Spray Drying And Crystallisation Of Ammonium Paratungstate

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Abstract

In this paper two basic processes of dried powder formation, spray drying and crystallization are being discussed along with the various process factors and condition affecting these two processes. Many authors have written about tungsten chemistry in aqueous solutions. Para tungstate is a type of tungstate. Through a series of reactions, an ion creates the normal Tungstate. The Existing Intermediates are of low concentrations. Tungsten concentrate impurities can form heteropoly tungsten anions but do not contaminate the APT crystals. At room temperature, orthorhombic decahydrate crystals crystallize. The APT tetrahydrate was used in this case. If the staring concentrations are not too high, monoclinic APT.4H2O cuboids generated at temperatures above 50°C. To obtain powders of higher quality, properties such as number, size and pretreatment of seeds in the case of crystallization, and concentration, air pressure, and temperature in the case of spray drying must be controlled. Spray drying has the advantage of producing a dry powder quickly and controlling the particle size distribution, but it has its own set of economic issues. Crystallization, on the other hand, can be accomplished using only a single beaker and filter paper.

Introduction

Spray drying is a critical unit operation and one of the most common dried particle formation processes in industry. It can be used in a variety of products and industries to produce dry solids in granulate powder or agglomerate form. It is used in the production of powder having specific properties. It is used in the build of a wide range of industrial and consumer products, including detergents, instant appetized food and pharmaceuticals.

Crystals are solids with sharp edges and regular faces that are homogeneous in nature. A lot of them have a clear shining appearance and a distinct shape. Crystals possess a high degree of 3D order as well as a distinct, albeit not always overall and stoichiometric composition.

The reversible equilibrium phenomenon of crystallization of molecules of any compound from its solution is driven by the minimization of the system's free energy. In general, the product must meet exact quality standards for particle size, bulk and particle density, distribution of size of particles, dispersibility, content of moisture and friability among other things. Spray drying is reliant on-air distribution and proper atomization. Product characteristics such as particle and bulk density are critical. All the above conditions and medium must be met to obtain the desired product.

Spray drying is the process of converting feed from a fluid to a dried state by spraying it into a drying heated medium. Spray dryers of various types are used for a variety of causes in fields starting from laboratory sales to industrial sectors. Modern equipment for drying can achieve the requirements for producing powder with the user's customized specifications. The working principle is to remove moisture from the feed product by applying heat and regulating the medium's moisture. The feed is sprayed into atmosphere of heated nature, resulting in an improved rate of drying.

Unit operation processes involved in this Spray drying are Atomization (formation of droplets), Liquid Pre-concentration, Drying in stream of heated moisture free air, powder separation from moist air, Cooling, Product Packaging.
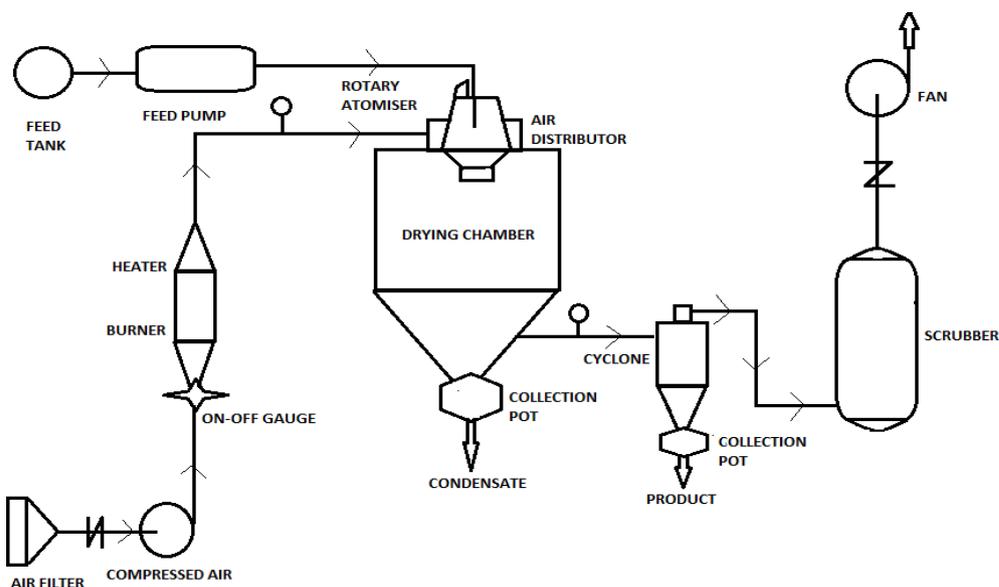

Figure-1- Flow diagram of Spray Drying

Pre-Concentration

Pre-concentration of liquid feed increases the liquid feed because each droplet contains more solids and increases particle density. As a result, powder separation is more efficient. Product dispersibility improves as the surface area is gradually reduced. The physical structure of the powder is determined by the concentration of the dried liquid. It influences both particle density and particle size.

Atomization

The atomization process is the first transformation that the feed goes through after entering the dryer. Atomization determines the size and uniformity of droplets. Atomization is critical to the process of spray drying because it affects the structure shape, size distribution of the droplets and velocity, and, and thus the nature of the final product and particle size.

Spray Air Contact

After the mass feed has been atomized to form small droplets, the droplets must come into direct contact with the hot gas. This allows for the uniform moisture evaporation from all droplets' surface. The critical requirement in this case is uniform gas flow to all parts of the drying chamber. Droplets typically collide with hot air in the spraying chamber, either flow of countercurrent or co-current. The medium of drying and product flow in the same direction through the dryer in co-current flow, whereas in countercurrent flow, drying medium and product enter at Completely opposite ends of the drying chamber.

Drying

Initially, the temperature rises to that of the wet bulb. The drop then develops a concentration gradient, and activity of water at the surface reduces, causing the temperature of the surface to jump up above the wet bulb temperature. Internal diffusion eventually becomes limiting. The surface successfully arrives at critical moisture content below which it becomes impassable.

Particle Separation

Separation occurs partially in between the chamber of drying and partially in peripheral equipment of separation. The spray drying chamber frequently has a conical bottom to make it easier to collect the dried powder. The powder, which become dry is gathered at the dryer's base during the primary separation. The evaporated moisture-laden gas stream is drawn from the cone's center up the conical bottom and sent out through the outlet of side position.
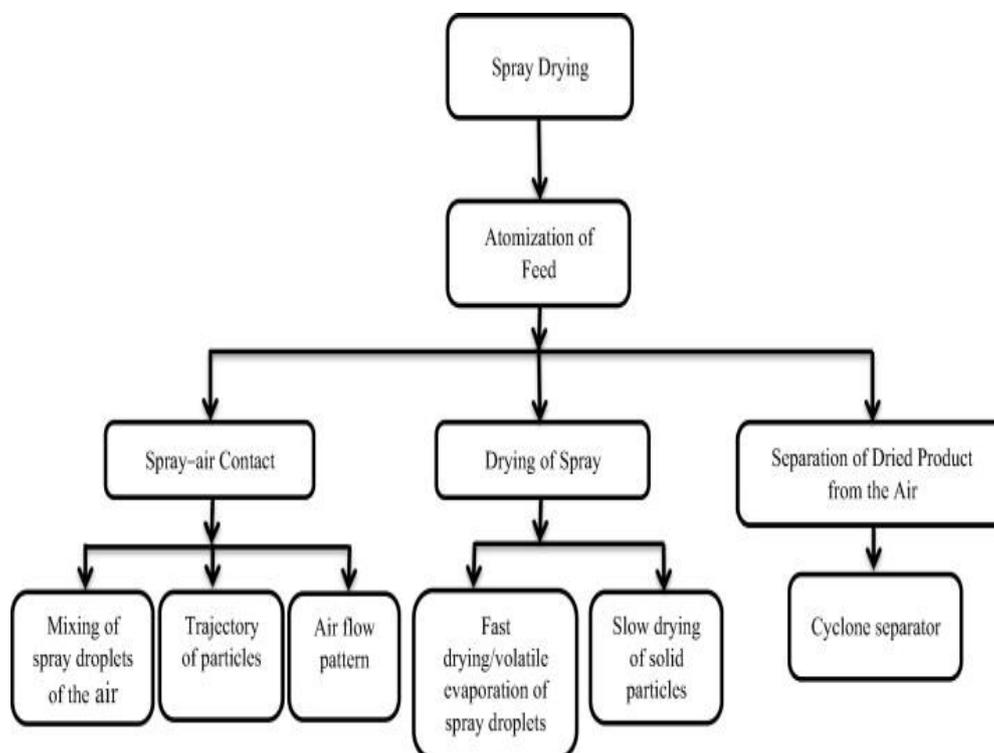

Figure 2: Overview of Spray Drying Process

The molecular crystallization of any compound which arose from its solution is a equilibrium phenomenon of reverse manner which is carried out by the minimization of the energy of free within the system. Solution where the molecules are fully miscible corresponds to an equilibrium system, in which the free energy is minimized. When a lot molecules were inserted to the solution, the system goes through internal changes until there is insufficient solvent to keep the molecules fully hydrated. No longer theexisting system will be in equilibrium under these conditions. As a result, it will be thermodynamically pushed toward a newly formed equilibrium of state with minimal free energy.

For many years, the crystal growth principles have been the attention of intense research. As a result, the practical and theoretical aspects of crystallization of molecules such as salts and compounds which are small and organic in nature are now well established.

Mechanism of Crystallization

The driving force for nucleation and crystal growth is supersaturated solution, a chemical potential for the crystallization process. It is calculated by dividing the concentration by the solubility (C/S). Supersaturation is established as any solution containing more dissolved solid (solute) than is found under saturation conditions. This supersaturated solution may be achieved by several methods:

a. Evaporating the solvent liquid
b. Metastable solid phase dissolution, such as anhydrous, amorphous, more soluble, and salt
c. Cooling the solution
d. Adding extra solvent that will partially mix with the solution and has a low solute solubility.
e. Adding precipitants or undergoing a chemical reaction that alters the solute's nature.
f. Changing the pH

Solubility Curve

The two-dimensional solubility curve provides a classical explanation of crystal nuclei formation and growth. The concentration space is divided into two areas by the solubility curve: undersaturated and supersaturated zones. Each point on this curve corresponds to a concentration where the solution and precipitating agent are in equilibrium. The solution is undersaturated in the area under the solubility curve, and crystallization will never occur. The supersaturation zone is located above the solubility curve; here, for a given concentration of precipitating agent, the protein concentration is greater than that at equilibrium.

This region can be divided into three zones based on the kinetics of reaching equilibrium and the level of supersaturation:
1. The precipitation zone is where excess protein molecules separate from the solution and form amorphous aggregates.
2. The nucleation zone is where an excess of protein molecules forms crystalline aggregates.
3. A metastable zone where unless mechanically shocked a seed crystal is introduced, a supersaturated solution may not nucleate for a long time.
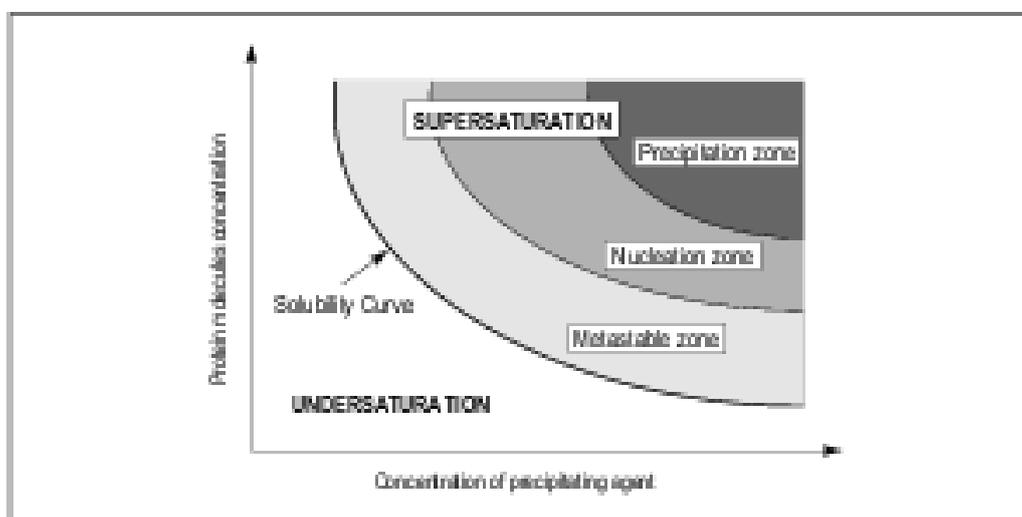

Figure-3-Supersaturation Zones

Materials and Methods

Ammonium Paratungstate is a crystalline material that is white and finely divided. Ammonium paratungstate (APT) is a byproduct of the production of tungsten metal powder from scheelite. It is used to make tungsten trioxide, tungsten blue oxide, and tungsten powders and carbides, among other things. Pure paratungstate crystals are obtained by evaporating purified ammonium tungstate solution. The quality and physical properties of ammonium paratungstate crystals are determined by time, temperature, concentration, and pH controls. These powders are then used to make a variety of products such as wire, cutting tools, billets, welding electrodes, mining tools, and so on.

Temperature Conditions

When APT is heated for extended periods of time at temperatures ranging from about 110° C. to about 205° C., the size of the average particle of the powder can be decreased by at least 20%. The finer the particle size becomes, the longer the APT is heated. At temperatures above about 205° C., however, the Para tungstate begins to decompose into Meta tungstate and tungsten oxide of yellow colored. The ideal conditions of heating are 72 hours for 177°C.

Basic Process

Differentiating tungsten from its ore yields ammonium paratungstate. For the case, the Ammonium Ptungstate used was derived from a synthetic solution rather than direct ore. The solution of ammonium paratungstate is then diluted to achieve the desired concentration. To realize the actual concentration of the solution, we take a sample and examine it using Atomic Absorption Spectroscopy. The powders can then be obtained by spray drying or crystallisation.
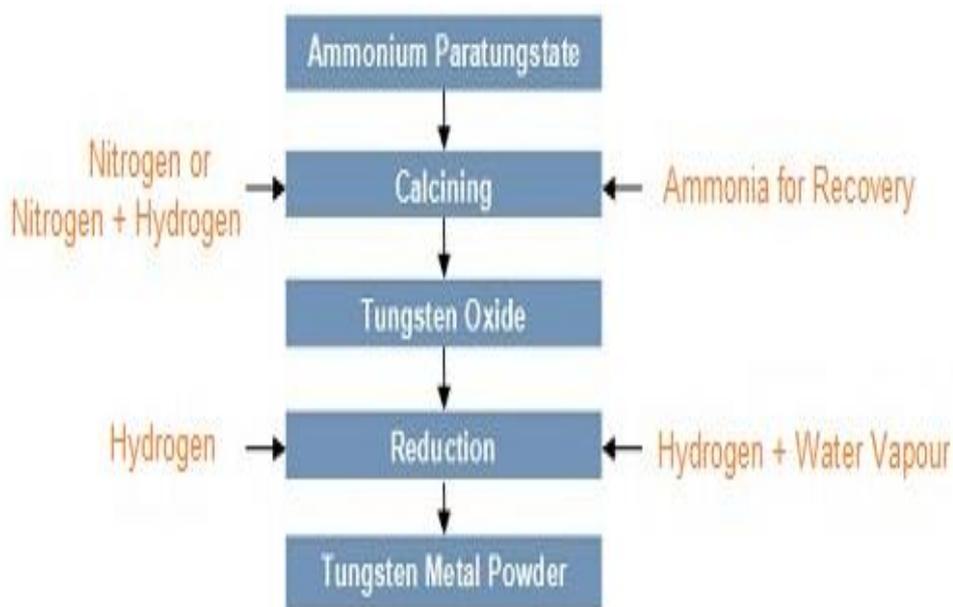

Figure-4-Production of Tungsten Metal From APT

Atomic absorption spectroscopy (AAS) is a Spectro-analytical technique for quantifying chemical elements based on the optical radiation (light) absorption by free atoms in a gaseous state. The method employs absorption spectrometry to determine the concentration of an analyte in a sample. It relies on the Beer-Lambert Law because it enquires known analyte content standards by establishing the relationship between measured absorbance and analyte concentration.

Experimental Method

Ammonium Para tungstate solutions of various concentrations were obtained by analyzing dilute solutions which were eventually filtered with an *atomic absorption spectrometer*. The concentration of "W" was measured by the help of parts per million (ppm) and finally successfully converted to grams per liter (g/l) for further calculations. The table below shows the percentages of various samples used. The first four samples were powdered using a spray drying process, and the final sample was powdered using crystallization.

Sample No.	Concentration of W (in gm/liter)
1	22.86
2	12.76
3	18.37
4	57.8
5	41.83

Table-1-Tungsten Concentration

Spray Drying Method

Various parameters throughout the experiment were obtained to get the products with varying yield and particle size. Feed flow rate or Feed pump speed, Air flow rate or Aspirator Speed, Inlet temperature, and Atomization pressure (Inlet air pressure) are the parameters. Ammonium Para tungstate solutions in various concentrations were analyzed.

- The Starting temperature is recorded constant for solutions of all concentrations i.e., at 160°C mostly.
- For each sample the feed flow rate varies with a particular concentration of solution. Here the various flow rates that were taken for the experimental purpose as 3ml/min, 5ml/min, and 7ml/min.
- The flow rate of air was maintained at $60Nm^3$/hr. throughout the procedure for every sample of different concentrations.
- The temperature of the plate is always maintained at 20°C.
- The pressure maintained during atomization operation was maintained using the pressure valve. The level must be kept such that no condensation occurs. It is a lab scale procedure with time bound operations. The volume of the sample was fixed at 100ml.

For one set reading, the parameter is first set, and then the computer's Start option is selected. The spray dryer is turned on for air until the outlet temperature reaches a steady state. After reaching a steady state outlet temperature, the feed pipe is inserted into the water beaker and the process is repeated until another steady state outlet temperature is reached. This temperature is recorded, and the set parameter is adjusted for a different set reading. The procedure is carried out again. The weight of different powders collected after spray drying of varying concentrations was observed, and Yield% was calculated. The particle size and particle size were examined.

SAMPLE-1

Experiment-1
Flow rate: 5ml/min
Atomization pressure: $0.89kg/cm^2$
No condensation observed
Weight of the sample obtained: 1.343g
Experiment-2
Flow rate: 3ml/min
Atomisation pressure: $0.91kg/cm^2$
No condensation observed
Weight of the sample obtained: 0.856g
Some amount of sample were obtained after both experiments which is treated as a mixture of the uncollected powders of sample 1. These have a varied particle size distribution.
Weight of the mixed sample obtained: 0.989g
Total weight of the sample obtained: 3.158g

SAMPLE-2

Experiment-1
Flow rate: 5ml/min
Atomisation pressure: $0.88kg/cm^2$
No condensation observed
In this case the particles were dispersed in both cylone1 and cyclone2 along with both the collection pots. The powders obtained from the cyclone1, collection pot1 and cyclone2, collection pot 2 were separately kept for particle size and particle size distribution analysis
Weight of the sample obtained from cyclone1: 0.598g
Weight of the sample obtained from cyclone2: 0.o47g
Experiment-2

Flow rate: 3ml/min
Atomisation pressure: 0.85kg/cm^2
No condensation observed
Weight of the sample obtained from cyclone1: 0.539g
Weight of the sample obtained from cyclone2: 0.0001g
Some amount of sample were obtained after both experiments which is treated as a mixture of the uncollected powders of sample 2. These have a varied particle size distribution but it can add up to the total amount of powders obtained.
Weight of the mixed sample obtained: 0.85g
Experiment-3
Flow rate: 7ml/min
Atomisation pressure: 0.80kg/cm^2
Vapours started forming and condensation observed. In order to stop condensation the temperature was increased to 180°c. Still condensation was seen. So now keeping the temperature at 180°c the flow rate was reduced to 6ml/min. The condensation stopped.
Weight of the sample obtained: 1.039g
Total weight of the sample obtained: 3.0731g

SAMPLE-3

Experiment-1
Flow rate: 5ml/min
Atomisation pressure: 1.02kg/cm^2
No particles were obtained upon drying. So the temperature was increased to 180°c
Weight of the sample obtained: 0.841g
Experiment-2
Flow rate: 3ml/min
Atomisation pressure: 0.85kg/cm^2
No condensation observed
Weight of the sample obtained: 1.496g
Experiment-3
Flow rate: 7ml/min
Atomisation pressure: 1.12kg/cm^2
No condensation observed
Weight of the sample obtained: 0.885g
Total weight of the sample obtained: 3.222g

SAMPLE-4

Experiment-1
Flow rate: 5ml/min
Atomisation pressure: 0.91kg/cm^2
Condensation observed but stopped after a while when stable conditions obtained
Weight of the sample obtained: 11.197g

SYNOPSIS
Total no of samples: 4
Total no of experiments: 9
Total volume used: 880ml
Total no of particle samples obtained: 14
Total weight of the sample obtained: 20.681g

CRYSTALISATION

The filtered solution was first checked for concentration using Atomic Absorption Spectroscopy. Since Ammonium Paratungstate will release ammonia fumes upon heating it was heated under a fume hood. A heat-pad was used for the constant heat supply and the solution is continuously stirred during the whole process.

SAMPLE 5

FIRST FILTERATION
Set Temperature of the heat pad= 200C
Initial temperature of the solution= 68C
Level of solution in the beaker=150ml
The rise in the solution temperature was checked
After 45 minutes:
Temperature of the solution = 84C
Reduced level of solution= 105ml
Clear solution changed to white milky fluid
After 35 minutes:
Temperature of the solution= 90°C
Level of solution= 55ml
Milky fluid thicked and settling down
Temperature of the heat pad reduced to 60°C
Solution temperature= 39°C
Level of liquid in beaker= 30ml
The heating and stirring were stopped and the solution was allowed to cool down
Solution was filtered into another beaker
A wet white layer was obtained on the filter paper
The paper was kept aside to dry
Weight of powders obtained= 9.536g
The filtered solution was again used for crystallisation so as to obtain more amount of powders
SECOND FILTERATION
Set temperature of the heat pad=200°C
Temperature of the solution= 54°C
Level of solution in the beaker= 100ml
White milky solution found after a while
Heat pad temperature reduced to 60°C
Temperature of the solution=73°C
Level of solution= 25ml
The heating and stirring were stopped and the solution was allowed to cool down
Solution was filtered into another beaker
A wet white layer was obtained on the filter paper (less than the!st time)
The paper was kept aside to dry
Weight of the powders obtained= 2.452g
Total weight of powders obtained= 9.101g

YIELD CALCULATION

Here we know the initial Tungsten and so weight of APT can be obtained
To calculate the yield of we require the initial concentration of APT respectively
Molecular Formula of APT: $(NH_4)_{10}(H_2W_{12}O_{42}).4H_2O$
Molecular Mass of APT: 3132.2g/mole
No of atoms of Tungsten: 12
Molecular mass of Tungsten: 183.84

$$\text{Conversion Ratio} = \frac{Mass\ of\ APT}{Mass\ of\ W \times No\ of\ atoms\ of\ W\ in\ APT} = \frac{3132.2}{183.84 \times 12} = 1.419$$

Initial APT concentration= Initial W concentration ×Conversion Ratio= 1.419 ×C

The table below gives the concentration of APT for different tungsten concentrations.

SAMPLE NO	W CONCENTATION (IN g/l)	APT CONCENTATION (IN g/l)
1	22.86	32.43
2	12.76	18.10
3	18.37	26.06
	15.86	22.505
4	57.8	82.018
5	41.83	59.356

TABLE-2-CONCENTRATION OF AMMONIUM PARATUNGSTATE

Now as we have the initial concentration, weight of the sample obtained and the volume of sample used we can calculate the Yield% of using the formula:

$$Yield\% = \frac{Weight\ of\ sample\ obtained\ per\ volume\ of\ sample\ used\ in\ l}{Initial\ concentration} \times 100$$

SPRAY DRYING

We have samples with various concentrations and each have a different yield%. Yield% is inversely proportional to the sample concentration and also for a particular sample and concentration we have obtained different weights of sample for different parameters. These parameters affect the yield in a no of ways. So it is necessary to take them into consideration while representing the yield% of the sample.

TABLE-3- YIELD CALCULATION BY SPRAY DRYING PROCESS

SAMPLE NO	CONCENTRATION OF W (IN g/l)	CONCENTRATION OF APT (IN g/l)	INLET TEMP (IN C)	ATOMISATION PRESSURE (IN kg/cm²)	VOLUME (IN ml)	FEED FLOW RATE (IN ml/min)	WEIGHT OF APT OBTAIN (IN g)	APT YIELD (IN %)
1	22.86	32.43	160	0.89	100	5	1.343	41.41
			160		100	3	0.856	26.39
			160			MIX	0.989	
2	12.76	18.10	160		100	5	CY1-0.598 CY2-0.047	35.63
			160		100	3	CY-1-0.539 CY-2-nearly 0 MIX-0.85	76.79
			160		105	7	VAPOURS FORMED	
			180			7	CONDESE	
			180			6	1.039	54.66
3	18.37	26.06	160	1.02	100	5	NO PARTICLE	
			180			5	0.841	32.27
			160	0.85	100	3	1.496	57.41
	15.86	22.505	160	1.12	75	7	0.885	52.43
4	57.8	82.018	160		100	5	11.197	136.51

Crystallisation

We have a single sample with known concentation. Powders were obtaion from both the filterations and weighed separately. The tables given below represents the yield% of the samples at different concentrations and parameters for Ammonium Paratungstate using Spray Drying Method and Crystallisation. It gives a view of the parameters are affecting the Yield%.

TABLE-4- YIELD CALCULATION USING CRYSTALLISATION METHOD

Filtration no	Concentration of W	Concentration of APT	Volume in ml	Weight of APT obtained in g	Yield %	Average Yield%
1	41.83	59.35	150	9.536	107.11	74.21
2	41.83	59.35	100	2.452	41.31	

Results and Discussion

From the experiment it has been observed that the spray concentration influences the particle size. The higher the concentration of the spray solution, the larger and more porous of the dried particles. The lower the concentration of the spray solution, the smaller and finer the dried particle.

The %Yield increases with increase in concentration and molecular weight whereas it decreases with the increase in inlet temperature, aspirator speed, pump flow rate and atomization rate.

Here we have used ammonium paratungstate tetrahyd rate. Crystallization of APT has shown that the tetrahydrate is always the stable phase under industrial crystallization condition. This means it will crystallize in the presence of tetrahydrate seeds. The supersaturation decreases at first during crystallizaion but increases later on due to solvent evaporation. This gives rise to generation of small crystals towards the end of crystallization. The pretreatment is important as damaged seeds tend to form aggregates. It is also seen that initial concentration also affects the particle size distribution in the sense that increasing high initial concentration result in decreasingly small medium sizes in narrowing of width of the population. Furthermore less agrigation occurs at higher concentration.

We have observed under microscope that the crystals obtained from the solution with higher concentration of WO has three shapes agglomerates of small cubic particles. This is because in high over saturation $(NH_4)_2WO$, aqueous, the supply of APT solute for APT crystalline grains growing is uneven.

Conclusions

Ammonium paratungstate is a metallised salt which is frequently employed in the manufacture of tungsten powder for use in the production of, for example, tungsten carbide tips for tools and tungsten filament lamps. It has been found that in the production of such items, it is desirable that the particle or crystal size of the ammonium paratungstate should be as small as possible.

The conditions under which ammonium paratungstate crystallises from solution are extremely critical and the conventional procedures for obtaining ammonium paratungstate of small particle size are expensive and time-consuming. Ammonium paratungstate of small particle size might be produced by spraying a solution into a container of liquid nitrogen so as to flash freeze the ammonium paratungstate, the solvent thereafter being removed by evaporation. Such a freeze drying technique would be expensive because it employs liquid nitrogen, and unless it was carefully controlled would not necessarily result in the formation of very small crystals of ammonium paratungstate.

Hence the process of spray drying of APT is much more useful as it is both cost economic as compared to freeze drying and conditions needed for crystallisation and time saving. Moreover the powders obtained by spray drying are less likely or free of contamination. We can also control and obtain the desired particle size if we thoroughly understand the parameters and operating conditions affecting the process.

References

1. J.W. van Put, G.J. Witkamp, G.M. van Rosmalen, and Formation of ammonium paratungstate tetra- and hexa-hydrate. I: stability, Hydrometallurgy, Volume 34, Issue 2, 1993, Pages 187-201.
2. M.J.G. Fait, H.-J. Lunk, M. Feist, M. Schneider, J.N. Dann, T.A. Frisk, Thermal decomposition of ammonium paratungstate tetrahydrate under non-reducing conditions: Characterization by thermal analysis, X-ray diffraction and spectroscopic methods, Thermochimica Acta, Volume 469, Issues 1–2, 2008, Pages 12-22.

3. J.W. van Put, T.W. Zegers, H. Liu, Hydrogen reduction of ammonium paratungstate into tungsten blue oxide—Part II: Experimental, International Journal of Refractory Metals and Hard Materials, Volume 10, Issue 3, 1991, Pages 123-131.

4. Hayat Khan, Marco G. Rigamonti, Gregory S. Patience, Daria C. Boffito, Spray dried TiO_2/WO_3 heterostructure for photocatalytic applications with residual activity in the dark, Applied Catalysis B: Environmental, Volume 226, 2018, Pages 311-323.

5. S. Endres, P. Kampe, J. Kunert, A. Drochner, H. Vogel, The influence of tungsten on structure and activity of Mo–V–W-mixed oxide catalysts for acrolein oxidation, Applied Catalysis A: General, Volume 325, Issue 2, 2007.

6. Ulla Kanerva, Juha Lagerbom, Marjaana Karhu, Anna Kronlöf, Tarja Laitinen, Erja Turunen, Synthesis of nano-WC from water soluble raw materials: Effects of tungsten source and synthesis atmosphere on chemical and phase structure evolution, International Journal of Refractory Metals and Hard Materials, Volume 50, 2015, Pages 65-71.

7. Hayat Khan, Marco G. Rigamonti, Gregory S. Patience, Daria C. Boffito, Spray dried TiO_2/WO_3 heterostructure for photocatalytic applications with residual activity in the dark, Applied Catalysis B: Environmental, Volume 226, 2018, Pages 311-323.

8. B.H. Kear, L.E. McCandlish, Chemical processing and properties of nanostructured WC-Co materials, Nanostructured Materials, Volume 3, Issues 1–6, 1993, Pages 19-30.

9. Joel B. Christian, M. Stanley Whittingham, Structural study of ammonium metatungstate, Journal of Solid State Chemistry, Volume 181, Issue 8, 2008, Pages 1782-1791.

10. Martin J.G. Fait, Elena Moukhina, Michael Feist, Hans-Joachim Lunk, Thermal decomposition of ammonium paratungstate tetrahydrate: New insights by a combined thermal and kinetic analysis, Thermochimica Acta, Volume 637, 2016, Pages 38-50.