Structure and Design Flow Injection Synthesis Method of Co-precipitation Forming Magnetic Materials Process

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ABSTRACT : *The Flow Injection Synthesis is the process has high reproducibility in volume and residence time, which is easy to do but still have a susceptibility to temperature and pH of the reaction co-precipitation process of forming magnetic materials. The second of the parameters be a reference for determining the processing of data, whether it is isothermal or non-isothermal, both have advantages and disadvantages. Isothermal process refers to the Avrami method, while the non-isothermal process has many choices of the methods such as ;Avrami-Ozawa, Kissinger, Matusita , Mahadevan, and etc.The FIS-apparatus is adapted to support the process. The isothermal process requires a reactor that can sustain of process temperatures, while the non-isothermal adiabatic nature should be able to maintain. The Piping system of fluid flow and using of the dosing pump or peristaltic pump following a pump electronic control circuit for use is an absolute terms. Using of data logger which use SD card will provide easier data processing. Know-how the FIS will base at know-how reaction process.*

2. Introduction

Either in the chemical or pharmacy laboratory, using of the flow injection process usually is used to precipitate of medicine in the imitate of liquid to obtained the process parameter matching as a natural process guanine, also able to apply in magnetic materials forming [1]

The process synthesis usually is faced with both temperature, pH parameter of the liquid raw material and yield. The process of formation material close to the FIS is the process by co-precipitation method.

The co-precipitation process is one of the oldest synthesis method. The process which is most easily and effectively generate yield with relatively small particle size of the nanometer sized. LaMer and 1950 Dinegar create diagrams that can be used for controlling syntesa co-precipitation process making it possible to generate yield relatively complete [2,3]

Some of the advantages of co-precipitation process namely;
1. It can be conditioned isothermal process or in the non-isothermal process and it to be estimated the value of t he activation energy process.
2. It can be estimated the speed of the process is based on both the temperature and pH of the reactants.
3. Ease of set up and record of the parameters either the process temperature or pH of yield or concentration of the reactants yield.
4. It can be estimated the cationic distribution and degree of the crystal spinel inversion [4]

2. The FIS Method.

The appropriate determination controlling FIS methods were needed knowledge of the chemical process mechanism, which consists of;

) Method FIS in bath.

This method Will obtains the yield has appropriate of the pH references . Both the reaction process and the equal treatment are done by the process of mixing of each the reactants of co-precipitation done simultaneously but gradually segmented mixing process. The first modern of the FIS models titration process conducted by German Salazar-Alvarez [5], who use a computer to perform the titration process, the

particle growth at pH constant. The Titration process use reactant injection-driven way of the peristaltic pumps and the injector .This method makes it possible to produce a uniform particle size or *mono- disperse particle.*

2) Method of the reactants injection.
a) Method of injection flow in the reactor basin (Flow Injection Synthesis in Bath)
b) The Flow injection synthesis in the interval references use coil of tube in many range depend of settling time of crystal particle forming and flow rate of raw material from peristaltic pump.

Comparing the tube coil of FIS construction, The FIS in bath construction has advantages such as;
1) More easy to operate..
2) More easy to use anti-oxidizing gas.
3) More easy to install and use stirrer.
4) More easy to install both pH and temperature sensor.
5) More easy both install and disassembly.
6) More easy to use data logger.

3. The criteria of construction and equipment FIS system.
To perfection of the way of operate of the FIS, both equipment and measuring devices must have the toughness is;
1. The reactor should be made either of glass or ceramic Easy to clean, resistant to heat treatment at high or at low temperatures.
2. The hose system must be made from rubber or flexible plastic resist to acid-base, not easily glued by chemicals will form a crust or clog and pipe damage.
3. Cleanliness peristaltic pump and hose.
4. Make sure the electrical circuit of peristaltic pump drive is still running in perfectly controlled.
5. Use data logger of data recording from both the pH gauges and a digital thermometer.
6. The FIS system has to complete with mixer to mix raw material in high speed mixing.

4. The Design and Construction of The flow Injection Synthesis in Bath.
4. 1 Theoretical Base Of the Co-precipitation Synthesis Kinetics Process
The co-precipitation synthesis is a synthesis reaction that

were characterized by the incorporation of atoms at the time of the precursor material in the precursor solution super-saturated conditions and growth nucleation occurs during the deposition process is taking place. The core growth follows exponent model, and the reaction occurs at the state super saturated-solution.

The nucleation and growth processes follow of the rules Avrami formulation, while the activation energy of the process will be based on the formulation of the Arrheneus.

Refers to the replication of the LaMer and Dinegar diagram, co-precipitation reaction of mono-disperse particle formation consists of three stages namely; saturation (saturation), nucleation (nucleation) and growth (growth). Saturation associated with the reactant solution saturation, nucleation associated with the formation of the core nucleus crystals, and crystal growth. [6] such as the following figure1

One application of FIS method is to estimate the activation energy and the entrophi of ferrite materials. Ferrite material is a material nanomagnetik that use nano-sized lot in the field of radio communication engineering, computer and electronics, catalyst materials, ferrofluid and etc.[9] Application of nano-sized materials development is quite rapid.
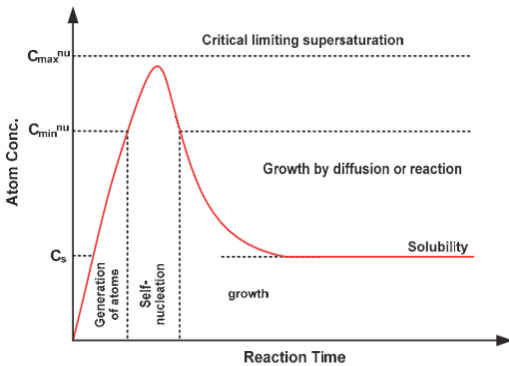

Figure 1. Nucleation and growth of particle formation process in co-precipitation synthesis by LaMer and Dinegar. [3,5]

The yield fraction f (t) can be calculated from the change in concentration of metal ions or metal ions or alkalinity changes in the reactant solution (pOH) with equality;
a) For the acid solution is injected in the flow of alkaline solution, so the pH of the solution changed from large to yield smaller, then the yield is expressed as a fraction [7]

$$f(t) = \frac{(10^{-pOH_0} - 10^{-pOH_t})}{(10^{-pOH_0} - 10^{-pOH_\infty})} \quad \ldots\ldots\ldots\ldots 1$$

pOH_0 = the previous pH

pOH_t = the pOH at t time

pOH_∞ = the pOH at steady state.

pOH = 14 – pH

b) For the base solution is injected in the flow of acid solution, so the pH of the solution changed from a small yield becomes larger, then the yield is expressed as a fraction

$$f(t) = 1 - \frac{(10^{-pH_0} - 10^{-pH_t})}{(10^{-pH_0} - 10^{-pH_\infty})} \quad \ldots \quad \ldots \quad 2$$

Fraction is in the range between 0% to 100% or 0:00 or 1:00.

a) The Isothermal of Kinetic Reaction Base..

The temperature constant reaction is in the bath condition where the temperature of process is in maintained be in constant state. To take this state is required the heats were not accumulated in the bath reactor , reversal the heat must fluent release out of the bath. Using of heat transfer fins is completed by minivans may practical and economical methods as the figure 2

The non isothermal bath is made from thin pyrex high quality glass, placed on a aluminum pallets is completed with fins and fan, in reversal of the isothermal bath is made of glass coated with thick a heat insulator layer

The reaction rate according to Avrami Behavior; phase transformation is expressed by the equation

$$f(t) = 1 - Exp(-k.t^n) \quad \ldots\ldots\ldots\ldots 3$$

t is reaction time
f (t) = fraction of the progress of the reaction (yield)
t and n are constants that depend on the reaction kinetics of the reactants environment such as ;pH, temperature-t, and concentration of precursor material products.

f(t) volume of fraction yield after t seconds, as the value of the exponent n depends on the kinetic and mechanism of crystal growth and size, K the reaction rate constant is generally expressed by the Arrhenius equation.

Following Christian,in the range in which the transformation curve becomes a straight line, nucleation saturation has occurred, and K may be interpreted by the equation

$$\frac{d \ln K}{d(1/T)} = \frac{-n.Q_E}{k} \quad \ldots\ldots\ldots\ldots\ldots 3a$$

where Q_E is the growth or diffusion activation energy, T is the absolute temperature, and k is the Boltzmann constant. Generally, we have the exponential relation.

which is an Arrhenius relation[8] , where K_0 is the frequency factor.

$$K = K_0 \exp(-\frac{Q_E}{kT}) \quad \ldots\ldots\ldots\ldots 3b.$$

The rate of crystal formation reaction yield at the constant temperature can be expressed as;

$$\frac{d f(t)}{dt} = n.K^n.t^{n-1}(1-x) = n.K(1-y)[-\ln(1-y)]^{\frac{(n-1)}{n}} \quad 4$$

In the isothermal treatment , both the values of frequency factor -K parameter ,and kinetic parameter exponent- n are obtained from the data f (t), ie with double logarithmic behavior Avrami equation as follows;

$$Ln[-\ln(1-y)] = n.\ln K + n \ln t \quad 4.b$$

N and K values obtained from fitting of the least square graph Ln {-ln (1-y) versus ln t, for each t different. The activation energy value-Q_E is obtained from fitting of the graph Ln.K versus 1 / T.

In the specific conditions, such as the particle shape is assumption as a ball, then the nucleation point such that there are N particles grows with velocity v, the parameter k can be written as[6] an equation;

$$k = N.\frac{\partial Vol_{pzrtikel}}{\partial t} = N\{\frac{\partial(\frac{4}{3}\pi R_p^3)}{\partial t}\} = \frac{4}{3}\pi.N.v^3 \quad \ldots\ldots\ldots 5$$

With;

N is particle number

v is rate of growth partikel.

Rp is particle radius.

In this case the parameter of n is 3.

By the half time-$t_{0.5}$ particle fraction f(t) has reached 50% - (t0.5, f (t0.5) = 50%). Then we should to arrange of t, pH_0, pH_t, f(t) from data logger t and pH_t .

Crystal growth by particles is a function of the Arrhenius activation energy and the temperature can be expressed by the equation ,

$$K(T) = K_0 . e^{-(\frac{Q_E}{R.T})} \quad ....6.$$

The equalization both equal 1.2 and 3 will be resulted of Avrami behavior either in the graph or the list of time forming could be obtained forming half time particle-$t_{0.5}$

Data processing to obtained usable necessary of parameter the data should be processed in the linier fitting of logarithmic methods.

b) The Non-Isothermal of The Kinetic Reaction Base.
If the relationship is obtained Avrami equation as in equation 4b as;

$$Ln[-\ln(1-y)] = n.\ln K + n \ln t .$$

to obtain the activation energy of crystallization at the crystallization process is in isothermal process.

Considering the non-isothermal crystallization being a rate dependent process, Ozawa extended the Avrami equation to the non-isothermal condition by replacing time variable in Avrami equation with a variable cooling rate and derived a kinetic equation as follows :

$$1 - f(t) = \exp\left[-\frac{K(T)}{\Phi^m} \right] \quad ....7$$

where K(T) was a cooling function, and m was Ozawa exponent depending on the crystal growth and nucleation mechanism, Φ was cooling rate [9].

In isothermal term the process temperature-T is constant but in the non-Isothermal activation energy-Q_E, the crystal growth process with more emphasis on the speed of change in the energy (heating or cooling) is constant.

Cooling rate unit is appropriate whether with time constant or half time of the process whether in seconds or in minutes.

Briefly the activation energy calculation stage non isothermal process shall be done by the following steps;

• Use both the data of temperature and pH from data logger, find t[K] and f[t] and linier graph of

$$Log[-\textit{h} (1 - f(t))] = Log k + n \log t$$

The values of the Avrami exponent n and the rate parameter Zt can be determined from the slope and intercept of the plot of log[−ln(1−ft)] versus log t, respectively. It was obtained Avrami parameter both n and k..

• Use the Ozawa equation;

Arrange the table of the Log(-Ln(1-f(t)) and log(Φ)

$$Log[-\ln - f(t) = \log(K(T) - m.Log(\Phi)$$

Find the linier graph, obtained ozawa parameter and K(T) parameter..

• Use the overall cooling rate equation

Get the linier graft Log(Φ) versus log (t), take design, linier layout, get the linier graph equation. analogy with equation

Log(Φ)=Lg F(T) –blog(t).

Obtained Φ, Log(F(T)) and F(T).

From equation of $F(T)^m = K(T)/K_c$ find Log K_c

Overall of temperatur rate is $\Phi = Log K/Log K_c$

• Get the data local of temperature exchange rate Φ and 1/T take layout of the linier graph $\textit{h} (\frac{\phi}{T^2}) = \frac{Q_E}{R} + Const$

It will find Overall cooling rate Φ. [kcal/mol K]

Use converse of energy unit, 1[J]=0.239 cal

R constant = 8.31 [j/mol K].

The Regression parameter do not use except to checking up of the really relation between parameters.

4.2 Equipment and measuring device.
4.2.1 Network Diagram Bath reactor.

Process diagram of equipment and device non isothermal bath reactor
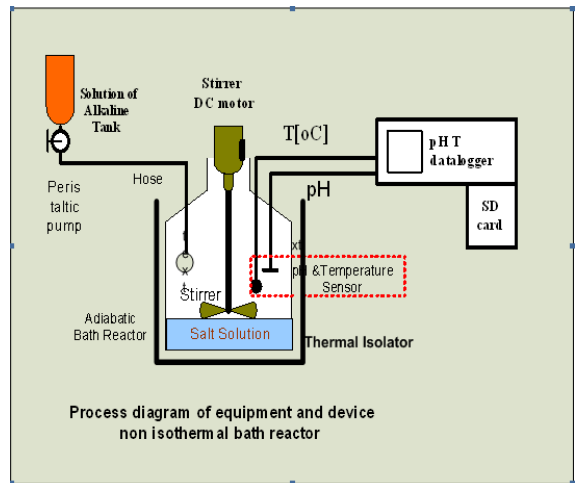
Figure2 Non-Isothermal FIS bath reactor of co-precipitation using thermal insulator as jacket of bath.
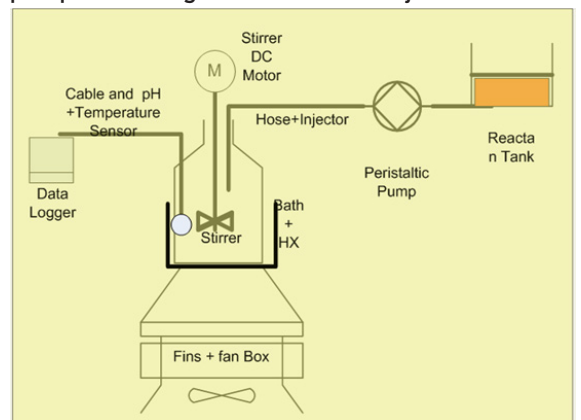

Figure 3. Isothermal FIS bath reactor of co-precipitation, Using Fins +vans inbox as heat exchanger of bath.

4.2.2 The equipment and measuring Device.
1) Adiabatic Bath reactor
2) Solution of alkaline tank
3) Hose and injector system
4) Peristaltic pump
5) Electric stirrer

6)   pH and Temperature data logger
7)   SD Card
8)   pH sensor
9)   PTC temperature sensor.
10) Variable DC power supply..
11) Pump speed controller.

4.2.3 The main equipment of the bath reactor.
a) Peristaltic Pump regulations
The peristaltic pumps may run continuously, or they may be indexed through partial revolutions to deliver smaller amounts of fluid, but it was able to drain the fluid precision. Under limited, liquid flow rate depend on rotation number of motor speed then flow rate able to vary by the voltage of DC motor mover.

The DC motor could be control by vary the DC voltage batteries, the indirect controller could be done by adjusting of positioning potentiometer at DC power regulator.

The Hose and injector of fluid requires mini tank as regulate of mixing liquid and gas. Adjusting of the fluids can be done by using of mini tank. This was due by the accumulation of fluid continuous carried peristaltic pump.

b).Stirrer Regulations.
The stirrer is the equipment to homogenize of liquid reactant in the bath reactor. It is driven by DC motor and use variable DC supply.

The rotation speed of etirrer can be regulated by regulate variable DC voltage power supply. Maximum speed of the stirrer rotation will give an effect to normalize of the co-precipitation reaction then timing of particle forming just depend on the number of raw material and temperature parameter. The proportional of both material yield and raw material can be determined by previous and last of the solution of the pH reactant such either as equation 1or 2.

c). Temperature and pH Data logger.
The advancement of computer technology and instrumentation, led the researchers of the chemistry of laboratory, capable of recording various process parameters such as pH, temperature, pressure and flow rate in very quick manner by using modern data logger complete with the external memory SD card. The memory can be quickly moved from data logger to computer in form data excel.

The readout of data logger have be seen as the following table;

Position	Date	Time	Ch1_Value	Ch1_Unit	Ch2_Value	Ch2_unit
1	1/4/2013	4:50:14	1.72	ph	28.6	Degree C
2	1/4/2013	4:50:16	1.72	ph	28.6	Degree_C
3	1/4/2013	4:50:18	1.72	ph	28.6	Degree_C
4	1/4/2013	4:50:20	1.72	ph	28.6	Degree_C
5	1/4/2013	4:50:22	1.72	ph	28.6	Degree_C
6	1/4/2013	4:50:24	1.72	ph	28.6	Degree_C
7	1/4/2013	4:50:26	1.72	ph	28.6	Degree_C

Figur4. The readout of the data logger memory, such as table of the excel datasheet.

The position content of data logger table have to rearrange either number of cell (column,rows) or cell content.

d). Determining of the temperature sensor and the pH Electrode.
Supporting of the measurement compatibility in this project require using of the PT 100 as the temperature sensor and the pH electrode-PE-03. PT100 is platinum sensor give a linear line of graphs around 100 C. PE-03 able to use pH liquid in range 1.00 [acid] until 14.00 [alkaline]

e) The selection of the isothermal or non-isothermal system.
Each system has advantages and disadvantages, depending on the point of view the emphasis on scoring system. One of the advantage of non- isothermal system is equipment of the bath is not complicated. The bath requires a jacket system to isolate the temperature of inside and outside the bath. Then the heat in the bath did not infiltrate from other system. The jacket is made either from rubber, stereo foam, plastic composite and etc.

Different with isothermal system, the process temperature usually vary, due by effect of the reaction require of heat or release of heat. To maintain of constant temperature need heat conduction well. The bath requires both more complicated and sophisticated equipment compare with the Jacket of bath.

f) Usage nitrogen gas and fresh raw material.
The nitrogen gas is one of anti oxidation in reactant and alkali liquid, especially of fero or ferri oxide.

4.2.4 Installing and operating direction.
Installing ; Place the reactor bath in space has fresh air, do not too close with either glass ware, electric cable but power supply, bottle of raw material.

Close all of the equipment, and install the support equipment such as; the glass funnel, ellemeyyer glass, thermometer, pH electrode, data logger, tubing, aqua DM jerry cans, Nitrogen gas cylinder.

The sequence of the installation process;

• Place the hose with mini tank in the reactant input .
• Connect mini tank, hose, peristaltic pump and injector. immersed the injector end in the liquid reactant
• Pairs of stirrer rod to the slot DC motors, immerse the stirrer into the bath reactor liquid.
• Enter the nitrogen gas hose into the bath.
• Install of pH electrode and PT100 electrode into the bath.
• Fill in to the bath alkaline liquid until the end of both the electrode and the stirrer immerse.
• Insert the electrodes to plug in slot data logger.
• Insert the SD Card to plug in slot data logger.

Operating Direction
• stream of the nitrogen gas in a liquid alkaline with a small stream.
• Fill in the tank by reactanct
• Switch on the data logger in recording mode.
• Switch on the stirrer
• Switch on the peristaltic pump at low speed.
• Wait until the reactants are runs out
• Switch off the peristaltic pump.
• Read the pH meter at the data logger
• If the pH meter showed the pH has not changed much, switch off recording of data logger.
• Remove the SD card from the data logger.
• Reinstall the equipment of bath reactor.
• Move the yield of the reactor bath to another container to continue by washing process of yield.
• Washing and precipitation process takes a long time until have pH around 7.

4.3 Data processing of SD Card
The SD card is memory have to move from SD slot of data logger and insert the SD to the SD slot computer is used. It has information of the chemical processing data in form

excel datasheet. Using of the data require a little act as the following;

The form of the previous data file such as figure 4, the data has to move be an operational data as the following data;

Table 1. The example of Extended table content at SD card DataLogger,

No	A	B	C	D	E	F	G	H	I	J
1										
2										
3										
.										
.										
n										

Where;

A = temperature [C]

B = temperature [K]

C= pH

D= pOH=14-C

E= $y = f(t) = \dfrac{(\emptyset^{-pOH_0} - \emptyset^{-pOH_t})}{(\emptyset^{-pOH_0} - \emptyset^{-pOH_\infty})}$

F = Log[-Ln(1-Y)]

G = Log α =Log $(t_2 - t_1)$

H= Log t

I = Ln (α/t^2)

J = $(1/t^2)$

From the table1, able to graph of
- Avrami behavior F versus H
- Ozawa behavior F versus G
- G versus H to obtain overall temperature exchange Φ=log k/log K_c
- I versus H to obtain crystal activation .

5. Discussion.
- The equation 1 is the percentage yield equations generated by changes konsentarasi reactants. In practice it turns out has a resemblance with the Avrami estimated based on the percentage change in the physical properties of materials forming. So that the percentage increase in yield can be traced by changes in energy levels. If the change is only based on physical properties of materials can be traced in the thermodynamic estimation using DSC apparatus while the changes are based on the chemical properties of the material traced yield estimates based on changes in concentrations of the reactants.

- The equipment network of FIS system is quite complex and prone to errors, it is necessary enforce operational procedures, such as calibration of measurement system, the series operating equipment and etc.
- The power supply which is used to drive weather peristaltic pump, stirrer, data logger must be guaranteed to run continuously.
- Related to the changes in temperature either the temperature increase or decrease, really there are in the certainty give to quality of product, in this system degree of particle size , such in mono disperse or poly disperse.
- The nucleation and growth of particle formation in co-precipitation synthesis, really depend not only on both temperature and pH parameter but also previous pH, steady state pH, speed of reactant homogenize and other of influent of environment. For example if the stirrer rotation is less the reactant not homogeneous so that the pH is not the same every time. This may illustrate the concentration yield is uneven. On the graph will appear jagged or saw tooth shape, if previous pH is too high the Avrami graph tend shape on the left side, reversely the Avrami graph tend gently sloping to right.
- From the chart of Lammer-Dinegar above, the initial pH of the alkaline solution will determine both homogenize and particle size of yield. If the initial pH is around 12.00 to 13.00 while approximately 1.00 pH reactant, The particles formation reaction and precipitation process will take place relatively quickly. This will have an impact on the coagulation process so that the homogeneity of the particle will be low.
- The synthesis of mono dispersed, uniform, and narrow size distributional Fe_3O_4 NPs (the diameter of NPs was 8.5 ± 1.3 nm) by co-precipitation without surfactants, there action in an aqueous solution with a molar ratio of FeII/FeIII= 0.5 and a pH = 11–12, and the colloidal suspensions of the magnetite can be then directly oxidized by aeration to form colloidal suspensions of c-Fe2O3 [10,11].It was able and easy to use FIS method.
- Determination of isothermal or non-isothermal system will determine whether or not a complicated system equipment, measurement systems and data processing systems. Using isotherm process has to Avrami and Arrhenius equation with reactor bath must in adiabatic system. Using Non Isothermal has to Avrami –Ozawa Equation and must use reactor bath have perfectly heat isolator.

6. CONCLUSIONS
The networking of flow injection synthesis –FIS methods were complicated whether isothermal or non isothermal. The system require not only satisfy equipments but also automatic record measurement device to support compactness of process pH and temperature measurement.

The FIS method able of magnetic material base on the chemical co-precipitation method. Using of non-isothermal system is recommended for researchers put forward the economical and practicality.

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