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SILICON CARBIDE EQUIPMENTS FOR PROCESS INTENSIFICATION OF SILICON REACTIONS

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Abstract. Bluestar Silicones, one of the worldwide leaders in silicones chemistry, proposes a R&D project, aiming to design new equipment for the transposition of batch to continuous processes. The safety and environmental issues linked to this type of chemicals, and the productivity targets as well require innovative technologies characterized by a fair corrosion resistance and high heat and mass transfer performances. A preliminary prototype of heat exchanger reactor made of silicon carbide plates has been developed by the LGC in collaboration with a SME specialist of SiC, Boostec. It has allowed the pilot feasibility with some reactions of industrial interest for a Bluestar Silicones to be highlighted. Now, it is necessary to pursue this effort and beyond the feasibility step to go on up to the design of an industrial reactor. This project corresponds to a programme of innovative process development in order to design cleaner, safer and less consuming devices.

Key-words. Process Intensification, Silicones reactions, Silicon carbide, Catalysis, Heat exchanger reactor

Bluestar Silicones represents one of the world's leading fully integrated global silicones players. Chemistry of silicones offers a wide variety of products in specialty market such as engineered elastomers, human care and textile and release coating. In that context, hydrosilylation is the most fundamental methods for the industrial synthesis of organosilicon compounds and organic silyl derivatives. The term of hydrosilylation refers to the addition of Si-H bonds to double bonds like C=C leading to oil functional silicones. Functional oil can be represented according to figure 1, where the R group due to its chemical nature, confers specific properties on the oil. Depending on this group nature, reactivity and surface activity of the oil can be controlled. The range of functional oil applications (and thus of market) is vast; let us quote for instance:

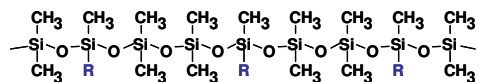


Figure 1: representation of functional oil

- Release coating.
- Antifoams.
- Hydrofugation (paints and coatings).
- Personal care.

The reactions of hydrosilylation involve oil possessing Si-H bonds (collectively called SiH oil). These oils present a major danger related to the strong amount of hydrogen they can release (auto-flammable at the rate of 4 % in volume in the atmosphere) or to formation of very flammable silanes when

SiH oil is put into contact with acids and bases. Moreover, this class of reactions generally consists of fast and highly exothermic reactions, traditionally operated in batch processes, which presents safety issues linked to hazards of different natures.

Such features make it as an ideal candidate to Process Intensification and to batch to continuous transposition¹⁻⁵. In this way, Bluestar Silicones proposes a R&D project, aiming to design new equipment for the transposition of batch to continuous processes. The safety and environmental issues linked to this type of chemicals, and the productivity targets as well require innovative technologies characterized by a fair corrosion resistance and high heat and mass transfer performances. A preliminary prototype of heat exchanger reactor made of silicon carbide plates has been developed by the LGC in collaboration with a SME specialist of SiC, Boostec. It has allowed the pilot feasibility with some reactions of industrial interest for a Bluestar Silicones to be showed.

INTENSIFICATION DEVICE

The present work aims to replace the industrial fed-batch reactor by continuous and intensified ones. In this way and taking into account the features of the considered hydrosilylation applications, plate heat exchanger reactor appears as the most suitable technology. In fact, thanks to specific design of channels⁶, this kind of devices offer the heat transfer performances of heat exchangers coupled with high mixing and plug-flow behaviour.

In front of the strong heat generated by hydrosilylation reactions (generally up to 300°C of adiabatic temperature raise), very high heat transfer performances are required to operate in a pure batch mode. As a consequence, the present project has been built around silicon carbide equipments that offer remarkable performances in terms of thermal control.

Silicon carbide hex-reactor

A first prototype of heat-exchanger reactor made of ceramic (SiC) has been developed in the frame of a collaboration between Boostec and LGC⁷ (figure 2). Boostec is an innovative SME, specialized in high-performance all-silicon carbide components and systems. Boostec sintered silicon carbide provides a unique combination of key advantages for the production of high performance components or systems:

- Nearly pure SiC, no secondary phase (to avoid interaction between the material and the reactive medium).
- Isotropic physical properties (that guarantees a good homogeneity of the reactor channels).
- High mechanical strength and stiffness, insensitivity to mechanical fatigue.
- High thermal conductivity.
- High stability in time and aggressive environments.

From a PI viewpoint, the use of ceramic allows strong corrosion resistance, high heat transfer capacity and temperature stability to be obtained in mini-structured plates. Therefore, such a reactor appears particularly suited to Process Intensification of highly exothermic and/or strongly corrosive applications. In fact, intensification allows reactions to be improved (increase of reactants concentration, of catalyst amount, etc) and then leads to the use of more aggressive and more corrosive products in an environment where thermal exchanges are enhanced.



Figure 2 : SiC hex-reactor

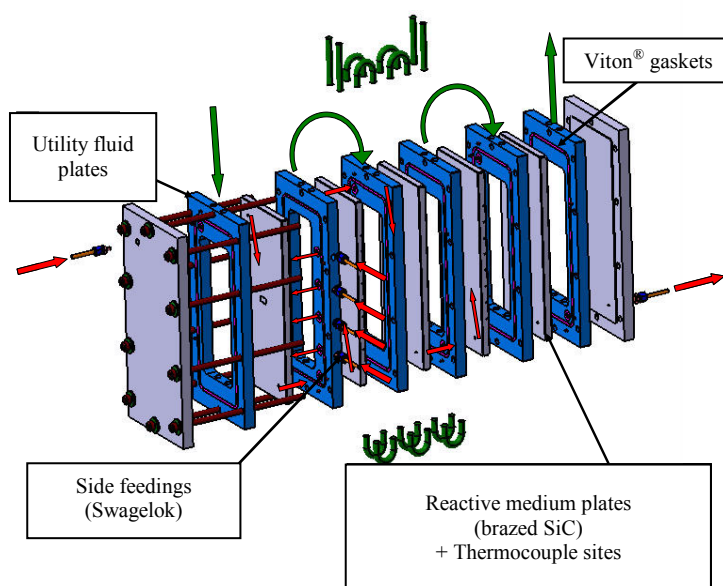


Figure 3: silicon carbide plate heat exchanger

Moreover, the reactor also offers promising perspectives in the fields of safety (reduction of reactive medium amount, minimisation of thermal runaway risk), of energy efficiency (high thermal transfer performances), of productivity (possibility to increase reactants concentration) and of environmental impact (reduction of solvent consumption and therefore of separation steps).

The concept of the reactor (figure 3) is based on a modular structure built by the alternative stacking of reaction plates (grey solid plates) and of utility plates (blue open plates) containing the utility fluid. On figure 3, the circulation (how the flow enters, fills and leaves the plates) of the reactive medium and utility fluid are respectively described by red and green arrows. Reaction plates are made of SiC, brazed and offer a volume with a specific design of about 35 mL for the reactive medium. Utility plates are made of SiC or stainless steel and end plates are made of stainless steel to facilitate the connection with the feed lines and the outlets. An advantage of the reactor lies in the thermocouples located all along the reactive channel that offer a measurement of the temperature in term of residence time at nominal flow-rates from 1 to 5 seconds.

Performances characterisation

A specific methodology has been set-up to propose a characterisation of the equipment performances in terms of hydrodynamics, of pressure drops, of mixing and of heat and mass transfer. Test reactions have also been identified to validate and emphasize these performances. Such an approach aims at proposing standard tests to be able to compare various equipments and technologies⁸⁻⁹. It would be very useful during the project to estimate the improvement related to the developed SiC equipments.

The first prototype has been designed for a nominal range of flow rates from 1 to 10 L/h. In such a range, the reactor offers interesting performances gathered in table 1. It is important to note that thermal performances are estimated from the product between the heat transfer area and the global heat transfer coefficient over the reactive medium volume. For a standard batch reactor, this parameter is nearly about 1 kW.m³.K⁻¹. Consequently, due to the large value of this factor combined with the strong conductivity performances of the SiC material, the heat exchange performances are expected to be very high.

Table 1: SiC reactor characteristics according to flow-rate

Flow rate (L/h)	Reynolds number (-)	Peclet number (-)	Residence time (s)	Pressure drop (bar)	Thermal performances (kW.m ³ .K ⁻¹)
2	300	> 100	60	0.4	9 600
5	760		25	0.7	20 000

FEASIBILITY STUDY

In a preliminary step the pilot feasibility inside silicon carbide equipments has been studied with a “simple” hydrosilylation reaction of industrial interest for a Bluestar Silicones.

Application case

Hydrosilylation refers to the addition of a Si-H bounds compound to an olefin or an acetylenic derivative, with C-Si bounds formation. Hydrosilylation reactions are conducted in the presence of a platinum catalyst between a liquid organic compound having in each molecule at least one aliphatic unsaturated bond and a liquid organosilicon compound having in each molecule at least one silicon-bonded hydrogen atom. Hydrosilylation reaction is normally carried out in a batch fashion in a compatible solvent (such as ethyl alcohol, isopropyl alcohol, or a similar alcohol; or benzene, toluene, xylene, or a similar aromatic solvent.) It is normally required for the above reaction that the mole ratio of the aliphatic unsaturated bonds to SiH be greater than 1 and the coefficient of conversion be greater than 0.9999. In order to satisfy such requirements, the reaction often took an extremely long time. In olefin case, hydrosilylation can be represented as on figure 4.

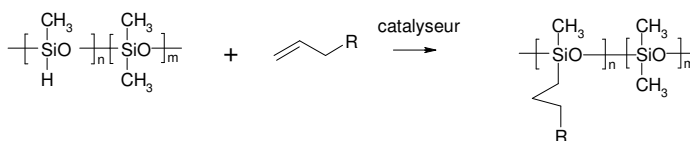


Figure 4: Reaction scheme

In the context of the feasibility study, a “simple” reaction of hydrosilylation was chosen for the demonstration. In that case, 1-octene constitutes the R group and H68 the silicon oil, which leads for the considered operating conditions to a fast and highly exothermic reaction with an adiabatic rise of temperature of about 340°C. As this application is an industrial and complex reaction based, only few data are available to provide the considered intensification methodology. In this way, specific experiments have been carried out on a lab batch reactor to characterize the application. An exhaustive knowledge is not required, but only a general understanding of the main phenomena occurring and of their impact on the intensified process key-points. As a consequence, the characterisation experiments are focused more precisely on the determination of the main reactions kinetics and on the estimation of a global heat generated by the reaction, to answer to safety and yield issues. For instance, figure 5 emphasizes the accuracy of the thermo-kinetics modelling for three different experiments with various temperature level and feeding time.

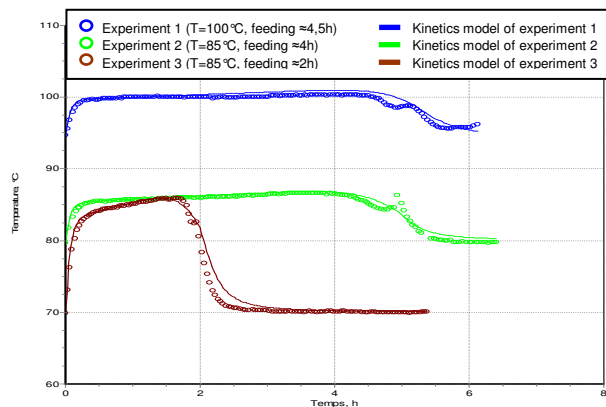


Figure 5: validation of reaction modelling

As a consequence, the characterisation experiments are focused more precisely on the determination of the main reactions kinetics and on the estimation of a global heat generated by the reaction, to answer to safety and yield issues. For instance, figure 5 emphasizes the accuracy of the thermo-kinetics modelling for three different experiments with various temperature level and feeding time.

Intensified process

The intensification of this application is considered for safety reasons related to the risk of thermal runaway¹⁰ and to hazards involved by SiH reactions (formation of H₂). Nevertheless and even if it favours the safety of the reaction by an enhanced thermal control and by minimizing the reactive hold-up, Process Intensification has to comply with a production objective of more than 99% of SiH converted at the end of the reactor to be satisfactory. The reduction of reactant excess and of catalyst amount, which can not be recycled, constitutes secondary objective of Process Intensification.

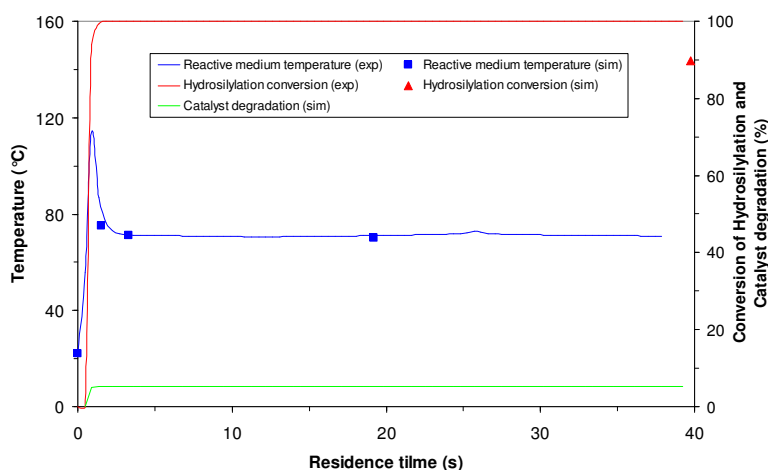


Figure 6: hydrosilylation in SiC reactor, with a 70°C utility fluid

According to the preliminary tests carried out on lab batch reactor and the resulting models that have been set-up, relevant operating conditions have been identified and applied to the SiC reactor. In a first step, it has been chosen to carry out a set of experiments at “low temperature” in order to validate the conditions and to test the feasibility inside the SiC reactor (figure 6). In this context, process fluid is introduced at 2.24 L/h with a molar ratio between Octene and SiH of 5.13 (Octene flow rate = 0.22, SiH flow-rate = 2.02). Utility fluid is introduced at 70°C with a flow rate of 20 L/h.

As expected, the results show that the reactive medium temperature is well controlled, in spite of the strong exothermicity (340°C of temperature adiabatic rise). The comparison between experimental and simulation data highlights the accuracy of our models in terms of temperature prediction, but also shows uncertainties on the final conversion. In fact, the measurement realized at the end of the reactor (only point available for the conversion estimation, no sample can be withdrawn inside the reactor) is about 90%, while the simulation predicts 100%. At this stage, it is important to note that the reaction modelling has been developed from batch experiments, where for safety reasons, operating conditions are radically different from the ones applied in the SiC reactor. Such considerations may explain somewhere the uncertainties observed on the final conversion. However, from a safety viewpoint, the modelling provides relevant information on the temperature of the reactive medium inside the reactor. Different parameters have been investigated in order to converge on optimal operating conditions. The influence of the ratio

between both reactants (Octene / SiH oil) has been studied in a 5 to 1 range (in moles) to measure its influence on final conversion (see table 2). Two different levels of temperature have also been considered by providing a utility fluid at 70 and 85°C.

Table 2: experiments carried out in the SiC reactor with an 85°C utility fluid

Octene	Flow-rates (kg/h)		Global	Molar ratio Octene / SiH	SiH conversion (%)
	SiH Oil				
0.24	2.10		2.34	4.85	91.3
0.40	2.02		2.42	2.82	93.1
0.55	2.02		2.57	2.05	92.8
0.96	1.94		2.90	1.12	94.0
1.11	2.02		3.13	1.00	93.7

Two sets of operating conditions have been studied but not allow the production constraint to be reached. Under these conditions, the residence time is assumed to limit the conversion to about 94%. In fact at high conversion level, kinetics appears to slow down and therefore the last conversion points require more time to be reached. Consequently, we have decided to experimentally estimate the residence time required to a 99% conversion. Since no additional plates made of SiC were available at the moment of the experimentation, a batch reactor has been added at the end of the process in order to control the residence time and to achieve the reaction. This stirred jacketed batch reactor is maintained at a temperature of 70°C. Different samples are withdrawn from the reactive medium at various times, to follow the final conversion according to time (figure 7).

The results shows that about 20 min are needed to reach more than 99% of conversion. These results allow a new process to be designed, coupling to the SiC reactor a continuous stirred tank reactor (CSTR) of 1L (to respect the required residence time), since the question of exothermicity no longer exists at this stage. This process offers interesting results in terms of conversion as it allows high conversion level to be reached (more than 99%). Another process, integrating solely a more conventional heat-exchanger reactor under unconventional conditions (utility fluid at 110°C, catalyst concentration of 15 ppm) leads to 99.8% of conversion. Unfortunately, through lack of time, such conditions can not be applied to the SiC reactor during the testing campaign. Some additional experiments have also been performed to test the influence of the catalyst amount on the final SiH conversion. The quantity of catalyst seems to have no influence on the conversion because there is not or little deactivation of the catalyst. It is thus possible to reduce the quantity of catalyst below 3ppm that is currently used in industrial production.

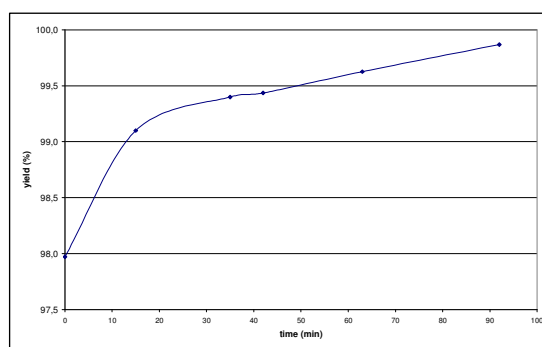


Figure 7: conversion according to time in the batch reactor

Conclusion and perspectives

Through this work, the feasibility and the intensification of a continuous process of hydrosilylation has been demonstrated. The intensified process is composed of two reactors, a plate heat exchanger reactor made of SiC to initiate the reaction and absorb the larger amount of the heat generated (95% of conversion) followed by a continuous stirred tank reactor to increase the residence time and then to achieve the reaction (more than 99% of conversion). This process shows under safe conditions a high efficiency: final conversions are close to 100 % with residence time of about 20-25 min instead of 5-6h in fed-batch reactor. Furthermore, the continuous operation allows an important gain on selectivity to be obtained and the amount of catalyst to be significantly reduced. Finally, in this kind of process, an excess of octene does not appear relevant and stoichiometric conditions could be applied that makes possible to avoid one post treatment operation (devolatilization of the reactive medium).

The good results obtained during this study lie more precisely on the enhanced heat transfer offered by the SiC reactor and on the reaction characteristics which include a fast kinetics associated to a slow catalyst deactivation. This feasibility study leads to a hybrid process composed of a plug flow and a CSTR. Nevertheless, from Process Intensification and safety viewpoint, operating in a single apparatus would be more convenient. In this way, various information on the operating conditions sensitivity has been collected to be able as a perspective to define a strategy and a novel process in a single apparatus.

In the context of the hydrosilylation reactions, this feasibility study offers interesting perspectives. In fact, the hydrosilylation class reactions present many issues that may be solved by process intensification and heat exchanger reactors, such as selectivity issues and the access to new products that can not be performed in batch reactor. These conclusions lead to the proposal by Bluestar Silicones of a R&D project, aiming to design new equipment made of SiC for Process Intensification and transposition of batch to continuous of hydrosilylation applications. This project, funded by the French ANR, is named HEXoSiC.

HEXOSIC PROJECT

The preliminary study has allowed the pilot feasibility inside silicon carbide equipments with some reactions of industrial interest for a Bluestar Silicones to be showed. Now, it is necessary to pursue this effort and beyond the feasibility step to go on up to the design of an industrial reactor, through the frame of a multi-partner R&D project.

It is expected that process intensification will lead not only to an enhancement of the operating conditions (better thermal control, efficient mixing) and of hazards management (hold-up decrease, strong thermal effusivity) but also to an increase of productivity (with the increasing reactants concentrations) and to a better selectivity with a better environmental impact (decrease of the solvent amount). It will be probably possible to imagine new chemical paths for new products. Some bottlenecks still remain in designing a reactor for silicones applications.

First, since the products of the studied reactions are viscous, the reactor has to be operated under pressure because of the expected high pressure drop. This question has to be addressed through a specific design of the reactive channels and thanks to a particular way of brazing the SiC plates, developed by Boostec.

Secondly, Bluestar Silicones would like to enlarge the applicability of this type of heat exchanger reactor to other exothermal reactions that require a precise control of two-phase mixing and a good resistance to corrosion. This latter requirement is a typical feature of silicon carbide. Simultaneously, two ways of catalysis will be investigated: one homogeneous studied by the LGC and the other one being heterogeneous with a supported catalyst, studied by the LGPC, specialized in catalytic process engineering. The objective is to find the most suitable commercial catalyst (acquisition of kinetic data, deactivation,...) and to study the ways of catalyst deposition and the production of interfacial area inside the reactor. This research is also considered by Boostec as a challenge and an opportunity to prove the versatility of this type of technology. One attempt is to open the market of this SME.

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