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An Experimental Approach to Compare the Percentage Yield of Oxalic Acid Dihydrate ($C_2H_2O_4.\ 2H_2O$) at Two Different Cooling Temperatures by Using L9 Orthogonal Array

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Abstract: Crystallization is one of the main unit operations performed in the many chemical industries. Crystallization process is driven by the nucleation and growth kinetics, which are based on the solute solubility and supersaturation. Effective optimization techniques are used to study the influence of the independent variables and their interactions on the dependent variables. Taguchi method, which is considered to be one of the effective optimization methods was selected for the process optimization. L9 orthogonal array was selected for the robust design of the experiments based on the selected factors with different levels in order to assess the impact on the yield of the oxalic acid dihydrate ($C_2H_2O_4.2H_2O$) in distilled water (H_2O). Based on the nine experiments performed as per the L9 orthogonal array revealed that the seeding temperature at various stirring speeds had a greater influence on the yield of the oxalic acid dihydrate ($C_2H_2O_4.2H_2O$) crystals. The solvent chosen with the solute for the experimental work was distilled water (H_2O) to understand the crystallization dynamics through the cooling crystallization method. The selected four significant factors were the agitator speed, seed ratio, seeding temperature and the linear cooling temperature. This article provides a profound understanding on the percentage yield comparison at two different end temperatures of $29^{O}C$ and $25^{O}C$ respectively and the factor, which is responsible to impact such a change. The solubility of oxalic acid dihydrate ($C_2H_2O_4.2H_2O$) at $60^{O}C$ was considered for the two sets of the experiments.

Key Words: Taguchi Method, Orthogonal Array, Crystallization and Optimization.

I. INTRODUCTION

1.1 Taguchi Method for Optimization

1.1.1 Optimization

Optimization is defined as a process of achieving the best possible results under the specified conditions. Optimization in the other terms can be describes as achieving maximum benefit with minimum cost. The objective of optimization can be expressed in terms of the design variables, which has a major role in providing the maximum or the minimum value of a function. These design variables are the controllable factors when properly determined and combined optimally give the best value of the desired response. However, the impact of the uncontrollable factors or the noise factors will certainly be there on the process or the system and minimizing the effect of such factors is also a necessary approach for the process optimization. The types of the optimization techniques include the cost optimization, process optimization, resource optimization, product optimization etc. All such optimization methods are a part of an operational research, which is considered to be a branch of mathematics. The methods of the operation research are categorized into mathematical programming techniques, stochastic process techniques and statistical methods. This article focuses on the design of experiments, which is related to one of the statistical methods. The design of experiments is a structural process having one or more independent factors that influences the output or the response of the process where in the response factor is considered to be the dependent variable. The design of experiments is beneficial to solve the complexity of a process that involves more than one variable and it is economically viable, helps to analyse the data in an effective manner and finally relates the conclusions from the analysis and the original objectives of the study. The focus on the optimization is followed in the various sectors, which include engineering, manufacturing, agriculture sciences, sociology, medicine, biology etc to reduce unnecessary costs and gain efficient function of the overall system by achieving the desired objective with proper design of experiments.

1.2 Taguchi Optimization Method

Dr. Genichi Taguchi a renowned Japanese electrical engineer and scientist who invented the Taguchi method, which is an optimization technique and a mathematical model based on the application of different types of orthogonal arrays for designing experiments to achieve the desired response. Orthogonal arrays are the set of experiments designed as per the matrix structure. According to Taguchi, quality is measured as the total loss to the society caused by a product and his method is based on the concept of design of experiments and is considered to be a strategic experimental strategy. This strategy is based on the interaction effect of the variables, supporting limited number of experiments to achieve the set objective of response, identifies the important factors for the experimentation and provides better yield for the expected results. The strategy provides completeness, efficiency and insight of the experiments to be conducted. It is specifically meant to optimize the experiments and achieve the quality in terms of the performance consistency, which is the primary characteristic of any process. However, consistency is attained with minimum variation in the performance closer to the objective. [1] The two step optimization steps proposed by Taguchi to improve the quality are as under:

- Find the factor-level combination that reduces performance variability.
- Adjust the factor levels that bring performance closer to the target. [1]

The experimental design is categorized in three different types that include full factorial design, fractional factorial design and orthogonal arrays. In full factorial design, the experiments are conducted by considering all the possible combinations of all the levels for each of the factors whereas the fractional factorial design encompasses a part of the total combinations. The experimental design based on the orthogonal arrays is a fractional factorial design with the matrices of orthogonal structure. Taguchi method is based on the selection of a correct orthogonal array to design the experiments in the research, which starts with the research question after acquiring prior knowledge of the subject considered for the research. Thereafter, the experimental research follows from which the data is obtained. The data, which is collected from such type of applied research, is analysed and interpreted based on the comprehensive knowledge gathered through the literature survey. Finally, new knowledge originates and it is always connected to the prior knowledge. *Figure 1* provides an easy understanding of the experimental design procedure through a flowchart.

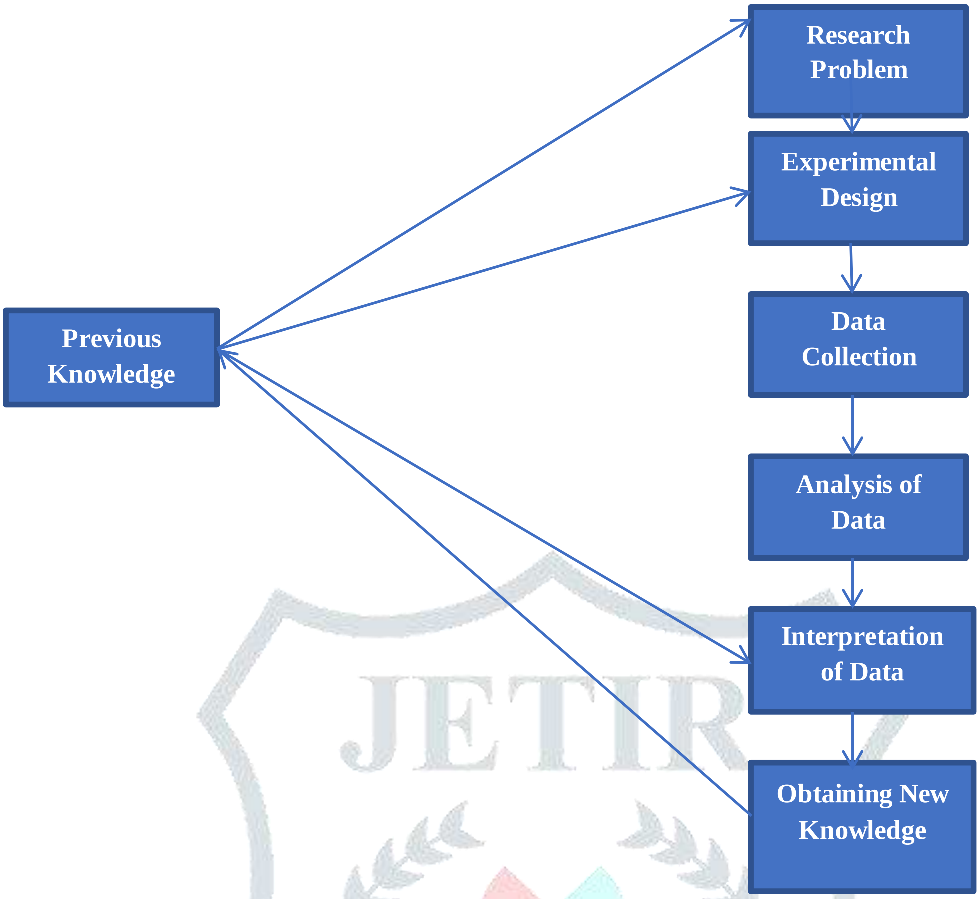

Figure 1. Flow Chart of the Design of Experiments

The Taguchi method is based on the fractional factorial design of the experiments described by the orthogonal arrays. These orthogonal arrays are the special set of tables used to denote the smallest fractional factorials for the experimental work allowing for a maximum number of main effects to be assessed from a minimum number of runs in the experiment while allowing for differences in the number if factor levels. Usually, in the conventional method, full factorials are used to conduct the experiments but the challenge is that the method is time consuming and is not cost effective because of the need to conduct multiple experiments. Another disadvantage of the conventional method approach would be variation in the output for the same experiment conducted with two different designs. Moreover, it may be difficult to interpret the experimental data obtained due to the involvement of larger number of factors in the experiment and because of lack of clear design and analysis strategies. [2] Most crystallization experiments usually involve important factors. Taguchi method reduces the number of experiments and the aim of this method is to reduce the variance in the targeted value and achieve quality [2]. If the levels and factors considered for the investigation are high then full factorial method can become a laborious task. However, if the fractional factorial approach is followed to minimize a large number of the experiments then only a fraction of the probable combinations of the levels and factors are possible to study. Therefore, Dr. Genichi Taguchi has found an effective solution by simplifying and standardizing the fractional factorial designs in such a manner that the results obtained as a result of selection of similar design by two or more engineers being far away from each other will be consistent. Taguchi technique follows the approach of robust design strategy, which means that the processes and the products are not affected to the influence of the noise or the uncontrollable factors. The improvements observed in the process or the product are quantified in the monetary units by the loss function, which is a mathematical model suggested by Taguchi. The loss function expresses the improvement in the results predicted from the design of experiments in terms of cost savings. The analysis of the results based on the design of experiments becomes much easier by using signal to noise ratio analysis instead of depending on the results alone for the multiple samples runs. The logarithmic conversion of the results in the terms of S/N ratios allows the prediction of the performance improvement from the analysis. Taguchi techniques created a significant change in the quality engineering methods and several industrial organizations applied these techniques and changed their approach towards the quality improvement activities. Therefore, based on the systematic approach for the problem solving, Taguchi method is considered to be a powerful tool to resolve difficult problems and mitigate the product failures thus improving the process performance, yield, productivity, reducing the scrap costs, re-work costs and production costs and eventually achieving the quality of the end product [3]. The Taguchi methods have originated after the Second World War, when the allied forced realized that the telecommunication systems were not efficient and cannot be continued for a long term communication purpose. Dr. Genichi Taguchi has understood about such need for an invention that improves the R&D productivity and increases the product quality. Therefore, he introduced Taguchi methods, which are considered to be the best optimization techniques used to improve the process efficiency by reducing the time and expenditure on the resources. Previously, a lot of time was utilized on the engineering experimentation and testing without focussing much on the process improvements to mitigate the unnecessary expenditure on the resources. Therefore, in order to address the need to reduce the cost and improve the productivity, Taguchi philosophy was originated on the three simple and fundamental concepts, which are below.

- Quality should be designed into the product and not inspected into it.
- Quality is best achieved by minimizing the deviation from a target. The product should be so designed that it is immune to uncontrollable environmental factors.
- The cost of quality should be measured as a function of deviation from the standard, and the losses should be measured system-wide [1].

Quality improvement starts at the beginning of the entire process especially at the design stage of the process and thereafter continues to the production stage and gives a final output in the form of the product carrying the quality as per the desired specifications. Taguchi method is based on the robust product design, which is insensitive to the uncontrolled environmental factors that interfere in the manufacturing process. It is a cost effective solution that can earn much return on the investment. Taguchi method aims at developing the manufacturing process by setting a target value. The minimum deviation observed towards the target value can be considered to be viewed as an ample improvement to attain the desired objective. The measurement of the deviations of the design parameter in terms of the overall lifecycle costs, which include cost of scrap, rework, inspection, returns, warranty service calls, and/or product replacement, is considered to be an important concept of Taguchi optimization techniques. The above costs give the direction to control the major design parameters. Taguchi method for optimization is an on-going effort to be striving for the ideal value of the target by reducing the variation towards the targeted value. Taguchi followed an approach for the quality improvement of the process with the help of orthogonal arrays, which were used for the design of experiments. Orthogonal arrays are the specifically built tables that are used to design the experiments in an easier and effective manner. Along with the controllable factors, uncontrollable factors are also involved in influencing the output of the system. These uncontrollable factors are considered as the noise factors, which cannot be controlled economically and can affect the response variable. Noise factors have a direct influence on the process output and are the major for the variation in response value. The effective optimization technique designed by Taguchi can examine the influence of the noise factors and reduces the repetition of the experiments, eventually abating the cost involved in the resources to perform repeated experiments. As a result, the design of the experiments is considered to be robust in its state with a higher value of S/N ratio with minimal noise. The desired product quality design can be achieved by three stage process as recommended by Taguchi. These stages encompass system design, parameter design and tolerance design.

1.3 General Process and the common terms used in the Taguchi method and Design of Experiments

It is usual practice in every field to have the common terms, which are assigned to a particular system. Likewise, in the Taguchi method there are exclusive terms that are used to understand the method. The common terms, which are identified with the different nomenclature are illustrated in the *table 1* below**.**

Table 1. Expressions used in Taguchi method and Design of Experiments

Terminology	Terminology
Input	Models {ANOVA – Analysis of Variance}
Process – Application of work (Production or Manufacturing)	Covariates {An uncontrolled quantitative variable that can be measured during the experiment, temperature}
Output (Responses Variables)	
Factors (Control Factors and Uncontrolled Factors) {Quantifiable & Non-Quantifiable}	Models {ANOVA – Analysis of Variance}
S/N Ratio is Signal to Noise Ratio	Experiments Randomization
Levels specified in the rows of an orthogonal array	Experiments Replication
Interactions of the variables during a process	Experiments Repetition
Experiments (Different number in different orthogonal array)	Blocking in a orthogonal array
Design of the Experiments	Confounding (Interactions of the tables in Orthogonal Arrays)

1.4 Definitions of the Terms used in Taghuchi Optimization Method.

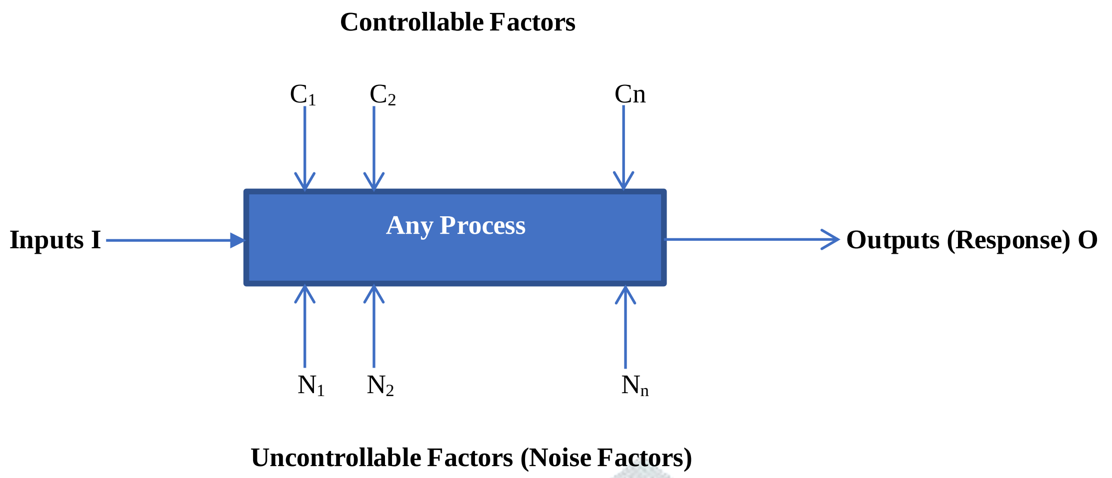

Figure 2. Flowchart of the Process or a System

Figure 2 clearly states about the various types of factors with which any process has to deal in order to achieve the desired output.
Controllable factors — Factors whose levels can be specified and controlled during the experiment and in the final design of the product or process [1].
Noise factors—These are the factors that are uncontrollable and have influence on the product or process results. Usually these factors are not maintained at specific levels during the production process or application period.
Inner array— It is an orthogonal array that has the controllable factors. All experiment designs with the controllable factors are considered for the inner array.
Outer array— The orthogonal array having an outer array is meant for the noise factors, which are the uncontrollable factors.
Experiments—These are different trials conducted with the combination of the factors and levels.
Conditions of an experiment – The inner array (orthogonal array) defines the unique combinations of the factors and the levels.
Repetitions or runs – The number of readings taken form an experiment having the similar conditions of the initial experiment [1].
Treatment – An experiment performed with the set of levels of all the factors.
Levels of Factors – The values of the factors that are studied in an experiment.
Experimental Unit – Facility like the setup, apparatus, person, test piece, material etc.
Response – The output or the result of an experiment. It is a dependent variable.
Effect – It is a change in the response or the output due to the change in level of a factor.
Experimental Error – It is a value, which is not obtained as per the expectation from an experiment. It is the residual value, which is found as a result of the influence of the uncontrollable or the noise factors.
Full Factorial Design – The total number of experiments conducted with all the possible combinations of all the levels of each factor.
Fractional Factorial Design - The experiments performed with a part of the total combinations of the levels of each factor.
Orthogonal Array - If the experiments are conducted in the fraction factorial design manner with an inclusion of orthogonally in them then the matrices thus obtained are considered as the orthogonal arrays.
Degree of Freedom - It is a measure of the amount of information that can be uniquely determined from a given set of data. As with factors, the DOF of a column is its number of levels minus one. Finally, the DOF of an array is the sum of its column DOF [1].
Sum of Squares - The deviation of the experimental data from the mean value of the data is measured from the sum of squares. Summing each squared deviation emphasizes the total deviation. [1]
Variance – The distribution of the data about the mean of the data is measured by the variance [1]. Variance is given by the formula sum of the squares divided by the degrees of freedom.
Taguchi Loss Function - Taguchi defined the loss function as deviation as a quantity proportional to the deviation from the target quality characteristic. At zero deviation, the performance is on target and the loss is zero. If Y represents the deviation from the target value, then the loss function L(Y) is: $L(Y) = k (Y- Y_O)^2$ where
Y = quality characteristics, such as dimension, performance, and so on.
Y_0 = target value for the quality characteristic
k = a constant, dependent on the cost structure of a manufacturing process or an organization [1]

1.5 Different Stages involved in Taguchi Experimental Design

Taguchi experimental design is considered to be a robust design of the experiments, which optimize to obtain the desired results. The method involves different stages, which are designed in a systematic manner to easily and swiftly meet the objectives of any project as shown in the *figure 3*. These stages begin with the confirming of the predicted results and followed by analysing the results. After analysing the results profoundly, the experiments are conducted to understand the knowledge of the influencing control factors on the system's performance. Thereafter, the control factors are selected that have an impact on the attributes of the response variables as desired. Such a selection of the control factors with different levels as per the suitable orthogonal array will define the design of the experiments, which appears as a fifth stage in the Taguchi's experimental design. Eventually, the planning of the experiments is done with a proper apparatus in order to achieve the desired results.

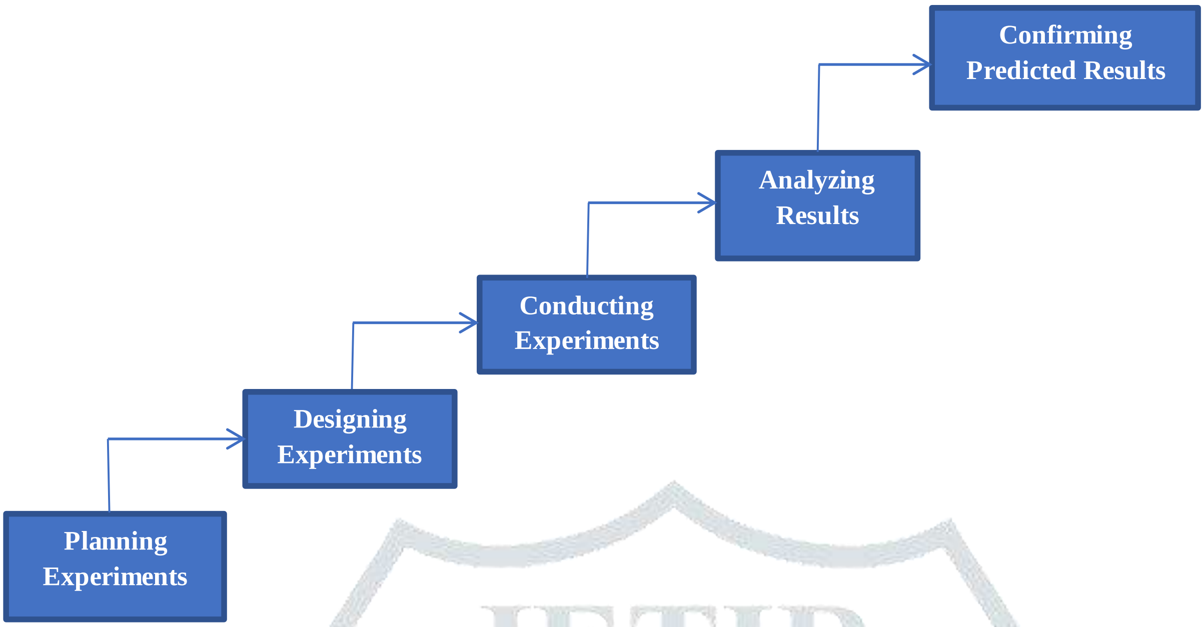

Figure 3. Flowchart of the Different Stages of Taguchi Experimental Design

1.6 Taguchi L9 Orthogonal Array

Orthogonal arrays are the mathematical structures that ensure a proper balance and a unvarying coverage of all the probable combinations of the factors and their levels. L9 orthogonal array is considered to be ideal or best for the robust design of the experiments if the significant control factors influencing the system are four in number. The effectiveness of each factor on the process is tested at three different levels to understand the behaviour of the system. The vertical columns represent the factors and the horizontal rows corresponds to the levels. Likewise, for each control factor, the values of three different levels are considered in the series of the experiments conducted as specified in the L9 orthogonal array designed by Dr. Genichi Taguchi, who is one of the renowned Japanese scientists. L9 orthogonal array is used for the robust design of the experiments and is a partial factorial method based on the use of the latin squares orthogonal arrays, which are used to optimize the results with the best combination of the factors and their levels by limiting the number of the experiments. The conventional method involves full factorial approach that involves conducting multiple experiments, which is a time taking process. The orthogonal arrays are the outcome of a mathematical process developed by the Dr, Genichi Taguchi in order to obtain swift results. The influence of the selected factors with different are tested for the optimization of the response variables. Overall, there are nine experiments, also called as trials are performed and the results obtained from these trials are compared with the standard expected values and nearest value to the standard one is considered as an optimized value. However, the researcher has to decide the response variables based on the objective of the research.

1.7 Standard Table of L9 Orthogonal Array

L9 orthogonal array is one of the Taguchi's methods, which is considered as a statistical tool used to optimize the system. The control factors and levels used in the optimization of the crystallization process as per L9 orthogonal array are four factors with each factor having three levels. A standard orthogonal array is represented with its columns and rows. The columns contain factors whereas the rows define the various levels for each factor. Overall, nine experiments are performed through L9 orthogonal array in order to obtain the optimized result. L9 orthogonal array assumes the main effects of the selected variables or the process parameters, which are evaluated and not the interaction effects between the variables. The information about the configuration of the experiments and the number experiments to be conducted will be defined by the orthogonal arrays. Orthogonal arrays provide an opportunity to analyse every factor at various levels. The orthogonal arrays are chosen based upon the list of important factors and the levels that can impact outcome of the experiments significantly. The advantages of using Taguchi's orthogonal arrays include swift testing of the influence of the process parameters on the system with minimal experiments or trials. It helps to simultaneously test the effectiveness of many interventions that occur during the process operation. The factors as per Taguchi design method are categorized into two types. One type is the process or the design factors and the another is the noise factors. Design factors are the process variables that can be controlled where as the noise factors are the uncontrolled factors that always involved in creating the disturbance to the system. *Table 2* and *table 3* describes the design of the L9 orthogonal array.

Table 2. Standard table with the columns and rows of L9 orthogonal array

Sr. No.	Factors/ Levels →	Level 1	Level 2	Level 3
1	A	1	2	3
2	B	1	2	3
3	C	1	2	3
4	D	1	2	3

Table 3. Taguchi L9 Orthogonal Array

Control Factors/Levels→	A	B	C	D	Response Factors
Experimental Run	**Stirring Speed**	**Seed Ratio**	**Seeding Temperature**	**Linear Cooling Temperature**	
1	1	1	1	1	
2	1	2	2	2	
3	1	3	3	3	
4	2	1	2	3	
5	2	2	3	1	
6	2	3	1	2	
7	3	1	3	2	
8	3	2	1	3	
9	3	3	2	1	

1.7 Oxalic Acid ($C_2H_2O_4$)

Oxalic acid is an organic compound that exists in two forms. One form of the oxalic acid is anhydrous in nature and the other exists in the form of dihydrate that is with two water molecules. Anhydrous oxalic acid has the formula $C_2H_2O_4$ whereas the dihydrate oxalic acid is given by the formula $C_2H_2O_4 . 2H_2O$. Oxalic acid exists in a solid crystalline form having a white colour. It forms a clear solution after dissolving in the water. It is grouped as the simplest di carboxylic acid. Oxalic acid is a reducing agent with its base being an oxalate ($C_2O_4^{2-}$). Oxalic acid in naturally found in many foods but it considered to be harmful to the human body if it is extremely absorbed in to it and also if the contact with the skin is persistent then it can be unsafe to the human body. The name of the oxalic acid appeared from the scientific name of genus oxalis, which is a flower-based plant universally recognized as the wood-sorrels. It is a very old process of preparing the salts of the oxalic acid from the plants that exists since 1745. The Dutch botanist and the physician Herman Boerhaave followed a separation technique to separate the salts of oxalic acid from the wood sorrels. In the year 1773, another notable scientist, named François Pierre Savary of Fribourg, Switzerland had separated the oxalic acid from its salts obtained from wood-sorrel. Oxalic acid was also obtained from the reaction of sugar and concentrated nitric acid and this innovative method was discovered by the Swedish chemists Carl Wilhelm Scheele and Torbern Olof Bergman in the year 1776 and the scientist named the acid as socker-syra or sacker-syra that is called as the sugar acid, which was compared with the naturally occurring oxalic acid and found to be similar. The experiment was conducted to achieve the oxalic acid by synthesizing the natural product was initiated in the year 1824 by the German chemist named Friedrich Wöhler. In this synthesis-based reaction, ammonia in aqueous solution was reacted with cyanogen to produce oxalic acid.

Other Names of Oxalic acid: Ethanedioic acid and Crab acid.
Formula: $C_2H_2O_4$
Elements Present: Carbon, Hydrogen and Oxygen
Molar Mass: 90.04 g/mol (anhydrous)
Solubility in Water: 90-100 g/L (20^{O}C)
Melting Point: 189.5^{O}C
Sublimation Point: 157^{O}C
Compound Type: Dicarboxylic Acid, Organic Acid
Available Form: Solid

1.7.1 Manufacturing Process of Oxalic Acid

Oxalic acid is usually prepared by the oxidation of the sucrose with the nitric acid by using vanadium pentoxide as a catalyst in smaller quantity. It the industry, oxalic acid is manufactured in large scale by a reaction comprising of sugar (sucrose, $C_{12}H_{22}O_{11}$), sulphuric acid (H_2SO_4) and nitric acid (HNO_3). The reaction is exothermic in nature where in the heat is released during the reaction. The reaction mass is taken in a specialized jacketed reactor, which is manufactured by steel of superior quality having a grade of SS 316. The process is continuous and the mother liquor obtained after the reaction is usually maintained at a temperature of 55^{o}C to 60^{o}C. Thereafter, the mother liquor having oxalic acid in it is sent for the crystallization unit for obtaining the desired crystals of the oxalic acid. The crystallization method, which is normally followed, is the cooling crystallization where in the temperature is reduced below 20^{o}C and the formation of the crystals of oxalic acid are observed. The crystals formed are separated from the remaining mother liquor and are further sent for the drying, which can be done either in the oven or by using the hot air drier. The extent of purity, crystal size and the crystal size distribution determine the efficiency of the process. The percentage of sugar influences the yield and purity of the product and it is desired to keep less concentration level of the sugar in the mother liquor. However, the internal molecular arrangements in the crystals depend upon the solute solubility, degree of supersaturation, nucleation kinetics and the growth kinetics. If the growth of the crystal is anticipated to be large then the width of the metastable zone is required to be increased. Similarly, the variation in the stages of the crystallization is done based upon the desired final product. There are different ways of cooling methods that are followed based on the specifications of the end product. These methods include, natural cooling, linear cooling, parabolic or controlled cooling and sudden cooling. Cooling crystallization is considered be the efficient method as it has an advantage to achieve definite shape of the crystals and also is an energy efficient process. Crystal seeding can be one of the methods to be considered to improve the yield and achieve specific sized crystals. Seeding method approach is based on creating a secondary nucleation to separate the phases. The usual quality tests performed on the crystals to understand the quality characteristics are X-Ray Diffraction method, Differential Scanning Calorimetry, Scanning Electron Microscopy, Gas Chromatography etc. These tests provide an insight about the structure of the crystals. The instrumental analysis also helps to know about the polymorphism where in the anhydrous crystals of oxalic acid exists in two different forms. One form has a chain like molecular arrangement whereas the in the other form the molecules are arranged like a sheet.

1.7.2 Common Applications of Oxalic Acid

Oxalic acid is used in the blade manufacturing process to remove the stains formed on the blades after the sintering process. About 25% of the oxalic acid, which is produced, is used in the dye processing as a mordant. It is also used as bleach and also as an ingredient in the baking powder. Oxalic acid is also used as a rust removal agent and as a miticide against the parasite that exists during the bee keeping. For cleaning the minerals, oxalic acid has an important role. Oxalic acid is used in an anodizing process to obtain the thin layer of the coat along with the lower surface roughness. Oxalic acid is used as a fungus acaricidal by inducing mortality in several tick species, including adult Ambylomma americanum (L), Ambylomma maculatum Koch and Ixodes scapularis Say [4]. Oxalic acid is key mineral transforming agent that converts cadmium, copper, lead and zinc into oxalates [5].

1.7.3 Toxicity

Oxalic acid is toxic in nature and it has harmful to the human body if swallowed or injected. Oxalic acid can cause skin rashes, redness, blisters, pain and slow healing ulcers, if it comes in contact with the skin repeatedly. The severe exposure to oxalic acid can result in the renal failure or the kidney damage, which occurs due to the formation of the calcium oxalates that are major cause for the kidney stones. The inhalation of the oxalic acid is considered detrimental as it can lead to the respiratory distress thus causing different respiratory diseases like pulmonary edema, pneumonitis, inflammation and edema of the bronchi. Common symptoms that are usually experienced after the exposure to oxalic acid include headache, dizziness, nausea, vomiting and convulsions. However, the toxicity of the oxalic acid can be useful for certain applications based on the lethal concentration levels to kill the fungus, mites and several tick species. Oxalic acid is used to control the varroa destructor that can damage the hives of the honey bees. It is less toxic to honey bees and highly toxic to the mites. [6]

1.8 Distilled Water (H_2O)

Distilled Water is a purified form of water obtained by the process of distillation. Ordinary water is boiled and the vapour formed is condensed separately and collected in a container. During the process of boiling, the impurities present inside the water are either left behind without boiling or may be boiled nearer to the boiling point of the water. Usually, distilled water is free from the salts, minerals and other organic materials. The uses of distilled water include sterilizing medical equipment, lead-acid batteries, automotive cooling systems, and other devices where mineral build up would cause damage to the equipment through scaling and corrosion of the equipment thus effecting the operational costs.

II. METHODOLOGY

2.1 Methodology Followed

2.1.1 Cooling Crystallization Method involving Seeding Technique

The principle involves heating the solution till it attains supersaturation followed by the cooling the process in a gradual manner with an intermittent addition of the oxalic acid dihydrate ($C_2H_2O_4.\ 2H_2O$) seeds of 250 microns size at different seeding temperatures. The yield and the properties of the final crystals seeds that are obtained are tested.

III. MATERIALS AND EXPERIMENTAL WORK

3.1 Materials

Based on the literature review, the raw materials considered for the experimentation are oxalic acid dihydrate ($C_2H_2O_4.\ 2H_2O$) and the distilled water. Oxalic acid dihydrate ($C_2H_2O_4.\ 2H_2O$) is used as a solute whereas the distilled water is used as a solvent. The experiments are conducted based on the L9 orthogonal array of Taguchi optimization method by considering different solubility levels of oxalic acid dihydrate ($C_2H_2O_4.\ 2H_2O$). The materials and the apparatus required to successfully perform the experiments are the magnetic stirrer with hot plate and temperature control sensor, oxalic acid dihydrate ($C_2H_2O_4.\ 2H_2O$), distilled water, seed size of 250 µm thermometer, 100 ml beakers, aluminium foil, glass measuring cylinder, turbidity meter, glass funnel, whatman filter paper, spatula and crucible.

3.2 Experimental Work

The experimental work is based on the design of the experiments of Taguchi's Method for Optimization. This method follows the path of conducting the experiment based on the partial factorial method, which uses different orthogonal arrays. This technique of designing limited experiments to achieve the desired results in a very short period was invented by a renowned Japanese scientist named Genichi Taguchi. Such a type of approach is very useful to reduce the number of experiments, eventually achieving better outcome in a lesser time as compared to the full factorial experiments, which are time consuming. The desired results with this method are obtained very quickly and also this method has an advantage of fulfilling the research requirements with the optimum utilization of time, material costs and energy of the researcher. The orthogonal array found suitable for the robust design of the experiments in the present research was L9, which was considered after careful evaluation of all the factors, which influence the crystallization process. The number 9 indicates a total of nine experiments are sufficient to be performed to achieve optimized results. The L9 orthogonal array accommodates 4 factors, which are analysed at 3 different levels to understand their influence on the overall thermodynamic system. The solubility of the oxalic acid at 60^{O}C temperature was considered for the experimental work. The solubility of the oxalic acid dihydrate ($C_2H_2O_4.2H_2O$) at 60^{O}C is 4.43 grams per 10 grams of distilled water [7]. The experiment starts by taking a 10 ml volume of the distilled water in a borosil glass beaker and is heated till 60^{O}C with a constant stirring by using an instrument, hot plate with a magnetic stirrer and a temperature control sensor. Then the oxalic acid dihydrate ($C_2H_2O_4.2H_2O$) of 4.43 gms quantity is added to the solvent at 60^{O}C and constantly stirred at a particular stirring speed. After attaining the saturation level of the solute in the solution, the cooling crystallization method is followed where in the temperature is gradually reduced in a linear manner. There are nine number of experiments that were designed and conducted in the initial phase as per the L9 orthogonal array of Taguchi optimization method. The seed technique was also followed by the addition of the seed crystals of 250 µm at a particular seeding temperature. During the crystallization process, the turbidity of the solution was captured with the help of the turbidity meter and the induction time and the induction temperature was measured. The linear cooling process was further continued till the temperature reached to the final temperature of 29^{O}C for the initial set of nine number of experiments. The final product from the mother liquor is removed by the filtration process by using the Whatman filter paper and eventually subjected to the natural drying for around 24 hours in the ambient temperature. Similarly, the above procedure as expounded was also followed for the second set of nine experiments with the final temperature being at 25^{O}C. The percentage yield obtained in both the set of the experiments was compared and analysed.

1V. RESULTS AND DISCUSSIONS

The importance of the seeding temperature and the cooling profile with the final cooling temperature was known through the series of the trials conducted as per the L9 orthogonal array of Taguchi optimization technique. The experiments were conducted by considering the seeding technique in the cooling crystallization process. Seed crystals of the size of 250 µm of oxalic acid dihydrate ($C_2H_2O4.2H_2O$) were added as per the planned seed ratios of 2%,4% and 6% into the solution at various seeding temperatures of 48^{O}C, 52^{O}C and 56^{O}C. The stirring speeds of 150 rpm, 250 rpm and 350 rpm were maintained in combination with the other factors throughout the experiments. The design of experiments was done based on the L9 orthogonal array of Taguchi's optimization method. The total number of the experiments performed were nine with various combination of the selected control factors with different levels thus eventually obtaining the different values of the yield, which is considered as a response variable. It was observed that there was a greater influence of the experiment's final temperature and the seeding temperature. The experiments in which the seeding temperature of 48^{O}C closer to the induction temperature has given a higher yield as compared to the seeding temperature of 56^{O}C, which was farther. Therefore, it is evident from the experiments performed that lower cooling temperatures can increase the formation of the number of crystals and the seeding done at the seeding temperatures closure to the induction times and temperatures can give better yield due to the high degree of supersaturation.

Design of the experiments based on L9 orthogonal array (Four Factors with Three Levels) at a solubility temperature of oxalic acid dihydrate ($C_2H_2O_4.2H_2O$) at 60^{O}C.

Solute: Oxalic Acid Dihydrate ($C_2H_2O_4.2H_2O$)
Quantity of the solute considered for the experiments at a solubility temperature of 60^{O}C: 4.43 grams
Solvent: Distilled Water
Volume of the solvent considered for the experiments – 10 ml

Table 4. L9 Orthogonal Array (Factors and Levels) design strategy for the experiments to be conducted at a solubility temperature of oxalic acid dihydrate ($C_2H_2O_4.2H_2O$) at 60^{O}C

Sr. No.	Factors/ Levels →	Level 1	Level 2	Level 3
A	Stirring Speed	150	250	350
B	Seed Ratio (%) on 4.43 gms	2	4	6
C	Seeding Temperature	48	52	56
D	Linear Cooling Temperature	4	6	8

Table 5. L9 orthogonal array with nine number of experiments conducted considering the final cooling temperature at 29 ^{O}C

Control Factors/Levels→	A	B	C	D	Response Parameters			
Experiment No.	**Stirring Speed (RPM)**	**Seed Ratio (%)**	**Seeding Temperature (^{O}C)**	**Linear Cooling Temperature (^{O}C)**	**Induction Time (Min)**	**Induction Temperature (^{O}C)**	**Final Weight (Gms)**	**Yield (%)**
1	150	2	48	4	39	46.90	1.93	42.70
2	150	4	52	6	28	46.50	1.69	36.66
3	150	6	56	8	29	45.50	1.96	41.70
4	250	2	52	8	29	45.50	2.10	46.46
5	250	4	56	4	35	46.00	2.00	43.38
6	250	6	48	6	29	46.50	2.06	43.92
7	350	2	56	6	30	44.50	1.88	41.59
8	350	4	48	8	28	45.00	2.09	45.34
9	350	6	52	4	36	45.50	1.82	38.81

Table 4 provides the information about the selection of the control factors that can influence the process during the formation of the product whereas the *table 5* contains the experimental values obtained based on the controlling the process by using the designated four factors of different levels. A total of nine experiments were performed as per the L9 orthogonal array design strategy with final cooling temperature set at 29^{O}C.

Table 6. L9 orthogonal array with nine number of experiments conducted considering the final cooling temperature at 25 ^{O}C

Control Factors/Levels→	A	B	C	D	Response Parameters			
Experiment No.	**Stirring Speed (RPM)**	**Seed Ratio (%)**	**Seeding Temperature (^{O}C)**	**Linear Cooling Temperature (^{O}C)**	**Induction Time (Min)**	**Induction Temperature (^{O}C)**	**Final Weight (Gms)**	**Yield (%)**
1	150	2	48	4	32	45.50	2.37	52.43
2	150	4	52	6	28	46.90	2.29	49.67
3	150	6	56	8	29	46.50	2.31	49.15
4	250	2	52	8	28	46.90	2.13	47.12
5	250	4	56	4	32	45.50	1.96	46.52
6	250	6	48	6	28	46.90	2.51	53.40
7	350	2	56	6	29	46.00	2.02	44.69
8	350	4	48	8	28	46.50	2.30	49.89
9	350	6	52	4	38	44.50	2.08	44.35

Table 6 contains the experimental values obtained based on the controlling the process by using the designated four factors of different levels. A total of nine experiments were performed as per the L9 orthogonal array design strategy with final cooling temperature set at 29^{O}C. The consolidated data obtained for the final temperature of 29^{O}C & 25^{O}C through the experimental work is mentioned in the *table 7*.

Table 7. Consolidated data containing the experimental values obtained at the final cooling temperatures of 29^{O}C and 25^{O}C

The comparison of the data between the final cooling temperatures of 29^{O}C & 25^{O}C is given in the *table 8* and the same data is also shown in *figure 4*, which is in the form of a graph.

Table 8. Final Cooling Temperature (^{O}C) v/s Yield (%)

Control Factors/Levels →	A	B	C	D		Response Parameters			
Experiment No.	Stirring Speed (RPM)	Seed Ratio (%)	Seeding Temp. (^{O}C)	Linear Cooling Temp. (^{O}C)	Final Cooling Temp. (^{O}C)	Induction Time (Min)	Induction Temp. (^{O}C)	Final Weight (Gms)	Yield (%)
1	150	2	48	4	27	39	46.90	1.93	42.70
2	150	4	52	6	27	28	46.50	1.69	36.66
3	150	6	56	8	27	29	45.50	1.96	41.70
4	250	2	52	8	27	29	45.50	2.10	46.46
5	250	4	56	4	27	35	46.00	2.00	43.38
6	250	6	48	6	27	29	46.50	2.06	43.92
7	350	2	56	6	27	30	44.50	1.88	41.59
8	350	4	48	8	27	28	45.00	2.09	45.34
9	350	6	52	4	27	36	45.50	1.82	38.81
10	150	2	48	4	25	32	45.50	2.37	52.43
11	150	4	52	6	25	28	46.90	2.29	49.67
12	150	6	56	8	25	29	46.50	2.31	49.15
13	250	2	52	8	25	28	46.90	2.13	47.12
14	250	4	56	4	25	32	45.50	1.96	46.52
15	250	6	48	6	25	28	46.90	2.51	53.40
16	350	2	56	6	25	29	46.00	2.02	44.69
17	350	4	48	8	25	28	46.50	2.30	49.89
18	350	6	52	4	25	38	44.50	2.08	44.35

Experiment No.	Final Cooling Temperature (^{O}C)	Yield (%)
1	27	42.70
2	27	36.66
3	27	41.70
4	27	46.46
5	27	43.38
6	27	43.92
7	27	41.59
8	27	45.34
9	27	38.81
10	25	52.43
11	25	49.67
12	25	49.15
13	25	47.12
14	25	46.52
15	25	53.40
16	25	44.69
17	25	49.89
18	25	44.35

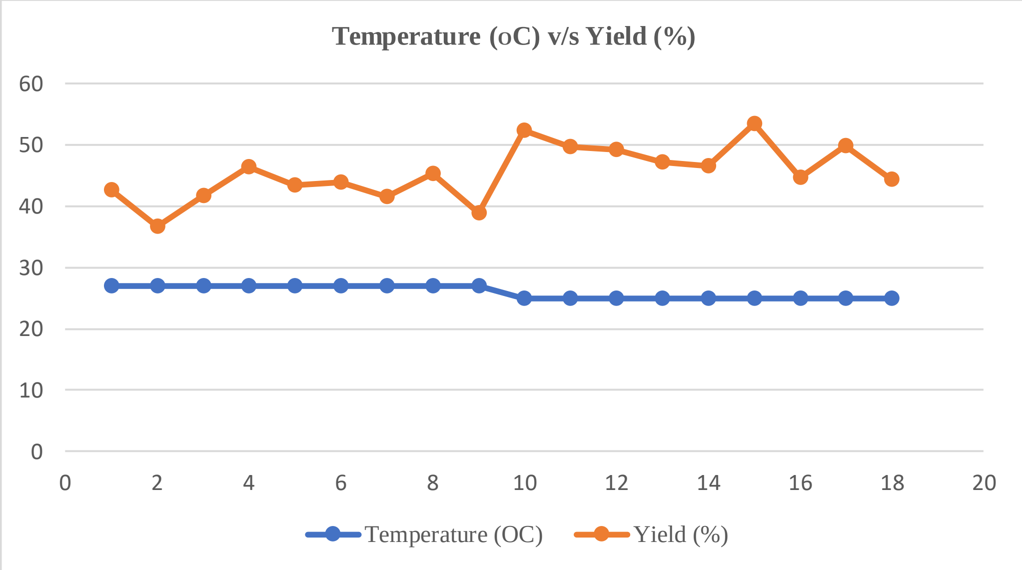

Figure 4. Final Cooling Temperature (^{O}C) v/s Yield (%)

Table 9. Consolidated data containing the experimental values of the percentage yield obtained at the stirring speeds and seeding temperatures.

Sr. No.	Stirring Speed (RPM)	Seeding Temperature (OC)	Yield (%)
1	150	48	42.70
2	150	52	36.66
3	150	56	41.70
4	250	52	46.46
5	250	56	43.38
6	250	48	43.92
7	350	56	41.59
8	350	48	45.34
9	350	52	38.81
10	150	48	52.43
11	150	52	49.67
12	150	56	49.15
13	250	52	47.12
14	250	56	46.52
15	250	48	53.40
16	350	56	44.69
17	350	48	49.89
18	350	52	44.35

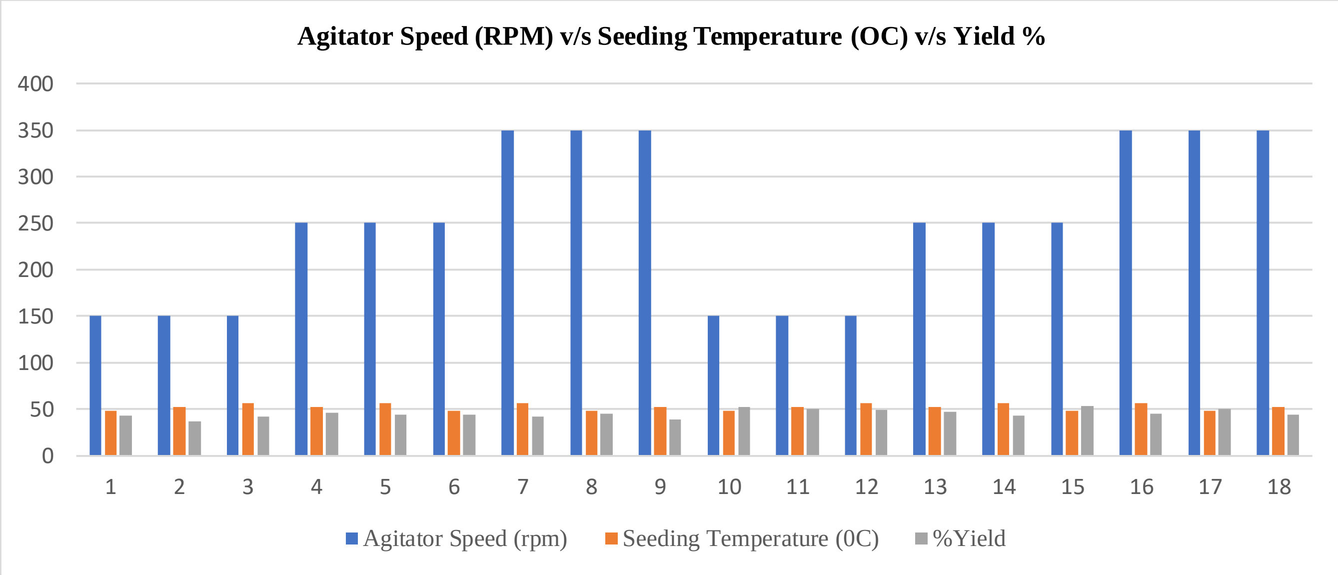

Figure 5. Graph showing the impact of the stirring speeds and seeding temperatures on the percentage yield of oxalic acid dihydrate ($C_2H_2O_4.2H_2O$)

It is evident from the experimental data that seeding temperature is pivotal to increase the yield or the percentage of the yield of the final product, which is oxalic acid dihydrate ($C_2H_2O_4.2H_2O$). The seeding temperature selected close to the induction temperature has produced more yield at all levels of stirring speeds as compared to the seeding temperatures, which are farther than the induction temperatures. *Table 9* with a relevant graph in the *figure 5* justifies the objective of understand the process to increase the yield of the substance.

The images shown in *figure 6* provides an idea about the onset of the nucleation, which is defined in terms of induction time and induction temperature. The induction time was different for different experiments. It depends on the factors, which include stirring speed, type of the solvent, degree of supersaturation, concentration and the mechanisms that occur during the crystallization process. The turbidity in the solution indicates the beginning of the crystal formation.

Figure 6. Images of the Induction Temperatures at 150 rpm, 250 rpm and 350 rpm

V. CONCLUSION:

The cooling crystallization method is considered to be an efficient method as it is not an energy intensive approach to obtain the desired crystals. The cooling profile designed for a gradual reduction in the temperature during the crystallization process can give better outcome in achieving good yield and crystal properties. In addition to the existing process, seeding in the crystallization can be considered as one of the best optimization techniques to improve the product properties. Seeding enhances the quality of the final crystals thus influencing the yield and the crystal properties. Supersaturation is an important stage in the entire crystallization process. It governs the nucleation kinetics and the growth kinetics. The degree of supersaturation determines the effectiveness of the final growth of the crystals and the yield. Therefore, seed addition at a right temperature is important to obtain the desired crystal characteristics. Seeding helps to obtain supersaturation swiftly and also widens the metastable zone in which the actual growth of the crystals occurs. Seeding temperature kept closer to the induction temperatures gave better yield. From the experimental work, $48^{O}C$ was considered to be a better choice to achieve better yield over the other two levels of seeding temperatures selected for the L9 orthogonal array. In order to achieve the optimization of the crystallization process within a lesser duration, L9 orthogonal array of Taguchi method was applied for robust design of the experiments. Orthogonal arrays are partial factorial experiments and are used to reduce the time, money and energy as compared to full factorial methods, which take longer time to give the results. The robust design of the experiments was done by using the L9 orthogonal array, which considered the testing of the process with four control factors at three different levels and with only nine experiments.

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