to saturated fatty acids by the hydrogenation of the double bonds	10 – 20	- lower formation of trans isomers
Fatty Acid Nitrilation		10 – 20	- continuous removal of water (equilibrium reaction) via external gas circuit
Oxidation		1 – 10	- safe operation due to nitrogen dilution
Alkylation with MeCl		10 – 20	- high reaction rate - good heat removal
Many others…		0.3 – 20	….

2.3 Known demonstration projects

(Are there any demonstration projects known related to the technology under consideration? In which process industry sectors are those projects carried out: large volume chemicals – specialty chemicals & pharma – consumer products – ingredients based on agro feedstocks? In Table 3 provide the short characteristics of those projects.)

Table 3. Demonstration projects related to the technology (existing and under realization)

Sector	Who is carrying out the project	Short characteristic of application investigated, including product name/type	Reported effects
	Buss ChemTech	Typically, reactions are optimised in BCT's pilot plant to be compared with the results achieved on the client's industrial plant	- shorter reaction times - lower catalyst concentration required - better yield

Reactor Technology (Industrial Scale Plants)	Power input (kW/m^3)	Bubble diameter (mm)	Mass transfer coefficient *kLa* (s^{-1})
Bubble Column	0.2 – 0.5	2 – 4	0.05 - 0.15
Stirred Tank	1 – 4	1 – 2	0.15 - 0.35
Advanced Buss Loop Reactor	2 – 5	0.03 – 0.07	up to 1.6

<u>A selection of reactions carried out in Stirred Tank Reactors and Buss Loop Reactors</u>

Chem. Com-pounds	Type of Reactor	Pressure (bar g)	Temp. (°C)	Cat. Conc. (%-wt)	Reaction Time (min)	Yield (%)
Aromatic Nitro Compound	Stirred Tank Reactor	40	150	0.1	360	-
	Buss Loop Reactor	40	150	0.01	100	-
Aliphatic Nitro Compound	Stirred Tank Reactor	75	30	2.6	480	72.0
	Buss Loop Reactor	30	55	2.6	120	96.5
4-hydroxy-4-methyl-2-pentanone	Stirred Tank Reactor	30	80	5.0	70	99.4
	Buss Loop Reactor	30	100	0.5	45	99.7
Cinnamic aldehyde	Stirred Tank Reactor	20	15	6.0	360	90
	Buss Loop Reactor	90	35	0.6	100	95
Benzaldehyde	Stirred Tank Reactor	10	150	2 (Pd/C)	120	96.5
	Buss Loop Reactor	10	150	1 (RaNi)	160	99.3
a – methyl cinnamic aldehyde	Stirred Tank Reactor	10	180	1.25	720	-
	Buss Loop Reactor	10	180	1.25	405 - 420	95 - 99.5

2.4 Potential applications discussed in literature

(Provide a short review, including, wherever possible, the types/examples of products that can be manufactured with this technology)

Some chemical reactions are carried out at conditions where the mass transfer from the gas to the liquid (and/or liquid to the solid phase, i.e. heterogeneous catalyst) is not limiting at all and where only the conversion rate will dictate the type and size of the reactor system. Actually, most chemists in the first trials will choose conditions in such way that in their laboratory autoclaves adverse effects due to mass transfer limitations will be negligible.

For developing a new chemistry and to investigate the kinetics thereof, the chemists normally choose:

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

After finding the specific kinetics, they will start to change parameters in order to improve the economics of the process. That's when reactions are mostly identified as mass transfer controlled. Changing the reaction parameters will probably result in problems such as undesired side reactions, difficulties in temperature control 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 becames a question of expertise and is releated to the desired capacity. The aspects of scaling-up stirred vessels and loop reactors have been reported by L.L. van Dierendonck, et al. From this publication, it may be concluded that the scale-up mass transfer limited reactions in stirred vessels can be very complex and difficult. The scale-up of the ABLR, is much easier and more reliable if you are experienced with these systems.

3. What are the development and application issues?

3.1 Technology development issues

(In Table 4 list and characterize the essential development issues, both technical and non-technical, of the technology under consideration. Pay also attention to "boundary" issues, such as instrumentation and control equipment, models, etc.) Also, provide your opinion on how and by whom these issues should be addressed)

Table 4. Technology development issues

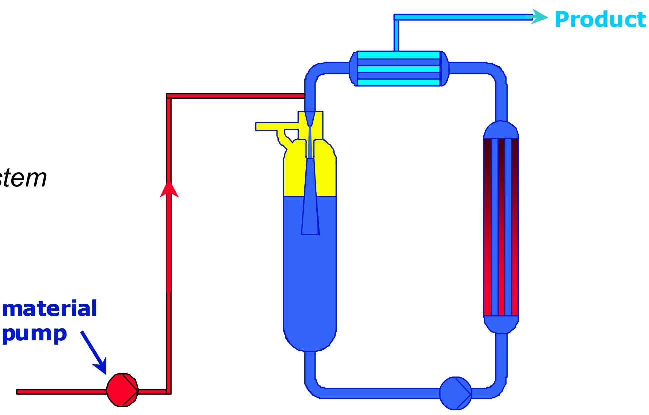
Issue	Description	How and by whom should be addressed?
Characterization / Optimisation of the Reaction Mixer	Mass transfer characteristics of a novel gas/liquid contactor, the Advanced Buss Loop Reactor (2001)	Swiss federal Institute of Technology Zürich, Dr. Frank Oliver Baier
Characterization / Optimisation of the Reaction Mixer	Hydrodynamics and mass transfer characteristics of liquid driven jet ejectors (2003)	Buss ChemTech AG Dr. P. H. M. R. Cramers

From Batch to Continuous Operation

As discussed, the reaction mixer generates very fine dispersed gas bubbles and offers very high local mass transfer rates. The highest energy dissipation takes place in the mixing shock zone within the reaction mixer, resulting in extremely fine gas bubbles and very high mass transfer coefficients. The concept of a continuous operated Advanced BUSS Loop® Reactor is shown in a simplified flow diagram (Fig. 4).

An excellent example for a reaction carried out in continuous ABLR reactor is the conversion of Nitro-compounds to the corresponding Amines. While maintaining a high loading of active catalyst in the reaction suspension, the Nitro-compound is fed continuously into the mixing zone of the reaction mixer. The conversion of the Nitro-compound will take place immediately and completely because of the presence of catalyst, the presence of hydrogen and the high energy dissipation in the mixing shock zone. The product is continuously filtered through the cross-flow filter system out of the reactor system. In a continuous stirred vessel system, this reaction would require a cascade of stirred vessels with a total residence time of 3 to 4 hours, whereas the ABLR required a total residence time of ½ hour only. Further, due to the high exothermic reaction stirred vessels would require the use of a solvent in order to dilute the solution and to reduce the heat released. This example shows that when using a stirred autoclave the total reaction volume would be at least a factor of 4 to 6 higher than when using the BUSS technology. That's why a continuously operated ABLR is a typical example of a high performance reactor using the concepts of **process intensification**.

Fig. 4:
Diagram of a continuous operated Advanced BUSS Loop® Reactor system



3.2 Challenges in developing processes based on the technology

(In Table 5 list and characterize the essential challenges, both technical and non-technical, in developing commercial processes based on the technology under consideration. Also, provide your opinion on how and by whom these challenges should be addressed)

Table 5. Challenges in developing processes based on the technology

Challenge	Description	How and by whom should the challenge be addressed?
Alternative materials of construction (MOC)	Typically, Loop Reactors are made from stainless steel of the SS 300 series or from Hastelloy. However, in some cases even Hastelloy is not appropriate and alternative solutions regarding MOC have to be found such as glass- or PTFE lining, ceramics etc.	

4. Where can information be found?

4.1 Key publications

(Provide the list of key publications in Table 6)

Table 6. Key publications on the technology

Publication	Publication type (research paper/review/book/ report)	Remarks
Cramers, P.H.M.R. et al., Hydrodynamics and Mass Transfer Characteristics of a Loop-Venturi Reactor with a down-flow liquid jet ejector	Chem. Eng. Sci. (1992), 47, 3557-3564.	Chem. Eng. Sci. (1992), 47, 3557-3564.
Cramers, P.H.M.R. et al., Hydrodynamics and local mass transfer characteristics of gas-liquid ejectors	Chem. Eng. J. (1993), 53, 67-73.	Chem. Eng. J. (1993), 53, 67-73.
Cramers, P.H.M.R. et al., Influence of the ejector configuration, scale and the gas density on the mass transfer characteristics of gas-liquid ejectors	Chem. Eng. J. (2001), 3770, 1-11.	Chem. Eng. J. (2001), 3770, 1-11.
Dierendonck L.L. van, et al., Scale up of Gas-Liquid reactions made simple with loop reactors	6th European Conference on Mixing (1988), Pavia, Italy	6th European Conference on Mixing (1988), Pavia, Italy
Dierendonck L.L. van, et al., Loop Venturi Reactor-a feasible alternative to stirred tank reactors?	Ind. Eng. Chem. Res. (1998), 37, 734-738	Ind. Eng. Chem. Res. (1998), 37, 734-738
Dutta N.N. et al., Mass Transfer and Hydrodynamic Characteristics of Loop Reactors with Downflow Liquid Jet Ejector	Chem. Eng. J. (1987), 36, 111-121.	Chem. Eng. J. (1987), 36, 111-121.
Havelka, P. et al., Effect of ejector configuration on the gas suction rate and gas holdup in ejector loop reactors	Chem. Eng. Sci. (1991), 52, 1701-1713	Chem. Eng. Sci. (1991), 52, 1701-1713
Henzler, H. -J., Das Sogverhalten von Strahlsaugern f Stoffsysteme	fIVT-Verfahrenstechnik. (1981), 15(10), 738-749.	fIVT-Verfahrenstechnik. (1981), 15(10), 738-749.
Henzler, H. -J., Zur Auslegung von Strahlsaugern für einphasige Stoffsysteme	Chem.-Ing. -Techn. (1982), 1, 8-16.	Chem.-Ing. -Techn. (1982), 1, 8-16.
Henzler, H. -J., Design of ejectors for single-phase material systems	Ger.Chem.Eng. (1983), 6, 292-300	Ger.Chem.Eng. (1983), 6, 292-300
Zahradnik et al., Hydrodynamic Characteristics of Gas-Liquid beds in Contractors with Ejector type gas distributors	Coll. Czech. Chem. Comm. (1982), 47, 1939-1949	Coll. Czech. Chem. Comm. (1982), 47, 1939-1949
Zahradnik et al., Design and scale-up of Venturi-tube gas distributors for bubble column reactors	Coll. Czech. Chem. Comm. (1991), 56, 619-634	Coll. Czech. Chem. Comm. (1991), 56, 619-634

4.2 Relevant patents and patent holders

(Provide the list of relevant patents in Table 7. Under "remarks" provide, where applicable, the names/types of products targeted by the given patent.)

Table 7. Relevant patents

Patent	Patent holder	Remarks, including names/types of products targeted by the patent
Several patents in the field of GTL (gas to liquid / Fischer Tropsch) reactions	BP and Davy Process Technology Ltd.	
Several patents under preparation	Buss ChemTech and partners	Confidential

4.3 Institutes/companies working on the technology

(Provide the list of most important research centers and companies in Table 8)

Table 8. Institutes and companies working on the technology

Institute/Company	**Country**	**Remarks**

5. Stakeholders

5.1 Suppliers and developers

(Provide the list of key suppliers/developers in Table 9)

Table 9. Supplier and developers

Institute/Company	**Country**	**Remarks**

5.2 End users

(Describe the existing and potential end-users, other than those already listed in Table 2)

Table 10. End users

Industry / Product Groups		**Remarks**
Pharmaceuticals		
Fine chemicals		
Speciality chemicals		
Resins, Petrochemicals		
Performance chemicals		
Ethylene oxide derivatives		
Agrochemicals		
Oliochemicals		
Oils&Fats		

6. Expert’s brief final judgment on the technology

- High performance is not only related to high-mass transfer rates or high throughputs, but also 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 a Buss Loop Reactor, because of the identical performance at all sizes.
- The Buss Loop Reactor may be used more for continuous reactions utilising the high-energy dissipation in the Gas-Liquid Ejector (Reaction Mixer).
- Loop Reactors, originally developed for hydrogenations may be used more for other gas-liquid reactions such as alkylations, aminations, carbonylations, oxidations and other gas-liquid reactions. This trend will continue.
- The Advanced Buss Loop Reactor is becoming more and more a standard in reactor design for industrial performed gas-liquid reactions.