CS22

Reactor design for a plug fluid flow through the textile

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Abstract

As the cellulose oxidation by NO_2 is highly exothermic, it is mandatory to design the reactor so as to obtain a radial fluid flow through the textile as plug as possible, permitting to avoid all dead zones where a reaction runaway may happen and to reach a very homogeneous degree of oxidation throughout the whole textile roll. The reactor was designed thanks to a detailed fluid modelling and use of a fluidic software for optimising the geometry of the fluid inlet ports and the characteristics of the cylindrical perforated support on which the textile is rolled. Moreover, the reactor was instrumented with many thermocouples to ensure a perfect control of temperature in all parts, leading to a safe and reliable operation.

The scale-up challenge

The main difficulty is related to the extremely corrosive and toxic character of the reactant NO_2 that demands very uncommon innovations on most parts of the equipment, at the difference with what we are accustomed to propose in "classical" supercritical carbon dioxide processes.

The "heart" of the process is the reactor where *Carbon dioxide* has four roles:
- *Moderator*: dilution of the reactant (NO_2) to moderate the reaction,
- *Mass vector*: of the reactant inside the porous material (cotton textile),
- *Heat vector*: for evacuating the reaction heat and controlling temperature at an optimal value for a good kinetics without risk of reaction runaway,
- *Solvent*: for withdrawal of unreacted reactant and unwanted nitric by-products after reaction completion.

The reactor, in which such functions will be completed, must be designed so as to obtain an as perfect as possible *plug flow* through the textile to reach a homogeneous oxidation advancement and to maintain a perfectly controlled temperature in all positions. This is much simpler at small scale where the textile width is limited to a few tens of cm, than at large scale: as the process is operated at high pressure, the reactor cannot be scaled-up in diameter only, but also in length! So, fluid distribution is the key-issue, the more because the pressure drop through the textile is extremely small and the fluid pattern is consequently modified by all geometrical details of the reactor.

Moreover, even if the reactor is the main system, many other parts are difficult to design and build:
-All parts of the equipment must be resistant to an extremely corrosive mixture of CO_2 and NO_2 that can lead to rapid oxidation of lubricants or seals if not correctly chosen to resist to this strong oxidant fluid;

- The need for a fluid circulation pump with high flow rate and low pressure head working at high pressure leads us to choose a specific centrifugal pump with the electric motor immersed in the fluid special: no need for shaft seals but special shaft bearings were particular difficult to find;
-Elimination of any NO_2 traces from all gaseous effluents: Several gas contactors filled with soda were designed for warrantying environmental safety in normal exploitation, but also in case of total rapid depressurisation of the equipment on critical situation;
- Another critical point of design is related to cleaning with the drastic rules to avoid any cross contamination between batches (in compliance to cGMP): the equipment must be designed to permit a complete withdrawal of all gas and liquid phases, without any dead volumes that might lead to accumulation of nitric reactants;
- A validated control system is required to ensure a safe and reliable operation, especially temperature control inside the textile roll to prevent any reaction runaway.

Reactor design

The reactor is a cylindrical pressure vessel in which a roll of textile around a shaft is introduced. The fluid percolates the roll radially and the radial flow, oriented from outside to inside the roll has to be plug flow. This means that the *longitudinal* (along z axis) pressure drops of the fluid (outside the roll, inside the roll and inside the shaft) must be negligible in comparison with the radial pressure drop.

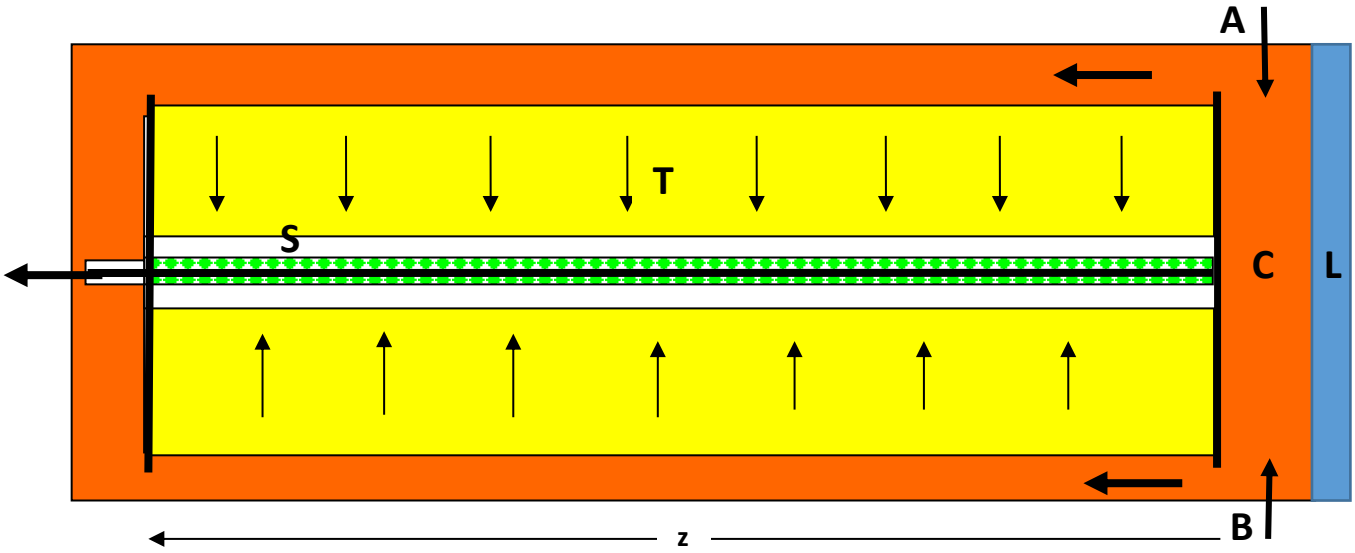


Figure 1: Oxidation reactor scheme

- Reactor shaft

So, the textile **T** is rolled onto a shaft **S** between two circular baffles. This shaft S is designed to create a large pressure drop, much higher than the pressure drop through the textile roll, permitting to damper all possible variations along the textile roll. For this purpose, we firstly tried to use a porous sintered metal tube, but we failed to find a metal alloy compatible with NO_2 presenting no risk of alteration and potential contamination of the textile. So, we designed a more complex system consisting in a perforated stainless steel shaft, on which the textile is rolled, and inside which a ceramic multi-tubular pipe is installed. This system has the advantage to present and homogeneous high pressure drop but also, as the radial flow is oriented from outside to inside the roll, to serve as filter for textile fibrils that may be carried by the fluid and may cause hazards when accumulating in some dead-ends with potential oxidation runaway.

Moreover, a rather simple calculation permitted to verify that the pressure drop along the internal tubings of the ceramic pipe remains very low in comparison with the radial pressure drop through the pipe.

- Fluid repartition

As the reactor has to be opened and closed at each batch, the fluid must be introduced through tubings fastened to the cylindrical part of the reactor, not through the lid **L** that shall remain easily moveable. The fluid is fed by two inlets (**A - B**) in opposite position and a specific geometry was studied to warranty a good fluid repartition whatever is the angle position relatively to the fluid inlets A and B.
For solving this challenge, we used a fluidic modelling (Navier-Stokes equation and turbulence model) to define the right geometry of the inlet chamber **C**, with the help of PROGEPI (Nancy – France) using *Fluent*® software; Among numerous results obtained with the different geometries that were tested, we present results showing the stream lines in the inlet chamber C (Figure 2) and the fluid axial (along z axis) velocity repartition according to the angle around the baffle when it enters into the textile roll zone (Figures 3).

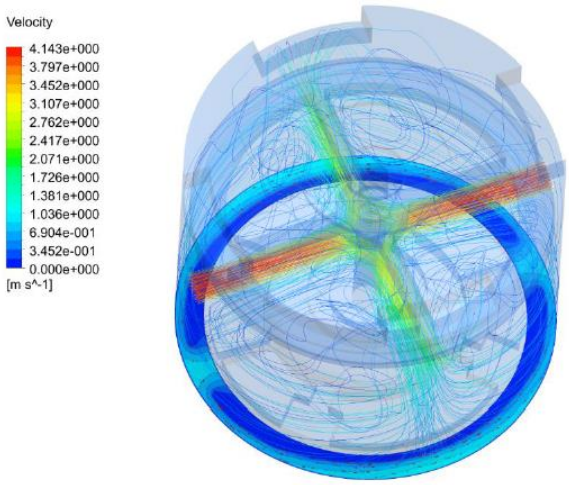


Figure 2: Stream lines in the inlet chamber

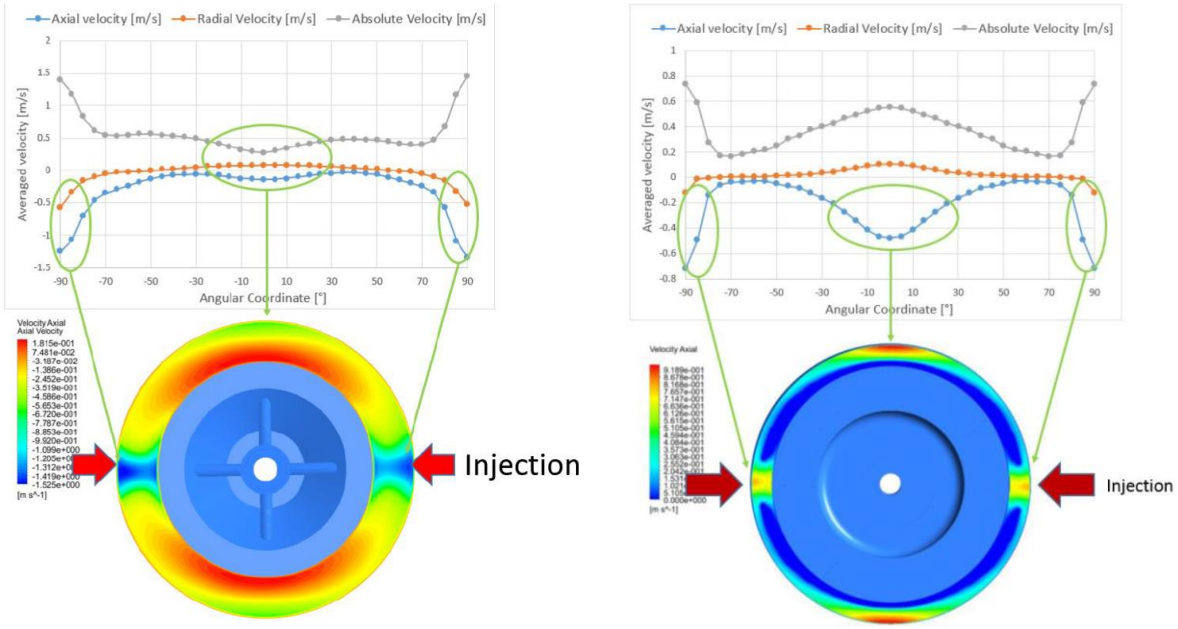
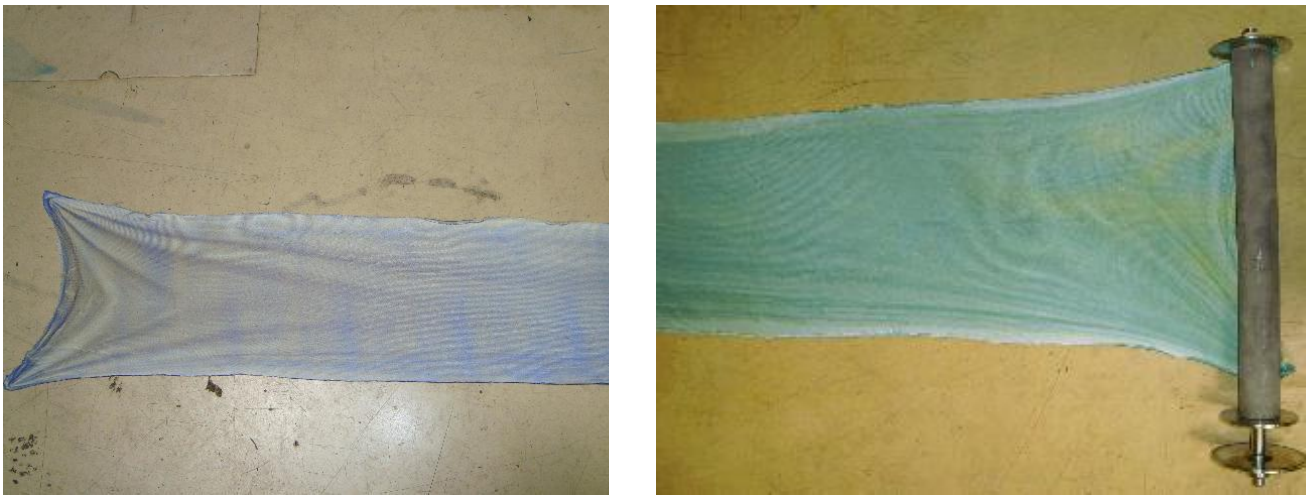


Figure 3: Fluid velocity repartition at inlet in the reaction zone for two different geometry of the inlet chamber

In order to validate this modelling, we also operated an (very rough) empirical residence time distribution measurement at pilot scale in two ways:
- The textile roll was impregnated by a colorant sensitive to pH (bromophenol blue: blue for pH>4.6 - green for 3.0<pH<4.6 – yellow for pH<3.0) and, after equilibrating the fluid flow, we injected a long pulse of acetic acid.
- The textile roll was impregnated by a colorant sensitive to pH (bromothymol blue: blue for pH>7.6 – green for 6.0<pH<7.6 – yellow for pH<6.0) in a range where CO_2 will change color.
In both cases, the textile was then unrolled and the color change gives a rough idea of the fluid repartition through the textile, as shown for the satisfactory cases presented on Figure 4a and 4b.



Figures 4: Bromophenol test (acetic acid in nitrogen): quasi homogeneous color (left)
Bromothymol test (CO_2): quasi homogeneous colour change to green (right)

But obviously, the only valuable test of the fluid flow homogeneity is to be made *in situ* during a batch production!

During the operation itself, the temperature map obtained from 12 thermocouples installed in the textile roll at different positions (along z axis and at various angles), is a first verification of the flow pattern. It appears that maximal temperature deviations remain below 2°C.

And finally, after the oxidation, the ultimate evaluation is the measurement of the oxidation advancement in all parts of the textile and consequently to assure on its quality for making the final product: Oxidation advancement was shown to be always near the target: 60%.

After months of validation, the process was certified for use at commercial scale, with a good reliability, demonstrating that all this work on reactor design was successful.