THESIS PROPOSAL

General information

Title : Simulation of TiO2 nanoparticles formation by Flame Spray Pyrolysis by discret element method and its coupling with CFD simulations.

Acronym : SimTiO2

***Keywords (4)* :** FSP, nanoparticle synthesis, MCAC

Scientific theme: Optimization and control of nanoparticle synthesis through improved modeling.

Funding: French ANR project "Toscana" ANR-24-CE50-4913-02, led by EM2C, Paris.

Gross salary : 3100 €

Thesis director : Jérôme Yon (jerome.yon@insa-rouen.fr)

Thesis co-supervisor : Eléonore Riber (Cerfacs, Toulouse, France) and José Morán (University of Ottawa, Canada).

Thesis location: CORIA, Rouen, Normandy, France.

CORIA is a Joint Research Unit (UMR) attached to the Institute of Engineering and Systems (INSIS) of CNRS, the University of Rouen Normandie and the INSA of Rouen Normandie. It is located on the Madrillet technology park, near Rouen, in Normandy. CORIA's research areas cover fundamental and applied studies in photonics, turbulence, atomization and reactive flows. The recruited person will join the Optics and Lasers Department of CORIA.

A trip to Canada is planned for the molecular dynamics part of the thesis.

Candidate's experience and training

The recruited student will be required to have a Master/engineer degree (Bac+5) in engineering or physics. He/she will need to have solid coding skills in C++ and Python. He/she should also have a good understanding of the physics of reactive flows. Good knowledge of written and spoken English is mandatory, knowledge of French or the willingness to learn would be an asset.
Computer skills are essential, including post-processing development in Python.

Candidate's application

Euraxess plateform : https://euraxess.ec.europa.eu/jobs/323242
Send your application by e-mail to jerome.yon@insa-rouen.fr

Your application should include your CV, a covering letter, the subjects you have taken as part of your specialization course, and your grades and rankings. You may add a letter of recommendation if you have one.
A limited number of applications will be selected for an oral interview (by videoconference). As the CORIA laboratory is located in Restricted Zones (ZRR), an administrative investigation will be carried out on selected applications. This will be based on your CV and proof of identity. At the end of this investigation, which can take up to 2 months, the final candidate will be notified and can begin the administrative registration process.

Corresponding recruitment timetable:

- Application deadline: March 6, 2025
- Closing date for application: April 6, 2025
- Interviews with shortlisted candidates: during April 2025
- Analysis of selected applications by the defense security officer: May - June 2025
- Administrative registration for selected candidates: July 2025
- Start of thesis: September 1 or October 1, 2025
- Duration of thesis: 3 years

Abstract

The ANR Toscana project aims to study experimentally and simulate numerically the synthesis of nanoparticles (metal oxides) in flame (FSP-flame spray pyrolysis). The goal is to provide the basis for optimizing hydrogen-based FSP technology for the "green" production of nanoparticles on an industrial scale, by enabling optical control of the synthesized objects and the numerical tool to simulate such nanoparticles with complex morphology.

The challenge is to better control turbulent combustion in order to master the characteristics of the nanomaterials thus produced in terms of size and morphology, parameters which modify their final performance. The project includes both experimental and numerical simulation aspects. This thesis is part of the latter. It aims to develop further the MCAC (Monte carlo aggregation code) code to enable it to simulate sintering, a phenomenon not currently taken into account by the code. Simulations of metal oxide formation will then be carried out on the basis of CFD simulations of the pilot flame using AVBP software developed at CERFACS. Finally, the morphological and radiative properties of the particles thus generated will be evaluated using the ADDA code developed by CORIA (Maxim Yurkin). These results will be compared with the experimental part of the thesis, which will be carried out by an EM2C PhD student, who will be supported by the CORIA team.

Résumé

Le projet ANR Toscana vise à étudier expérimentalement et simuler numériquement la synthèse de nanoparticules (oxydes métalliques) en flamme (FSP-flame spray pyrolysis). Il vise à fournir les bases pour l'optimisation de la technologie FSP à base d'hydrogène pour la production « verte » de nanoparticules à l'échelle industrielle en permettant un contrôle optique des objets synthétisés et à l'outil numérique de simuler de telles nanoparticules à morphologie complexe.

L'enjeu est de mieux contrôler la combustion turbulente afin de maitriser les caractéristiques des nanomatériaux ainsi produits en termes de taille et morphologie, paramètres qui modifient leurs performances finales. Le projet développe en parallèle un volet expérimental et un volet simulation numérique. La présente thèse s'inscrit dans ce second volet. Elle vise à élargir les fonctionnalités du code MCAC (Monte carlo aggregation code) afin de permettre à ce dernier de simuler le « sintering », phénomène actuellement non pris en compte par ce code. Des simulations de formation d'oxydes métalliques seront ensuite effectuées sur la base de simulations CFD de la flamme pilote à l'aide du logiciel AVBP développé au CERFACS. Enfin, les propriétés morphologiques et radiatives des particules ainsi générées seront évaluées à l'aide du code ADDA développé par le CORIA (Maxim Yurkin). Ces résultats seront confrontés au volet expérimental de la thèse qui sera assuré par un doctorant de l'EM2C et soutenu par l'équipe du CORIA.

Detailed description of the subject

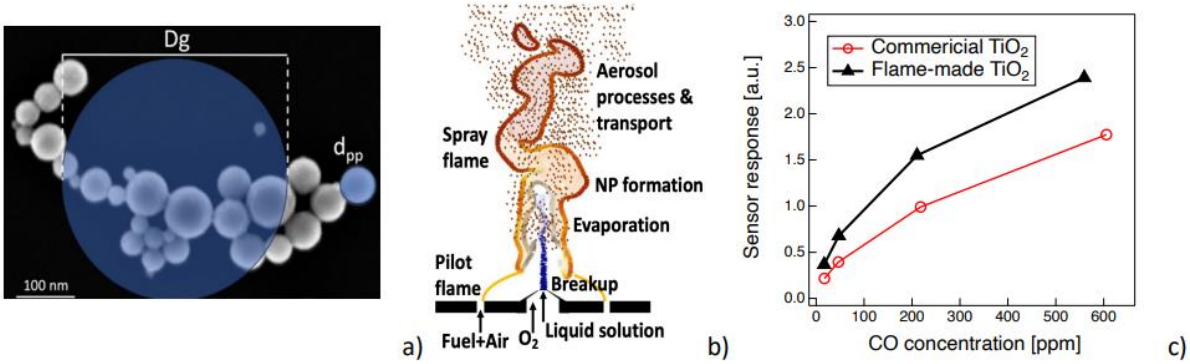

Figure 1 : . a) SEM image of flame-synthesized TiO2 aggregate of gyration diameter Dg composed of primary particles of diameter dpp . b) Schematic of a FSP system. c) Response to CO concentration for a sensor made of commercial (red) or flame-made (black) TiO2. In some applications, superior performances can be obtained when using flame-made metal-oxides

The thesis is part of the Toscana project led by EM2C (Benedetta Franzelli) in collaboration with two other laboratories (CORIA and CERFACS). It aims to study experimentally and simulate numerically the synthesis of nanoparticles (metal oxides) in flame (FSP-flame spray pyrolysis). These particles are used for biomedical, pharmaceutical wastewater treatment, catalysis, and energy storage applications among others. The project aims at providing the basis for optimizing hydrogen-based FSP technology for the "green" production of nanoparticles on an industrial scale.

The aim of the project is to better control turbulent combustion in order to master the characteristics of the nanomaterials thus produced in terms of size and morphology, parameters which modify their final performance. To achieve these objectives, in-situ diagnostics and CFD models will be developed and their results compared. The impact of operating conditions on the particle formation process will be studied by spatially and temporally characterizing nanoparticles within the flame.

The CORIA laboratory is involved in both experimental and numerical/modelling aspects of the Toscana project. The experimental one will be through the participation of Marek Mazur and Jérôme Yon in light scattering and extinction experiments at

EM2C lab to apply our optical techniques to TiO2 flame synthetized nanoparticles. The local PhD (EM2C) will participate in these experiments.

The present thesis concentrates on the numerical aspect of the project. It consists first in incorporating sintering in the code MCAC previously developed at CORIA in the framework of José Moran's thesis. Indeed, MCAC has been developed to simulate the formation of soot aggregates by discrete element methods considering nucleation, aggregation[1], [2], surface growth [3] and oxidation [4] processes by considering the change of flow regime occurring the particle growth. This original code is able to generate virtual aggregates having realistic morphologies. Its coupling with a CFD simulation of the holding flame has been demonstrated [4] proving the potential of this code since it enables to provide additional information on particle size and morphology compared to other approaches.
The current thesis aims at extending the capabilities of MCAC to simulate metal-oxides particles experiencing an additional phenomenon, namely sintering. Sintering corresponds to the thermal reorganization of an aggregate of primary particles towards a single spherical particle, a phenomenon which lies beyond MCAC's current capabilities yet which has a high potential for extending the code to new applications.

Accurate sintering models must take into account the change in kinetic energy due to the increase in binding energy associated with the sintering process [5], [6]. However, these authors have not modeled the effect of energy transfer on practical parameters for sintering modeling such as its characteristic time. In addition, a realistic model of sintering should include the initial deformation of particles upon collision which is not accounted in models found in the literature. Molecular dynamics (MD) simulations of two titania primary particles collisions will be carried out using LAMMPS [7], an open-access, fast and versatile MD code. This project will be carried out in the University of Ottawa, supervised by José Morán, and will be funded by a Mitacs globalink research award with duration between 3-6 months.

The PhD will also conduct LES simulations on the experimental laminar Flame Spray Synthesis in collaboration with CERFACS (AVBP code). These simulations will be used to provide necessary inputs for the MCAC code.
The PhD will finally characterize the radiative properties of the so virtually generated nanoparticles. For this purpose, the ADDA code developed by Maxim Yurkin [8] will be used and the exploitation of the internal electric field will follow the methodology developed during the Clément Argentin's thesis [9], [10], [11]. Maxim Yurkin, Clément Argentin and a PhD student working on this aspect will also be present and will be able to support the PhD student recruited on these aspects. Finally, the so simulated TiO2 particles with the knowledge of their radiative properties will be compared to experimental results in terms of volume fraction, size and morphology.

Thesis program (36 months)

First year : A review of the most recent literature concerned by its modeling will allow to retain the most effective strategy for an optimal implementation in MCAC. The student will implement sintering to MCAC. Also, to manage the simulation of the formation of a necking at the junction between spheres, a "necking parameter" will be added in the MCAC aggregates descriptors and will evolve during time based on mass

conservation laws to be established during this work. This will enable the generation of very realistic virtual aggregates. It should be noted that, for this part of the thesis, the PhD student recruited will be assisted by José Moran and Alexandre Poux, who developed the MCAC code. This can include a research stay in Ottawa at J. Moran's laboratory in order work on the MCAC code.

Second year : Once the sintering phenomenon added to MCAC, simulation of particle synthesis will be possible by imposing to MCAC the temporal evolution of governing parameters (temperature, nucleation and growth rates, ...) provided by AVBP. The PhD student will then work in close collaboration with CERFACS (E. Riber and PhD students of CERFACS) to simulate a limited selection of flame conditions that will be chosen by the consortium after the investigations of WP1 (experimental characterization). At this stage, the simulated Transmission Electron Microscopy images of TiO2 aggregates at different stages of their formation will be compared with experimental ones (WP1) to ensure the validity of the simulation. The statistical morphological analysis of the virtual aggregates will be done.

Third year : A systematic evaluation of the radiative properties of the virtually generated particles will be proposed. This is the only way to link simulation of the formation of aggregates with optical measurements in flames (WP1) for the interpretation of light scattering and extinction measurements. The exact radiative properties of representative clusters will be determined by solving Maxwell equations by using Discrete Dipole Approximations (ADDA). As explained above, for this part, in addition to the expertise of the thesis director, the recruited PhD student will find the necessary help and support in the group. This could enable the proposition of correction factors to be brought to RDG-FA for the simulation of TiO2 radiative properties under morphological restructuration. Such corrections will be useful to enable an efficient and accurate control of the nanoparticles synthesis by optical methods.

References

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