isrjournals

International Journal of Advanced Research in Chemistry and Chemical Engineering

Volume: 1 Issue: 1 Feb,2016,ISSN_NO: xxxx-xxx

Use of Nanoparticle Tracking Analysis (NTA) for particle size determination of dispersed catalyst in bitumen and heavy oil fractions

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ABSTRACT-The use of Nanoparticle Tracking Analysis (NTA) for size determination of nano-catalysts dispersed in bitumen or heavy oil fractions is investigated. A method for sample preparation is proposed and comments on the technique adaptation and troubleshoot are addressed and discussed. The NTA was able to measure the particle size of a tri-metallic catalyst dispersed in bitumen obtaining a mode size of 111nm, with particles ranging from 40 to 1000nm and 80% of them between 57-176nm. NTA data was confronted with the particle size obtained by depositing the catalyst on sand and analyzing it through SEM-EDX, obtaining the same particle size range. Refinement of the sample preparation method and measuring parameters are suggested.

Keywords: Nanoparticle Tracking Analysis (NTA), particle size, dispersed catalyst, bitumen and heavy oil fraction processing

1, INTRODUCTION

The measurement of particle size is of great importance in different applications over a wide range of industrial processes. From food products to cement or emulsions and aerosols the particle size conditions substantially the product quality.

The desired particle size varies for each application, some prefer them as small as possible i.e suspensions and emulsions, and others target larger particles; on the other hand certain applications need to produce particles in a specific size range in order to obtain the desired effect, i.e. pharmaceutical.

With the increase of the world energy demand the exploitation of heavier oils and bitumen has significantly increased during the last years and with it the challenges to efficiently process these feedstocks. One of the most promising ways to tackle the challenges posed by heavy oils and bitumen is catalysis. However conventional supported catalysts are not suited to process these kind of feedstocks since they are based in porous supports that are easily plugged by the large molecules present in bitumen and heavy oils with the consequent loss of catalytic activity.

The development of dispersed catalysts, also used in pharmaceuticals, has provided an innovative pathway way for the processing of heavy oil feedstocks. In these type of catalysts the active phase is encountered in the surface of small particles that are nonporous and therefore do not have the risk of being plugged by large molecules present in the feedstock. The advantages of the dispersed catalyst involve high specific surface area and the ability to penetrate the heavy molecules network of the bitumen, among others.

The preparation (method and conditions) of the dispersed catalyst has a direct effect on the resulting particle size and therefore has to be carefully controlled. A key step to do so involves an accurate measure of the resulting particle size, which the effect of the different variables in the preparation cannot be accounted for.

There are several techniques available to measure small particle sizes, each of them with its own strength and disadvantages, they can generally be classified in two groups: single particle and ensemble measurement. The single particles techniques measure individual particle size and are usually based on high powered microscopes such as: Transmission electron microscopy (TEM), atomic force microscopy (AFM) and scanning electron microscopy (SEM) [1-3]. While the ensemble techniques are normally indirect techniques where all the particles in the sample are measured at once, the most common of these are: dynamic light scattering (DLS), laser diffraction (LD) and electrophoretic light scattering (ELS) [2, 3].
The selection of the measuring technique has to be carefully considered based on several parameters such as: the range of the particle size, available sample amount and other specific conditions referring to the nature of the particles and the media to guarantee a reliable, precise and valid measurement. [4]

When dealing with bitumen or heavy oil fractions a combination of different challenges for the particle size measurement arises due to the nature and compositions of the bitumen that serves as the continuous media. The high viscosity and strong black color pose as the most significant physical properties that can affect the measure of particles dispersed in the medium. The presence of metals in the initial feedstock as well as clay particles still embedded in the oil matrix product of the exploitation can also be an important source of error. The presence of agglomerates of large molecules such as asphaltenes that can be mistaken by particles in some analysis are another factor to keep in mind.
We have developed a preparation technique to obtain dispersed catalyst on bitumen [5] that has been successfully tested under different processing conditions to upgrade bitumen and its heavy fractions, however the determination of the particle size obtained in this preparation still has not been done.
Several authors have attempted the measure of these particles through various techniques, most of which requires intermediate steps of processing or using other hydrocarbon media. Alkhaldi (2013) used centrifugation after dilution to separate the particles and later let them dry at room temperature before taking it to TEM for particle size determination [6]. Another alternative has been to deposit the particles in a sand media [7-9] and analyze the deposited particles through TEM and SEM. When observing their results it can be noted that most of the particles are found in agglomerates of various sizes and the particle size is estimated by measuring what seem to be the constituent particles of the agglomerate, however it is impossible to tell if the agglomerates where formed during the catalyst preparation (and therefore existed as though in the bitumen media) or they are the result of the after processing steps[7-9]. Another source of incertitude regarding the measures involving single particle techniques refers to the sample size; the total number of particles obtained in the preparation is unknown, therefore the selection of the sample size (how many individual particles are measured) in order to ensure that it is representative stands as an incognita, while analyzing the full sample is not an option.
A different approach for nano-catalyst size characterization has been taken by Galarraga (2011), Thompson (2008) and Contreras (2010) where the catalyst has been prepared directly in different hydrocarbon media such as Base Oil; the Base Oil is a clear hydrocarbon that will allow the use of ensemble measuring techniques like DLS [7, 10-12]. The results presented by these authors show that the particles can be measured using this procedure with acceptable levels of the polidispersivity index (PI), around 0.18 (a good PI is considered to be under 0.1, in order to ensure a monomodal distribution) [7, 10].

Contreras (2010) tried the same approach by using Vacuum Gas Oil (VGO) as the continuous medium, however she faced problems regarding agglomeration and sample stability [11]. Another option has been to dilute the bitumen until the sample allows the pass of light. These approaches result in measures with high PI index in DLS, with several error warnings involving the quality of the measure due to the light pass and the possibility of settling of the particles which creates high levels of uncertainty in the results.
The preparations on different hydrocarbon media (Base Oil and VGO) are valid only under the assumption that the preparation will not be affected by the difference in the nature of the continuous medium; while the dilution process may cause the loss of the larger particles that will not stay in suspension, shifting therefore the particle size to lower value and conducting to misleading results.

It has been reported [2, 13, 14] that for samples including particles that are not monodispersed the results obtained via DLS are not reproducible even when samples are prepared by mixing two specific particle size. The particle size of the catalyst depends on the droplet size formed in the micro-emulsion which is controlled by the degree of mixing achieved. This may be controllable at a lab scale but even at bench-scale pilot plant it is almost impossible to guarantee a monodispersed catalyst particle size; therefore, despite the efforts done in this regard DLS doesn't look like to be able to aid in the characterization under these circumstances.
The nanoparticle tracking analysis (NTA) technique potentially combines the advantages of the single and the ensemble particle sizing approaches [2, 14-16]. The NTA starts by identifying the particles suspended in the fluid by detecting the light scattered by each one present within the viewing range when irradiated by a laser source and viewed through a charged couple device camera. Later each particle's movement is tracked while inside the viewing range, being the particle size obtained by the relationship between the distances moved over a set period of time. The hydrodynamic radius of the particle is given by the Stokes-Einstein equation (eq. 1) [2, 15].

$$\overline{(x,y)^2} = \frac{2kTt}{3r\eta} \qquad (1)$$

Where *x* and *y* are the position coordinates, T is the temperature, t time the particle is tracked (s), k the Boltzmann constant, η the viscosity of the medium and r is the hydrodynamic radius (m). Therefore NTA follows each particle individually and measures it as the single particle techniques, but does the procedure over all the particles in sight as the ensemble techniques. It must be noted that the measured particles only count if they are tracked by a minimum amount of time, anything tracked under this minimum time will not be counted in the final result [4].
The NTA technique is able to measure particles in any solvent as long as the particles scatter sufficient to be visible and sizes are as small as 9-15nm [15]. Additional data required are Temperature and viscosity of the sample and no additional pre-treatment is required except dilution to obtain an appropriate particle concentration for the NTA [15].
The NTA technology is widely used in the bio and toxicological industry with many possibilities such as: cellular vesicles [17], drug nanoparticles delivery and protein aggregates [16] and, casein micelles [18], with very satisfying results.
The NTA technique results have been compared with both single and ensemble techniques. Boyd (2011) compared the results for TEM, AFM, DLS and NTA using 100 and 200nm supplied latex particles in water, being able to compare their results and providing a good explanation of how the results comparison should be performed [2]. Montes-Burgos (2011) compared as well the performance of DSL and NTA techniques using gold nanoparticles in *relevant biological media* (plasma) for nanotoxicological purposes, again with satisfying results [14].

Based on the inherent challenges of measuring the particle size of a dispersed catalyst in bitumen or heavy oil fractions and the different approaches and techniques employed until now to try to characterize such catalyst, this work investigates the possibility of using NTA technology to measure the particle diameter of a dispersed catalyst in bitumen or heavy oil fractions. The necessary procedure to implement this technique as a fast and reliable manner to measure the particle size was developed.

2, METHODS AND MATERIALS

2.1, CATALYTIC FEED PREPARATION

The catalyst that used in this work is a trimetallic nano-catalyst containing Ni, Mo and W, prepared by the transient emulsion method [19] Athabasca bitumen (ATH) with aqueous solutions of the transition-metal salts: nickel acetate (98%, Aldrich), ammonium metatungstate (98%, Aldrich) and ammonium heptamolybdate (99%, Stream Chemicals) [5]. A detailed description of the production of the catalytic emulsions has been presented by Galarraga et al. [20]. The preparation of the catalytic feed can be done in two ways: the first one carried on in the laboratory where the aqueous solutions are added slowly to the bitumen while heating and stirring in order to assure the proper dispersion [5]. The second option employs a continuous mode of online compact preparation (manufacturing) unit (CMU) consisting on water solution pumps, bitumen pumps, additives pump to drive the synthesis, mixing zone with both static mixers and mechanical rotational mixers, followed by a decomposition zone from which the dispersed metal sulfides are obtained.

The final products obtained are: Bitumen with incorporated nano-catalyst and a mixture of diluent and water. A general scheme of the CMU is shown in Figure 4.

In this work the catalyst has a final target concentration of 1200ppmw of metals respect to the bitumen, distributed as follows: 211ppm of Ni, 604ppm of Mo and 385ppm of W.

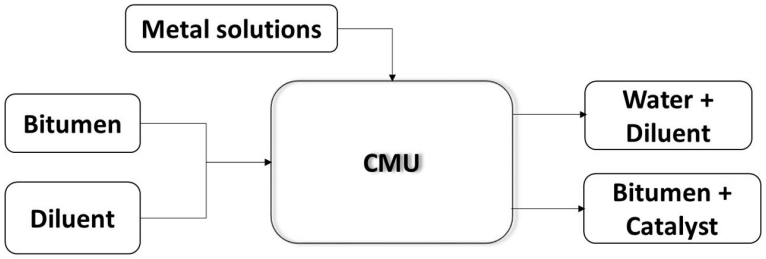

Figure 4.- Catalyst preparation flow scheme

2.2, SAND PACK CATALYST DEPOSITION

The catalyst deposition over a sand pack was performed in a reactivity test unit (RTU3) using a vertical reactor in up flow configuration (35cm long and 1in OD). The sand pack was prepared following the guidelines of Coy (2012) and Zamani (2010), using sand 70-100 US Sieve and synthetic brine at 1%wt; the obtained sand packed media results with a porosity around 35% and a permeability of 13.5 Darcys, similar and in accordance with the preparations presented by Coy (2012). The catalyst deposition consists in flowing the catalytic feedstock through the sand pack at moderate temperature that will allow enough viscosity reduction so the catalyst particles can move and attach to the sand, producing no or very little conversion on the bitumen; based on the works of Coy (2012) and Zamani (2010) the selected conditions were a temperature of 300˚C and 24h of residence time based on the Pore Volume. Deposition was carried out during 7 days, monitoring the exit product in quality and metal content. Afterwards aliquots of the sand at

different lengths along the reactor where taken and calcined in an oven under a nitrogen atmosphere at 500˚C for 12 hours to later be analyzed by SEM-EDX.

Simulated Distillation

The liquid products of each stage of the process were analyzed through Simulated Distillation to observe their composition and detect any level of change on the feedstock. The results are reported in terms of typical cuts for the oil industry according to their boiling points: Naphtha (IBP-216˚C), Distillates (217-343 ˚C), Vacuum Gas Oil (VGO) (344-550 ˚C) and Vacuum Residue or just Residue (VR) (550+ ˚C). Errors obtained in SimDist are 1% relative for lighter fractions (Naphta, Distillates and VGO) and 4% relative for VR.

Inductively Coupled Plasma-Atomic Spectroscopy

An Inductively Coupled Plasma (ICP) together with an Atomic Spectroscopy (AS) (IRIS Intrepid II Optical Emission Spectrometer-ICP Spectrometer, Thermo Electron Corporation) is use to determine the amount of metals present in the bitumen before and after the incorporation of the catalyst as well as the amount of metals remained after the processing through the sand pack. The error of the technique is 1% in the concentration of each of the metals. In order to transform the sample into an aqueous solution phosphoric acid and Nitric acid are added to an aliquot of bitumen and placed in a Microwave digester (CEM Mars 6) and finally diluted to an appropriate concentration.

Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy

The sand samples collected at different heights along the reactor, after been calcined to remove the hydrocarbon phase covering them, where taken to a Scanning Electron Microscope (FEI QUANTA FED 250) in order to analyze the surface of the sand to look at the deposited catalyst particles. The SEM is coupled with an Energy Dispersive X-ray Spectrometer (EDX or EDS, BRUKER X FLASH 5030) that allows to perform an elemental analysis over different zones (particles and background), used to guarantee that the measured particles are actually catalyst particles and no other type of particles generated during handling and processing.

Nanoparticle Tracking Analysis

A sample produced during the catalytic feed preparation was set aside and taken to the Nanoparticle Tracking Analysis (NTA) using a NanoSight NS300 equipment and a NTA 3.0 software for the data analysis in order to obtain the particle diameter suspended in the feed.

2.3, ATHABASCA BITUMEN SAMPLE PREPARATION AND MEASUREMENT WITH NTA

Based on the previous discussion the general sample preparation method proposed for bitumen with dispersed catalyst analysis through NTA is: a sample of the ATH bitumen is diluted in toluene and submitted to mechanical agitation for 10min, after verifying that there are no distinct phases, the mixture is placed during 10min in an ultrasound bath (Branson 3510, 100W-42kHz) to further increase the homogeneity of the sample. An aliquot is taken using a plastic syringe and injected into the NanoSight sample chamber making sure there are no visible bubbles in the chamber, sample is flowed through the chamber (approximately 1ml 4 times the chamber volume, 0.25ml). It is verified that there are no stuck particles in the chamber and a drift is induced. The focus and camera parameters should be adjusted to obtain the best possible view of the particles, following the guidelines provided by the equipment manufacturer [4] although they have no influence in the final calculation. Five videos of one minute length each are taken advancing the sample in between each video or leaving enough time for the drift to “replace” the sample, this allows to measure a

larger variety of particles across the aliquot. The analysis settings are later fixed depending on what is observed in the videos.

Further dilutions are prepared by taking an aliquot of the already prepared sample and adding toluene, mechanical agitation and ultrasound steps are repeated for each sample and the procedure is repeated each time. In between samples clean solvent (toluene) is flowed through the chamber (about 2 or 3ml) to ensure no sample remains and checked with the camera to make sure it is clean (no particles observed) if so the chamber should be open and cleaned.

3, RESULT AND DISCUSSION

3.1, CATALYTIC FEED PREPARATION AND SAND PACK CATALYST DEPOSITION

The product quality was tracked along each of the process steps during the catalytic preparation and deposition through SimDist. The cut distribution for each intermediate product is show in Table 1. The addition of gasoline for the CMU processing is clearly observed in the increased Naphtha fraction (Feed CMU) as well as its almost complete removal when comparting the catalytic feed and the original Bitumen.

Table 1.- Unit Performance and product distribution

	ATH BIT	Feed CMU	Catalytic Feed	MB 1	MB 2	MB 3	MB 4	MB 5	MB 6	MB 7	MB 8	MB 9
	%wt											
Naphtha	2.66	14.5	5.5	8.5	7	7.5	7.5	8	8	8	8	7.5
Distillates	15	13	13.5	14	14.5	15.5	15	15.5	15.5	15.5	15.5	15.5
VGO	35	29	32.5	34	33	33.5	34.5	34	34.5	33.5	34	34.5
Residue	47.4	43.5	48.5	43.5	45.5	43.5	43	42.5	42	43	42.5	42.5

During the catalyst deposition on the sand pack intermediate samples were taken during the process, the results show a slight increase in the lighter fractions and the quality was consistent along the experiment that serves as an indicator of correct operation of the unit.

The metal content was measured with ICP-AS in each step stage of the bitumen processing. The original Athabasca Bitumen was analyzed as well in absence of any manipulation to account for the initial metals in it, so they can be subtracted since these will not be converted into the active phase of the catalyst. The results of the catalytic Feed preparation are presented in table 2.

Table 2.- Catalytic Feed Preparation metal results

	Mo (ppm)	Ni (ppm)	W (ppm)	Total (ppm)
ATH BIT (C_0)	10.0	88.0	1.0	99.0
ATH BIT+CAT	601.4	274.5	295.5	1171.4
incorporated by CMU	591.4	186.5	294.5	1072.4
desired	604	211	385	1200.0
difference	12.6	24.5	90.5	127.6
%error	2.1	11.6	23.5	10.6

Athabasca Bitumen has approximately 100ppm of metals naturally most of it been Nickel, this amount is subtracted for the catalyst incorporation and removal analysis. In case a negative values are obtained they mean a removal of intrinsic metals form the original bitumen. The incorporated (dispersed) catalyst during the preparation was very close to the target with a 10% error. During

the sand pack decoration (catalyst deposition) it is noticed that from the very beginning almost all the catalyst is left in the sand pack since the metal content goes back to the initial metal composition of the bitumen or lower, results of it are expressed in Table 3 and Figure 1.

Table 3.- Metal Analysis (catalyst amount) for each mass balance in the catalyst deposition (C-C_0)

	Mo (ppm)	Ni (ppm)	W (ppm)	Total (ppm)
incorporated in CMU	591.4	186.5	294.5	1072.4
MB1	16.2	11.0	3.6	30.8
MB2	16.1	2.6	3.6	22.3
MB3	7.8	0.8	2.1	10.7
MB4	2.1	-1.3	1.5	2.3
MB5	0.0	1.8	4.7	6.5
MB6	-0.7	1.6	1.3	2.2
MB7	-1.5	1.0	0.8	0.2
MB8	-2.0	-0.1	0.6	-1.5
MB9	-2.5	0.9	-1.0	-2.6

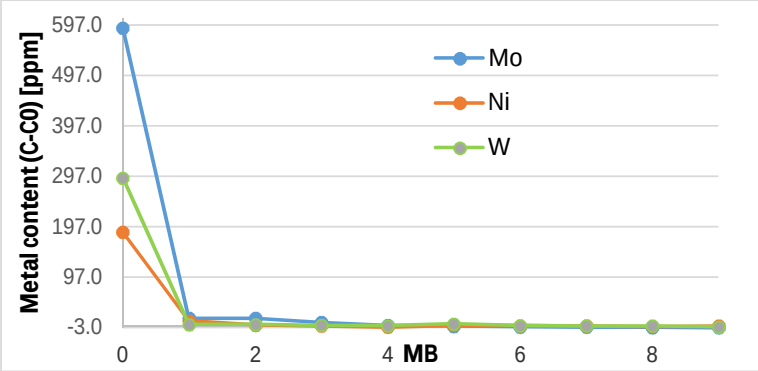

Figure 1.- Metal content evolution during decoration

3.2, SEM RESULTS

While the sand pack was removed samples of the sand were taken approximately every 5cm along the reactor starting from the bottom (since the reactor was operated in an up flow configurations) sand samples where labelled Bottom 1 through 7 and finally Top 1, with a total result of 8 samples. The approach taken for the SEM analysis was to measure as many particles in each of the samples as it could be reasonably performed during the machine time allocated (a few hours), making sure that all the measured particles were in fact catalyst, to ensure this EDX was performed in every case over the particle under focus. The presence of a W or Mo signal is definitive indicator of the presence of a catalyst particle since the natural amount of these metals in the bitumen is very small. The sole presence of Ni was not considered as a catalyst particle due to the significant presence of it in the bitumen, which could leave Ni particles deposits, however the occurrence of that seems not to take place as per our results.

As mentioned before measuring a reasonable large number of particles was intended, also searching for the different sizes possible to encounter. Also in many cases, as Figures 2f shows, particles where found to be grouped in small cluster in which case they were attempted to be

measured individually in as many different grains and various locations on each grain when possible. Figure 2 shows a series of photos taken with different zooms for the case of Bottom 1 sample.

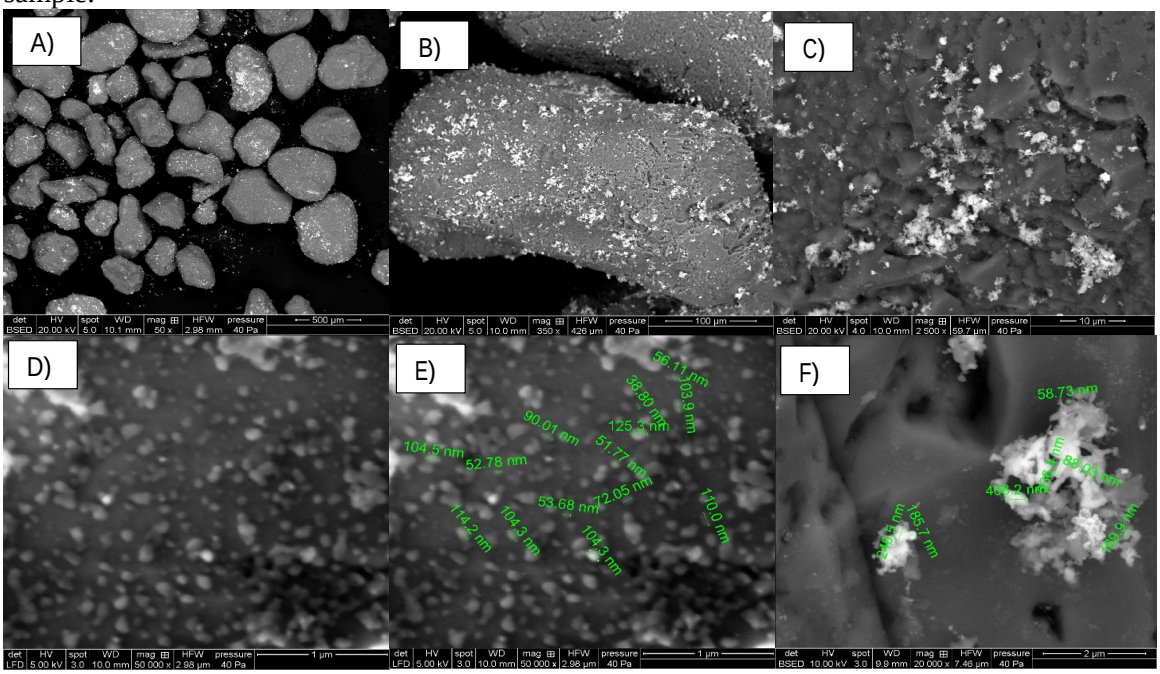

Figure 2.- Bottom 1. A) Grains view. B) Single grain. C) Zoom on a particular zone of the grain. D) Particle identification image. E) Particle identification with labeling of catalyst particle sizes. F) Cluster with individual particles labeled Bottom 5.

In general it was found that catalyst particles are spherical and look like bright spots, even though this affirmation may be used as a first approximation on to where to look at for catalyst particles it is by no mean a fixed rule, therefore the importance of the EDX analysis. Figure 3 shows the EDX analysis performed in one specific are of a grain of Bottom 2 sample. There five spots were analyzed (3 particles and 2 background sites as reference). EDX for points 1 (background) and 5 (catalyst particle) are showed where the difference in the signals is quite evident. Point 1 shows no presence of neither of the catalyst metals contrary to point 5 where Ni, Mo and W signals are significant. The EDX analysis was performed in every one of the particles measured.

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International Journal of Advanced Research in Chemistry and Chemical Engineering

Volume: 1 Issue: 1 Feb,2016,ISSN_NO: xxxx-xxx

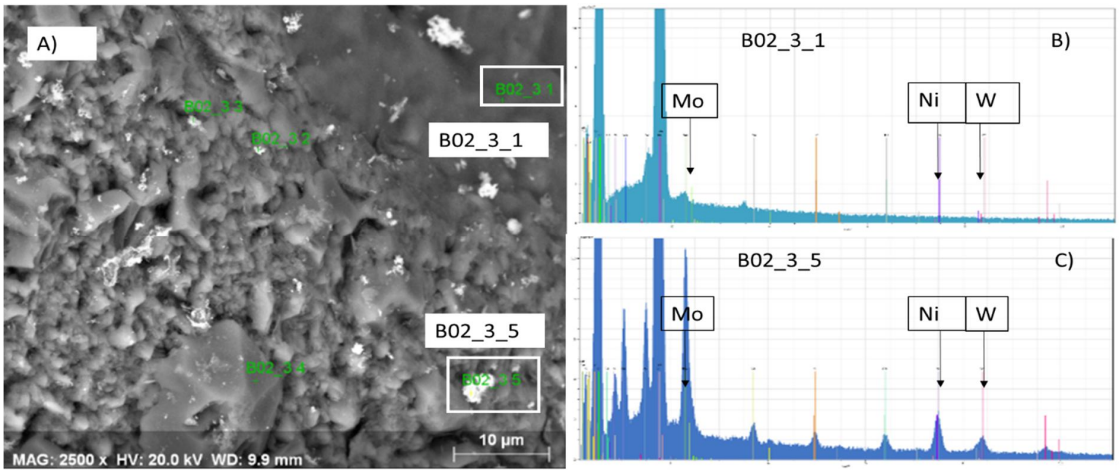


Figure 3.- EDX analysis on spot on Bottom 2. A) Spotted places of analysis. B) EDX point 1. C) EDX point 5.

As we moved along the different samples further up on the reactor the sand grains where much cleaner and catalyst particles were harder to be found, as well the presence of individual particles over the grains was much scarcer and they tended to be found in small cluster or groups. Figure 4 shows examples of this at different positions in the reactor. Among the identified particles it was noticed that the presence of smaller particles (40-80nm) are rarely found as we advanced to the top of the reactor, while particles between 100-400nm were found all along the reactor.

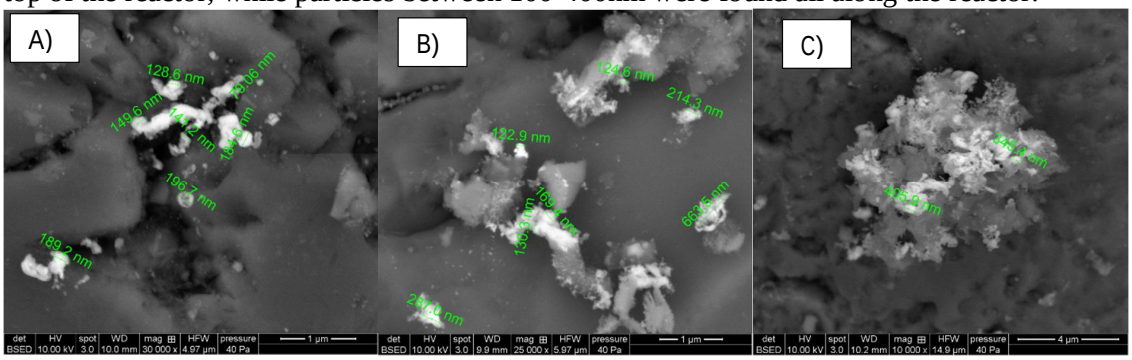


Figure 4.- Particle identification. A) Bottom 4. B) Bottom 6. C) Top 1

In total 127 particles where measured averaging a size of142nm. It also is observed that the average particle size increases along the reactor. Table 4 shows the number and size of particles measured at the different heights of the reactor with the average for each sample. The smallest particle measured was around 39nm and the largest is 1046nm.

Table 4.- Particles measured along the reactor length

	Bottom 1	Bottom 2	Bottom 3	Bottom 4	Bottom 5	Bottom 6	Bottom 7	Top 1
Distance from entrance (cm)	0	5	10	15	20	25	30	35
Particles #	41	16	19	14	12	12	11	2
Average	85	89	100	157	223	311	165	376
Total particle	127							
overall average	142							

3.3, NTA ADAPTATION TO SAMPLE CHARACTERISTICS

The use and operation of Nanosight NS300 is pretty simple and straight forward, there are few parts that should be assembled and the sampling is easy to perform, however there are several aspects and problems that were faced during the use of the equipment due to the particularities of the treated sample. This section addresses the troubleshoot of those problems. These observations are the result of many and systematic trial and error procedures in order to obtain a good measurement with the NTA technique.

The NTA technology is principally used for aqueous samples, as reported in the literature, and to the knowledge of the authors there has been no published attempts to use this technique for the analysis of hydrocarbon samples, specially bitumen or its heavy fractions. Ensuing a short discussion of addressed points:

- Viscosity: There is no specification for viscosity of the sample in the equipment, however viscosities of 60cP or higher already present challenges for properly filling the flow cell and restrict significantly the movement of the particles making tracks harder.
- Color: The NanoSight NS300 has no restriction regarding sample color but when dealing with dark samples they might be thick enough to prevent the laser from going through the sample. This has to be managed through dilution to make possible the measurement. An initial dilution of 1/20 has been found to work.
- Presence of initial particles: sample with no catalyst and the solvent has to be analyzed previously to ensure that they have no initial or very few particles that will interfere with the catalyst particle determination. In case of presence of particles the settings to view and measure they should be noted, if they are similar to the ones for the catalyst measurements there might be interference. For the case of Toluene and Bitumen the initial presence of particles is very scarce and require very sensible settings compared to the ones with catalyst.
- Dilution level: the dilution level is important not only to control the viscosity and color of the sample but it also must guarante the proper amount of particles in sight. Too many particles can cause severe interference, while few particles might not be representative both cases leading to misguiding results.
- Sample drift: the presence of a general sample drift was found to enhance the detection and tracking of the particles for the bitumen sample. This has no effect on the final result since the NTA3.0 software recognizes the non-random movement and subtracts it before fitting the particle movement to the Stokes-Einstein equation. The sample drift allows to measure more particles, however large velocities should be avoided to guarantee particles are in sight enough time.
- Length of the Video: this variable has no effect on the final measurement however larger videos allow to have more time to track the particles successfully. Videos of 1 minute were found to be most suitable for the type of samples used in this work.
- The “falling” particle phenomena: Another challenging phenomena observed was the “falling” of particles that were in sight the movement doesn’t appear to be random. The movement in the z-direction is not expected to the thickness of the sample chamber (0.5mm) and may raise the alert for settling of particles; this phenomena was observed primarily in samples with low dilutions and disappeared at higher dilutions. The presence of falling phenomena leaves to a very small particle size result since the “falling” particles do not stay in sight enough time to be tracked and measured. The falling may suggest

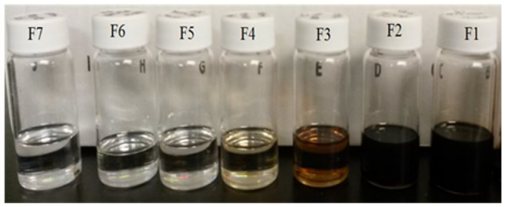
settling of large particles, when analyzing the results this aspect has to be considered to see if it has really an impact on the measurement.

3.4, NANOPARTICLE TRACKING ANALYSIS (NTA) RESULTS AND DISCUSSION

A total of 7 samples were prepared starting with the lowest dilution possible until a level at which not enough particles are in sight was reached . Table 5 presents the name, dilution level and approximate catalyst concentration (ppm, by weight) of each sample, Figure 5 gives a visual image of the samples starting from the right with F1 to F7 on the left.

Table 5.- Samples name, dilution level and catalyst concentration. Samples shown from F1 (right) to F7 (left)

Name	Dilution level	Catalyst concentration (ppm)
ATH bitumen	-	1072
F1	1/20	54
F2	1/200	5.4
F3	1/2000	0.54
F4	1/20000	0.054
F5	1/200000	5.4e-3
F6	1/2000000	5.4e-4
F7	1/20000000	5.4e-5



Based on the sample appearance F1 and F2 would not be able to be measured by DLS, while F3 may be on the limit of DLS range.

The viscosity was measured for the first 3 samples (F1-F3) obtaining a value of 0.6cP at room temperature (25˚C) very close to the toluene viscosity (0.59cP at 20˚C) and this value was used in every case. The samples were prepared and measured the same day and let standing for 5 days at room temperature and another aliquot was taken from the top of each without any agitation and analyzed again, after which a visual inspection of each flask was performed noting no sedimentation of particles in any of them. So there were 10 videos taken for each sample.

Samples F5, F6 and F7 showed throughout the whole analysis very few particles in sight, although the measurement was performed both days, so they are discarded to avoid misleading results.

F1 showed a couple of the previously discussed problems: in the first place the high concentration of particles causing overlapping and poor tracking of the particles; in second place the “falling” phenomena was abundantly present in the sample and thus they do not remain enough time in sight to be tracked and sized. Both of this problems generate misleading data since they tend to lower the particle size obtained since the particles that remain long enough to be tracked are the smallest ones. Figure 6 shows the merged results for this sample for both days.

The results show a very monodispersed sample with very small particles, but with a bigger diameter after 5 days. These results give some insight regarding the influence of the “falling” phenomena over the results, if this phenomena actually referred to a settling process the particles measured in day 5 could not be larger by any means than the ones measured in day 1. It seems that when the falling phenomena is present only the smallest particles are able to be tracked properly. The F1 sample although it is not good for the particle size characterization, due to the high concentration and presence of the falling phenomena, aids in understanding the impact in some of the unconventional phenomena happening due to the characteristic of the sample treated.

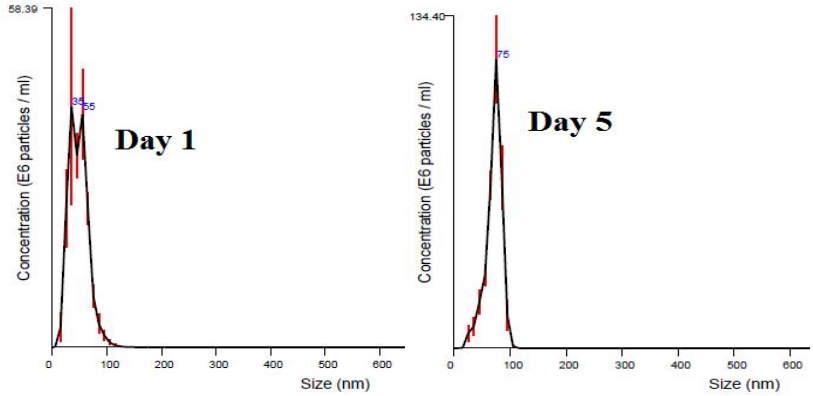


Figure 6.- results for F1 particle size measure

When analyzing sample F2 the amount of particles on sight was abundant but not overwhelming as in F1; the falling phenomena was limited to a few particles in each video, however, in general the data collection and analysis was proper with long tracks over the particles on sight. Samples F3 and F4 showed a good amount of particles in sight and tracked during all the videos with no significant appearance of falling particles. Therefore the result of the NTA will be focused on these three samples (F2, F3 and F4) and the technique will be assessed based on these results.

It is important to mention, at this point, that a set of data (5 videos) is considered good or valid by inspection and comparison of each of the individual video results, this is, that the results have to show certain level of agreement. A total agreement or overlapping of the peaks is not expected since the particles measured in each video are different on the other hand, it is not expected that the particles diameter measured in each video are radically different. A measure will be not considered if for example video 1 shows diameters of 60nm, video 2 at 300nm, video 3 at 100nm, etc. It is expected that all videos show peaks in the range of 20-70nm, 100-130nm, 200-300nm, etc., since otherwise may be an indicative of sample inhomogeneity or another problem. This behavior was observed in samples F5, F6 and F7 where due to the small amount of particles tracked each video was significantly different form the others, while samples F2, F3 and F4 show a high overlapping among individual results. Figure 7 shows and example of the previous discussion

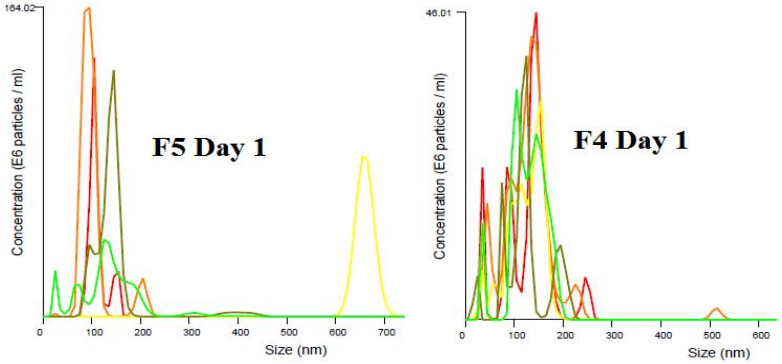


Figure 7.- agreement among videos in a sample. A) F5 day 1, results differ strongly among individual videos. B) F4 Day 1 high overlapping between each video result

Figure 8 shows the merged results for samples F2, F3, and F4 for both days and the results are summarized in table 7 for each of the cases. Results are showed in terms of mean, mode, standard deviation (SD), D10 (10% of particles under this value), D50 (50% of particles with diameters under this measure) and D90 (90% of particles below this diameter size)

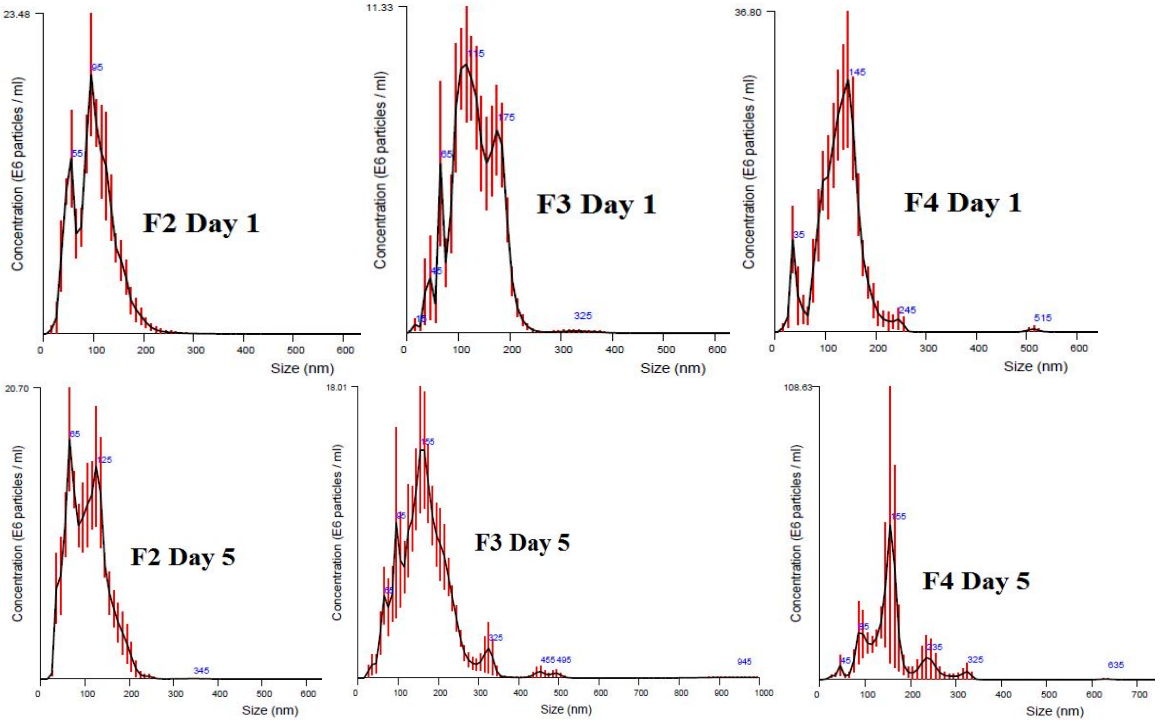


Figure 8.- Merged results for samples F2, F3 and F4 for both days

Table 7.- Result summary for samples F2, F3 and F4

	Diameter (nm)						
	F2		F3		F4		Average
	Day 1	Day 5	Day 1	Day 5	Day 1	Day 5	
Mean	95.5 ± 2.0	99.9 ± 3.7	123.8 ± 3.9	167.0 ± 5.7	122.0 ± 1.5	126.8 ± 11.9	122.5
Mode	89.5 ± 14.2	89.6 ± 13.7	97.1 ± 8.9	130.0 ± 9.9	132.1 ± 8.4	129.4 ± 10.9	111.3
SD	40.0 ± 4.5	42.2 ± 2.4	45.5 ± 2.1	85.8 ± 15.8	45.2 ± 4.6	46.6 ± 6.1	50.9
D10	36.7 ± 3.5	42.5 ± 5.0	63 ± 6.1	77.2 ± 9.8	64.1 ± 5.5	59.8 ± 10.3	57.2
D50	89.2 ± 2.6	92.9 ± 3.8	116.0 ± 3.4	150.5 ± 5.2	119.8 ± 2.8	121.8 ± 9.0	115.0
D90	145.7 ± 7.6	152.3 ± 8.9	177.2 ± 1.3	246.2 ± 15.4	165.1 ± 5.3	169.4 ± 22.2	176.0

The NTA shows particles diameter in the same range than the estimated via SEM. Modes are between 90nm and 132nm and in general the means and modes are pretty close, with the equipment detecting particles in all the expected range from the small particles (35nm) to the largest one (500, 600 and1000nm), see Table 7. We will discuss in detail on each aspect of these results.

Comparing results of the same sample during different days it is observed that all three samples show results in the same range in both days. Samples F2 and F3 show modes slightly higher for day 5 however they are still in the same size of particles found with the SEM analysis. The cause for a higher particle size could be result of some agglomeration within the sample or simply that the aliquot taken contained particles a little larger; since the values are in the same range agglomeration does not seem to have a considerable effect.

The NTA technology identified in all cases most of the particles in the range of 45 to 200nm, but also identified particles in the 300, 400, 500, 600 and even in the 900nm range (Figure 8); these larger particles are present in smaller quantities but are still present in the sample and the NanoSight could resolve and measure them, when present. An important observation is to highlight

the incorporation of the sample drift and the proper length for each video, when large particles show up they can hide the smaller ones present in the sample and then point towards a misleading direction; with the presence of drift, large particles are measured but come in and exit the camera range, and can be properly pondered in the total sample. The presence of large particles even in small amounts such as in sample F3 day 5 can drive the mean value to a higher range, so this is a good example of why the mode is a preferred measure for the particle size.

Sample modes and means are in all cases in the range of 90-130nm (except for F3 day 5, were the mean is higher due to the presence of large particles). By looking at the standard deviations (SD) it is observed that the values vary between 40-47nm showings that in general the distribution of the particle sizes in the sample are similar in all cases. Values of D10, D50 and D90 serve to identify the size range in which most of the particles are found and to weight the presence, proportion and importance of outsider particle sizes. Looking at the D10 results only 10% of the particles are smaller than 65nm in general (57nm in average), while the same proportion of particles are found to be larger than 176nm (D90 values) so based on the analyzed samples we have that in general terms 80% of the particles produced are in the range of 65-180nm, this may vary when looking at specific samples, with the highest amount of particles measured in the middle of that range [90-130nm (mode)].

By comparing the results obtained from each sample it is noticed that F3 and F4 results match up very well while F2 lays on the smaller particle side, although still within the same range. This result is in accordance with the previous discussion regarding the dilution level of the sample and the falling phenomena encountered while taking the measurements. Sample F2 had some presence of the falling particle phenomena and, this might account for the slight lower particle diameter, similar to why sample F1 showed particle diameters of 50nm. However, dilution levels in F3 and F4 show no difference among them.

The calculated error by the NTA 3.0 software can reach values of 15nm in some cases, which is relatively high, however, due to the characteristics of the sample it is not considered important and with further development of the methodology (dilution level, sample preparation, sample drift, etc.), it is expected that errors in the measurement will be reduced.

4, TECHNIQUES COMPARISON

The use of NTA technology for particle size measurement of dispersed catalyst in bitumen or heavy oil fractions as intended for the first time required the comparison with another technique in order to validate the obtained results to assure their pertinence and also validate the use of the NTA technique. The deposition of catalyst particles over a sand pack at mild conditions was selected as a manner of freezing them in order to be able to observe and analyze through SEM-EDX.

The SEM-EDX allowed to identify particles size varying from 40 to 1046nm based on a total of 127 particles measured along different heights in the reactor, with and average particle size of 142nm. The NTA data through various samples and repeated measurements identified particles from 40 to 945nm; with an average mean value of 122.5nm and 111.3nm as the mode value. Consequently, it may be affirmed that both techniques identified particle sizes in the same range, so the NTA did not leave any particle without measuring. The average value obtained by NTA is slightly lower than the one measured by SEM, however it is not possible to consider the SEM average representative of the entire population due to the intrinsic nature of the analysis, but even after this considerations the mean value is found in the same range of particle diameter.

The NTA analysis indicates that around 80% of the particles measured are between 57nm and 176nm, with 10% under 57nm and 10% above 176nm. Looking at the SEM data collected 15% (19 particles) are found to be smaller than 57nm and 19% (24 particles) above 176nm, values that are higher in both cases, but helps to confirm the NTA analysis accuracy for the determination of the sizes of particles dispersed in bitumen.

5, CONCLUSIONS

A method and procedure has been developed to use NTA technology for the particle size measurement of dispersed sub-micron size catalyst particles in bitumen and heavy oil fractions, consisting basically in dilution of the sample to adjust viscosity and color to the capacities of the equipment (NanoSight NS 300) and, to obtain a proper particle concentration.

NTA results compared to particle size measurement perform through SEM-EDX of the same catalytic dispersions “anchored” over sand show particles in the size range between 40nm to 1000nm. Average particle size are in the same range but show around a 16% difference on value.

The particle size was successfully measured by NTA obtaining an average diameter of 111nm (mode), with 80% of the particles having sizes between 57nm (D10) and 176nm (D90).

Adequate procedures were developed to cope with factors such as: sample color, viscosity and presence of initial particles. Best practices to improve the measurement are proposed regarding dilution level, length of measurement and incorporation of sample drift for submicron particles dispersed in bitumen were identified and a solutions were proposed for most of the cases. While it was found that some other issues, such as the “falling particle phenomena”, that could not be procedurally established seem not to have a significant effect on the measurement observed.

Most intermediate handling steps that cause uncertainty in the particle size determination having been successfully overcome during this detailed application of the NTA technology to the uncommon system of mineral particles suspended in a dense, viscous and dark media, this work has found the NTA to be a fast, reliable and acceptably accurate technique to measure particle size in the nanometer sub-micron scale for bitumen and heavy oil fraction as the suspending media, taking advantage of the combination of single and ensemble particle measurement of the technique.

ACKNOWLEDGMENT

The authors are grateful to the Natural Sciences and Engineering Research Council of Canada (NSERC), Nexen-CNOOC Ltd, and Alberta Innovates-Energy and Environment Solutions (AIEES) for the for the financial support provided through the NSERC/NEXEN/AIEES Industrial Research Chair in Catalysis for Bitumen Upgrading. Also, the contribution of facilities from the Canada Foundation for Innovation, the Institute for Sustainable Energy, Environment and Economy, the Schulich School of Engineering and the Faculty of Science at the University of Calgary are greatly appreciated.

The authors specially thank Dr. Chris DeBuhr of the Department of Geoscience at University of Calgary for his valuable help with the SEM-EDX data acquisition, imaging and analysis.

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