CFD investigation on 3D printed reactor for hydrothermal continuous synthesis of beta zeolite

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Introduction

- FLOW4SOLID is a collaborative project within the framework of the ERDF program (Project portfolio INTENSE4CHEM), which aims at the intensified manufacturing of Zeolite beta. The project globally looks on the whole process from synthesis to crystal formation, growth and drying.
- Zeolite beta has shown great potential as heterogeneous solid catalyst in petroleum refining and chemical/petrochemical industries [1][2]. It is one of the high silica synthetic zeolites, which was first hydrothermally synthesized from a reacting mixture containing Silicon Oxides, Aluminum, Sodium and TEAOH at a temperature between 75°C-200°C. Various methods for zeolite Beta synthesis have been described in the literature [3][4]. However, this work is based on the Clearfield and Borade model [5] due to its capacity to synthesize Zeolites beta molecules with a low Si/Al ratio. The hydrothermal synthesis of zeolite particles is mostly carried out in stirred batch reactor which causes many limitations in terms of working pressure and time cost. Recently, continuous flow systems, which are frequently used in heat exchangers and chemical reactors, have received more attention, due to their potential ability to overcome batch system drawbacks [6][7]. Continuous synthesis involves strong interactions between different phenomena (crystal growth, rheology and hydrodynamics). To optimize this continuous system, it is thus necessary to perform a coupled-modeling study of all phenomena, to be able to predict the complex behavior of the reacting medium (solid suspension).
- In the present work, the rheology and hydrodynamic behaviors of the Zeolite beta suspension in a 3D printed reactor is modelled, with the objective of optimizing the reactor design.

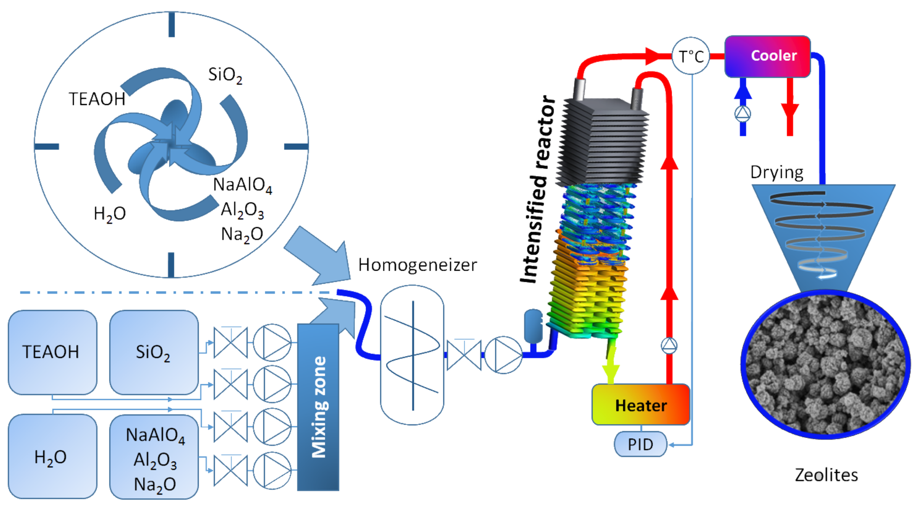

Figure 1 – Flow4Solid complete project

Process Description & Case Study

PROCESS DESCRIPTION

The complete process combines crystallization kinetics, rheology and fluid dynamics. Gel particles utilize water, to form zeolite crystals. In a continuously operating reactor the individual particles have different sizes at different times. Hence particle size distribution (PSD) varies with time, it is described as main source of rheology and flow regime changes.

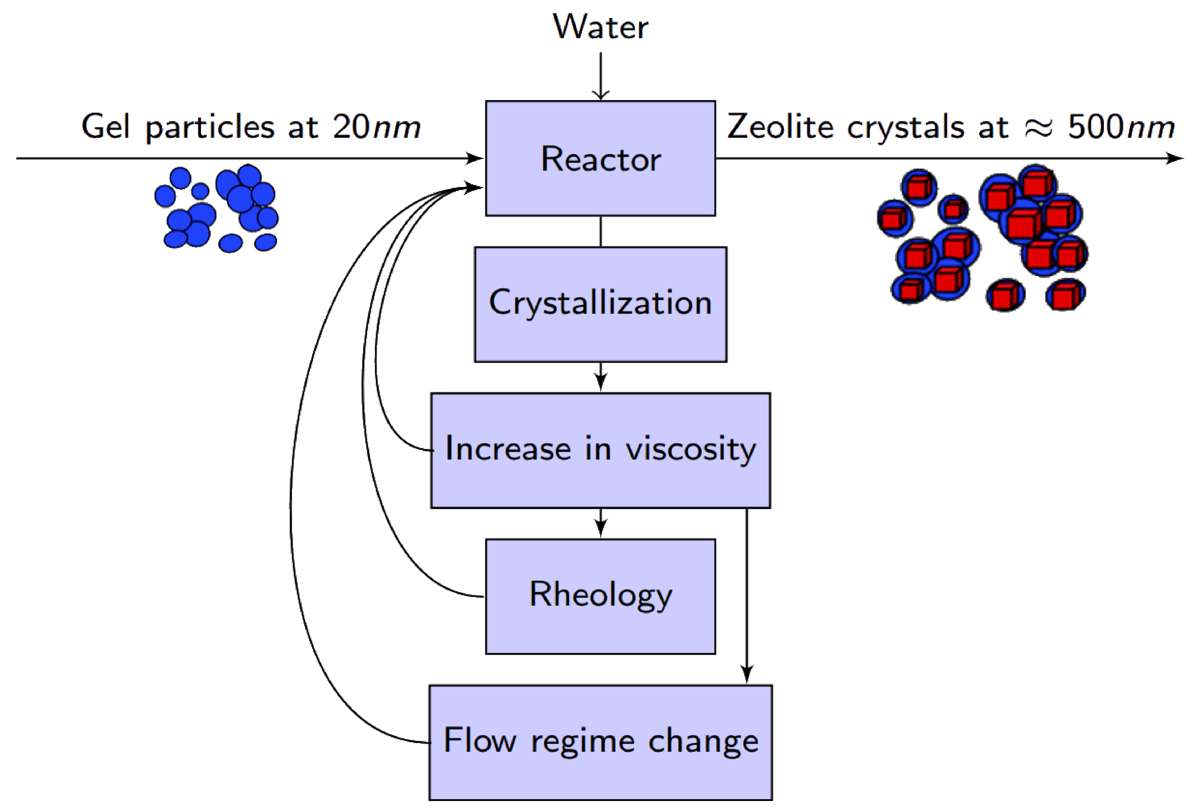

Figure 3 – schematic diagram of process where rheology and flow regime are directly affected by crystallization

CASE STUDY

3D printed plate reactor (22×22 stages)

Plate reactors usually operate isothermally, which is desired for hydrothermal synthesis, as the reaction can occur at optimal conditions. In the first stage of model development, the geometry of the 3D printed plate reactor designed by CERTECH (fig.2 left) was set up in Ansys DesignModler simulation platform (fig.2 right), in order to simulate fluid dynamics and heat transfer. Fluent 18.2 energy based model was used to describe heat transfer between the reacting medium and the heating fluid (oil).

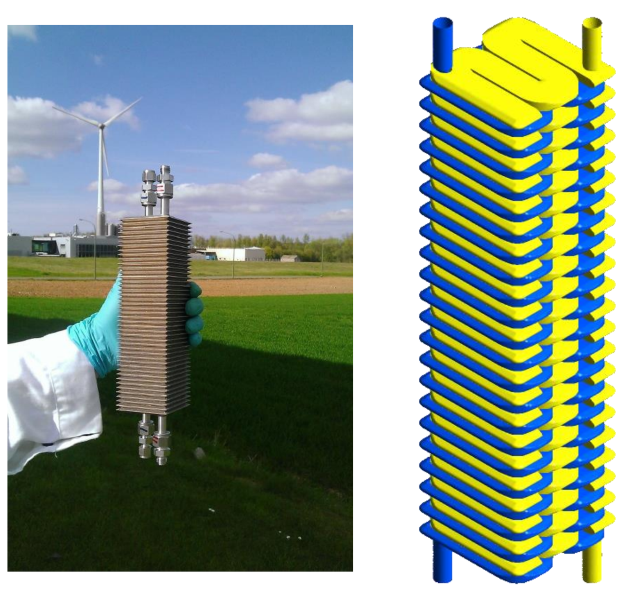

Figure 2 – experimental and numerical plate reactor

RESULTS
I. CFD validation

Test	Operating conditions		Results			
	Q_{water} inlet (gr/s)	T_{oil} outlet (°C)	T_{water} outlet (°C)		ΔP (bar)	
			CFD	EXP	CFD	EXP
1	1	90	90	86.7	0.003	0.05
2	31.167	90	27.2	28.5	1.78	2.8
3	41	90	25.67	26.9	2.93	5
4	31	120	29.8	34.6	1.8	2.8
5	40.33	120	28	31.3	2.9	4.9

The CFD approach was validated on the basis of experimental tests performed by CERTECH. For these preliminary tests, water was used as working fluid. Its inlet temperature equals 20°C. The water flowrate and the heating fluid temperature were varied.

- The experimental and simulated temperature profiles are in good agreement, especially for the lower temperature of the heating fluid.
- The pressure profiles are of the same order of magnitude, but the simulated pressure drop values are systematically lower than experimental ones. The gap increases with the liquid flowrate.

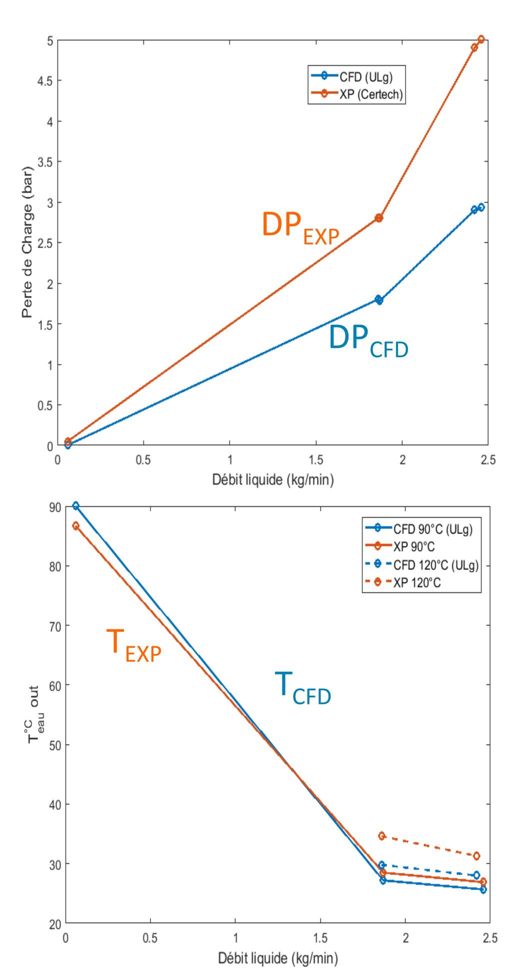

Figure 4 – Results comparison

RESULTS
II. Hydrodynamic regime

The reacting medium is much more viscous (μ=20Pa.s) than water (μ=0,001 Pa.s). If one considers a Newtonian behavior of the reacting medium, this higher viscosity implies a significant decrease of the Reynolds number for a given flowrate (3.6 kg/h). At 20 Pa.s, the Reynolds becomes very small compared to the unity and the viscous forces dominate the dynamics of the flow.

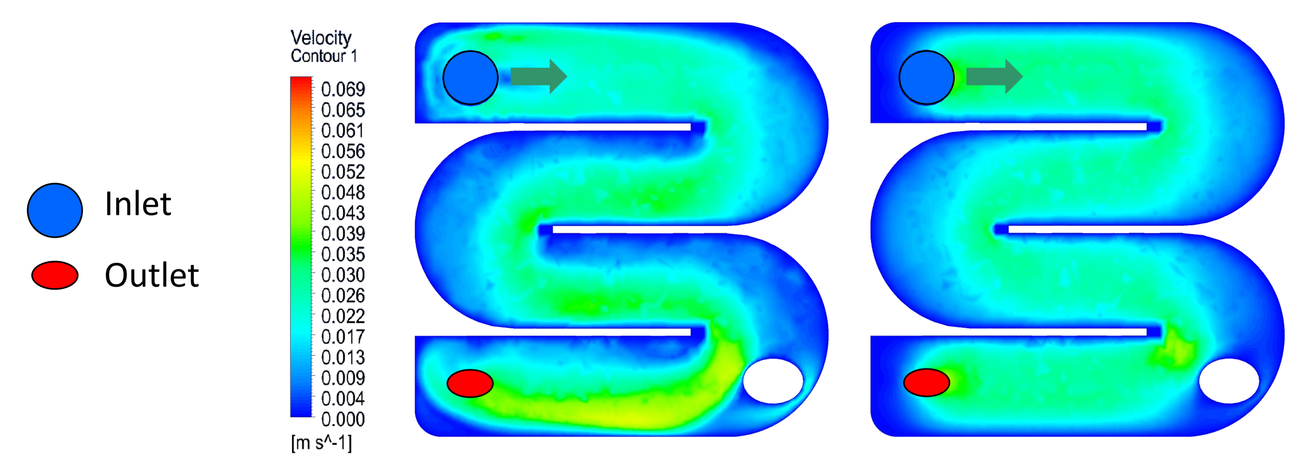

Figure 5 – Flow fields for a Newtonian fluid at 0.001Pa.s. (left) and 20Pa.s. (right)

On Fig.5, the velocity field varies less along the flow when the viscosity is increased and it is obvious that flow regime changes from laminar to stokes [8]. In this case, the non-stationary terms may be removed from Navier-Stokes equations, which becomes linear:

$$\nabla p - \nabla^2 u = 0$$
$$\nabla \cdot u = 0$$

RESULTS
III. Rheology : Non-Newtonian fluid

The reacting medium is a solid-liquid suspension with a very high solid volume fraction (40 - 55%). If added to high shear rates, it is highly probable for this suspension to have a non-Newtonian behavior [9]. In order to determine the effect of this potential non-Newtonian behavior, a power-law model [10] was applied and the resulting flows were simulated in the 3D printed reactor:

$$\mu = k \cdot \dot{\gamma}^{n-1}$$

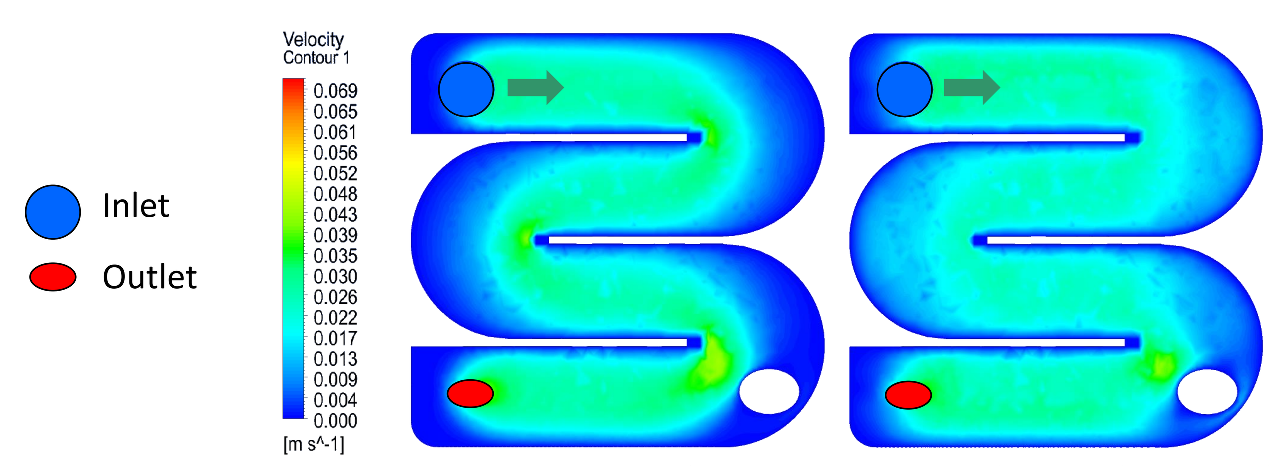

Figure 6 – The viscosity results for a pseudo-plastic and dilatant fluids respectively

Pseudoplasticity (fig.6, left) leads to important dead zones in the reactor, linked to high viscosity values and thus low velocities at low shear rates. This behavior is obviously undesirable because a big part of reactor becomes useless.
For a dilatant fluid (fig.6 right), the velocity profile is more sharped, dead zones are less important and non-zero fluid velocities are obtained throughout the domain.

CONCLUSIONS & PROSPECTS

CONCLUSION

- Numerical investigations were carried out and results were compared to experimental values.
- CFD modeling has been used to evaluate the impact of the reacting medium rheological behavior on the flow field in the reactor.
- The impact of fluid viscosity on flow regime was first evaluated. In the reaction conditions, the high viscosity of the fluid leads to Stokes flow regime.
- The potential non-Newtonian fluid behavior has a significant impact on the velocity field. A dilatant behavior has potentially positive consequence. A pseudoplastic one would lead to a flow fluid degradation and to important dead zones.
- Despite the need of more details on rheological behavior, these simulations offer a good basis for the understanding of flow behavior.

PROSPECT

- Define the actual rheological law of the reacting medium
- Establish the relation between operating conditions, particle size distribution and fluid rheological behavior. As future investigation, we plan to add more features on these simulations in order to improve and complete our model.

References

[1] K. A. Sashkinaa, N. A. Rudina, A. B. Ayupov, E. V. Parkhomchuk, Materials Today: Proceedings, Vol. 4, 11418-11424, 2017.
[2] G. Huang, P. Ji, H. Xu, J.G. Jiang, L. Chen, P. Wu, Microporous and Mesoporous Materials, Vol. 248, 30-39, 2017.
[3] K. Shanjiao, G. Yanjun, D. Tao, Z. Ying and Z. Yanying, Petrolium science Jurnal, Vol. 4, 70-75, 2007.
[4] A. Sakthivel, A. Iida, K. Komura, and Y. Sugi, Journal of Nanoscience and Nanotechnology, Vol.9, 475-483, 2009.
[5] A. Clearfield eand R. B. Borade, Journal of Microporous Materials, Vol. 5, 289-297, 1996.
[6] B. Kriedemann and V. Fester, Chemical Engineering Journal, Vol.281, 312-321, 2015.
[7] J. A. Darr, J. Zhang, N. M. Makwana, and X. Weng, Chemical Reviews, Vol. 117, 11125–11238, 2017.
[8] T. Tran-Cong and J. R. Blake, Journal of Mathematical Analysis and Applications, Vol.90, 72-84, 1982.
[9] M. Rhodes, Introduction to Particle Technology, John Wiley & Sons, Ltd, second edition, 117-152, 2008
[10] G. W. Scott. Blair, J. C. Hening, and A. Wagstaff, The Journal of Physical Chemistry, Vol. 43, 853-864, 1939.

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