Chemical Engineering Journal 238 (2014) 66–77

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Flow field simulation and mixing efficiency assessment of the multi-inlet vortex mixer for molybdenum sulfide nanoparticle precipitation

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HIGHLIGHTS

- MoS_2 nano-lubricants with primary particle sizes from 60 to 135 nm were obtained.
- MoS_2 nanoparticle synthesis was performed in a multi-inlet vortex micro-mixer.
- The mixer flow field was computed at a *Re* of the mixing chamber of 832, 4160 and 8320.
- The reactants were fully macro-mixed (mixture fraction = 0.5) already at *Re* = 4160.
- The micro-scale variance of the mixture fraction was 0.03 at *Re* = 4160 and 0.008 at *Re* = 8320.

ARTICLE INFO

Article history:
Available online 25 September 2013

Keywords:
Lubricants
Molybdenum disulfide
Nanoparticle
Precipitation
Micro-mixer
CFD modeling

ABSTRACT

Molybdenum sulfide nanoparticles (NP) have been successfully obtained, for lubricant applications, by means of a wet chemical synthesis in an aqueous solution employing ammonium molybdate, citric acid and ammonium sulfide as the reactants. The production of MoS_2 NP has been performed in a multi-inlet vortex mixer, which has the ability to ensure fast mixing, induced by a confined turbulent flow inside the precipitation chamber, to suitably control the NP size distribution.

In particular, three inlet flow rates, corresponding to Reynolds numbers in the mixing chamber (hereafter named Re_c) of 832, 4160 and 8320 were employed, which resulted in NP primary particle average sizes of 135 nm, 84 nm and 60 nm, respectively.

The flow field of the multi-inlet vortex mixer was therefore investigated through computational fluid dynamic simulations, in order to assess the mixing efficiency of this device, with respect to the different operating conditions leading to these size differences in the MoS_2 product.

Both laminar and turbulent (LES and RANS k–ε) models were employed to simulate the profiles of tangential and radial velocity inside the micro-mixer. From the comparison with μPIV measurements, it was found that the laminar model was the most suitable one for the case at a Re_c equal to 832, while turbulence had to be taken into account for higher Reynolds numbers (namely 4160 and 8320).

The degree of mixing was assessed through the mean mixture fraction approach by resorting to a micro-mixing model. The degree of segregation of the reactants was assessed at the macro-scale, as well as at the micro-scale (i.e. the molecular level). It emerged that the only satisfactory condition in terms of micro-mixing was the one at a Re_c of 8320, which ensured that an effective mixing of the reactants down to the molecular scale was reached within the mixing chamber.

The operating conditions ensuring optimal mixing were assessed, and the experimental results were discussed based on these evaluations.

1. Introduction

Advanced lubricant nanomaterials are nowadays of great interest for their potential in reducing friction and enhancing protection against wear, when incorporated in full lubricant formulations in a stable way [1]: as a matter of fact, they can contribute to substantial energy savings, as well as to reduce equipment maintenance and lengthen the life of the machines.

Transition metal dichalcogenides with the generic formula MX_2 (M = W, Mo; X = S, Se) seem to be very promising materials to be dispersed as nanoparticles in the engine oil matrix [2].

Several nanoparticle synthesis techniques and morphologies have been investigated: a pioneering work in this field has been carried out by Tenne and co-workers, who first synthesized these materials through the reaction between MO_3 and H_2S in a fluidized

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http://dx.doi.org/10.1016/j.cej.2013.09.065

Nomenclature

List of symbols

C_φ	mechanical-to-scalar timescale ratio
C_μ	constant for turbulent diffusivity calculation
D	hydraulic diameter of the inlet channel
D_c	diameter of the mixing chamber
f_ξ	probability density function (PDF)
k	turbulent kinetic energy
K	number of inlet channels in the MIVM
N	number of environments
p_n	volume fraction of the environment
Re_c	Reynolds number in the mixing chamber
Re_j	Reynolds number in the inlet channel
Re_l	local turbulent Reynolds number
Sc_t	turbulent Schmidt number
$\langle u_i \rangle$	Reynolds-averaged velocity
V	mean velocity in the inlet channel
x	position vector in the computational domain

Greek letters

ε	turbulent dissipation rate
λ_M	micro-mixing rate
Γ_t	turbulent diffusivity
ξ_n	local mixture fraction
ξ_n	mixture fraction
$\langle \xi \rangle$	mean mixture fraction
$\langle \xi'^2 \rangle_{LS}$	large scale variance
$\langle \xi'^2 \rangle_{SS}$	small scale variance
v	kinematic viscosity

Subscripts

n,1,2	Environments (n: generic, 1 or 2: specific)

Abbreviations

CIJR	Confined Impinging Jets Reactor
CFD	Computational Fluid Dynamics
DLS	dynamic light scattering
LES	Large Eddy Simulation
LS	Large Scale
MIVM	multi-inlet vortex mixer
MIVR	multi-inlet vortex reactor
NP	nanoparticle
PDF	probability density function
PSD	particle size distribution
RANS	Reynolds-Averaged Navier–Stokes
SS	Small Scale
μPIV	micro-Particle Image Velocimetry

bed, in a reducing atmosphere at high temperature, to obtain the corresponding sulfide (WS_2 or MoS_2) [3]. The lubrication mechanisms of these metal sulfides, often called inorganic fullerenes due to their peculiar structure of spherical concentric layers, is currently debated; however, several studies indicate that an exfoliation process of these layers, and the consequent liberation of nanosheets directly inside the surface contact area, is the prevalent lubricating mechanism for these systems [4,5].

Other techniques can be used for the sulfidization of MO_3 into WS_2 or MoS_2, such as spray drying [6], or chemical vapor condensation [7]; however all these methods are characterized by high temperatures (800–1000 °C) in the presence of H_2 or H_2S, which involves a certain complexity of the equipment. Milder conditions can be used for liquid phase synthesis of the sulfides, either in aqueous [8] or organic solution [9].

One major requirement for the application of these nanoparticles as lubricant oil additives, in substitution to the currently adopted ones, is their constraint not to produce any related harmful emission, which could modify the nominal performances of the catalytic substrates present in the after-treatment line, through sulfur-related catalyst aging or excessive ash formation [10,11], and possibly affect their lifetime durability.

The present study focuses on the synthesis of MoS_2 nanoparticles which have to be incorporated in engine lubricant oils, and specifically on the micro-fluidic device to achieve this synthesis. A technique has been devised [12], which is based on the preparation of an aqueous solution of citric acid and ammonium molybdate to form a complex of molybdenum(IV), to which a suitable amount of ammonium sulfide was added to obtain MoS_2. It is worth mentioning that the chemistry of molybdenum and molybdenum compounds is quite complex and it is very difficult to provide exact and reliable reactions [13]. The ammonium molybdate is supposed to decompose, in an acid environment, into molybdenum trioxide and its hydrated forms, also referred to molybdic acid. The citric acid can react with both molybdic acid and molybdenum trioxide. In the first case, some various Mo-citrate complexes are formed, the composition of which is not defined and for this reason it is difficult to draw up univocal chemical reactions. In the second case, the citric acid reduces the Mo (VI) to a lower (IV) valence state, in the form of molybdenum dioxide. This compound reacts with the ammonium sulfide with the final formation of molybdenum disulfide.

This synthesis resorts to a simple and scalable process, and involves low-cost reagents, instead of other above-mentioned complex reaction methods. This synthesis route is extremely versatile since it can be adapted for continuous MoS_2 particle production, in specific devices that allow to control the particle diameter and obtain reproducible results in terms of particle size distribution [12].

MoS_2 precipitation is a fast process and thus the rate and extension of mixing is determining for the process outcome: because of their ability to achieve the high mixing efficiencies necessary in the precipitation process, passive micro-mixers are here investigated for this application. The term micro-fluidic device strictly refers to systems with characteristic length-scales that are in the range of micrometers. Small dimensions lead to behaviors strictly controlled by molecular phenomena [14], allowing rapid diffusive mixing with time-scales ranging from tens to hundreds of milliseconds. Very interesting is also the recent investigation of large micro-mixers (with characteristics length-scales ranging from hundreds of micrometers to a few millimeters) in which some flow instability is allowed to develop resulting, under particular operating conditions, in turbulent flow and turbulent mixing [15]. These devices present the main advantages of passive micro-mixers, such as more controlled process conditions, better and faster homogenization of the feed streams, short mean residence time and narrow residence time distribution, combined with other additional advantages, such as limited power consumption (when compared with traditional micro-fluidic systems) and ease of scalability for process intensification.

Examples of these kind of mixer configuration are the T-Mixer [16], the multi-inlet vortex mixer (MIVM) [17] and the Confined