Paraffin Wax: The Effect of Particles on Crystallisation Kinetics

By

Raja Mohammad Arif b Raja Hassan

A project dissertation submitted

in partial fulfilment of the requirement for the

BACHELOR OF ENGINEERING (Hons)

(PETROLEUM ENGINEERING)

JANUARY 2014

Universiti Teknologi PETRONAS
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CERTIFICATION OF APPROVAL

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Approved by,

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(Dr Lukman b. Ismail)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

JANUARY 2014

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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(RAJA MOHAMMAD ARIF B RAJA HASSAN)

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ABSTRACT

This project is mainly about to study the effects of different particles properties on the crystallisation kinetics of paraffin wax. In the oil and gas industry, the crude oil that have a high amount of wax is considered a hassle as it is easily deposited in the pipeline and increase the pump load which resulting in increasing of energy consumption. Sometimes, there is some salt particles extracted along with the crude oil during production as well as sand particles. Thus, it is important to observe and study how these particles with different properties can affect the growth and dimensions of the wax deposits. The properties of the particles such as different mass, different salt type and grain size will be the manipulated variables for this project. These data results is then inputted into the Avrami equation to observe the growth rate and crystal dimensions.

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CHAPTER 1

INTRODUCTION

1.1 Background Study

The paraffin wax crystallisation is one of the main problems in the pipeline system as they will block the pipeline and stop the fluid from flowing. Usually, the oil is pumped continuously from the platform to the land using the subsea pipelines. When the productions stops due to well testing or technical failure, the heat will easily dissipates to surrounding and cause decreasing in temperature. This phenomenon will cause the crystallisation to occur especially when the crude oil have a high amount of wax content.

This project is mainly to study about the effects of salt and sand particles on the crystallisation kinetics of paraffin wax. However, this project is focusing more on the crystallisation process of the waxy crude oil that contains a lot of salt and sand particles extracted from the formation. Thus, the properties of the particles will be changed according in this project in term of amount, type and sizes. This includes on how the different amount of salt crystal and different surface area of the particles can affect the crystallisation process of paraffin wax contained in the crude oil.

This project also covers the effect of salt type and particles size on the crystal growth. During crystallisation process, the nucleus of the crystal are commonly formed through a process called nucleation. However, for this cases, the nucleus for the crystallisation will be the salt and sand particles. As the temperature drops below its Wax Appearance Temperature, the monomers or a crystals will be starts to be deposited on top of the nucleus and the growth will be increasing with time.

By using the Avrami theory, it is possible to estimate the dimension and the growth of the crystal. From this, we can identify whether the crystal formed with or without the present of these particles is actually the same or not. From this result, we can identify which properties of the particles that can affect the crystallisation kinetics. The crystal strength is depending on the texture or dimension of the crystal growth which can be determined by this analysis.

1.2 Problem Statement

The particles can behave differently in the crude oil. The salt especially can exist in two forms together with crude oil which are either as a salt solution or salt crystal. Most of the salt solution exist as emulsions in the crude oil can usually washed out by the brine. However, this salt crystal mostly remained in the crude oil as there is a thin layer of oil is encapsulating these crystal that prevent the salt from contacting and dissolving in the brine. The salt crystal and sand can acts as a nucleus for the wax crystallisation and can somehow change the properties of the deposits. Thus it is essential to understand the effect of those particles on the crystallisation kinetics.

1.3 Objective and Scope of Work

1.3.1 Aim and Objectives

The aim of this project is to study the effect of different salt properties on paraffin wax crystallisation kinetics.

The experiments will be conducted based on the following objectives:

- To study the effects of salt concentration on wax crystallisation kinetics
- To study the effects of salt type on wax deposition
- To study the effects of particle size on nucleation process.

1.3.2 Scope of Work

The scope of studies in this project would be entirely experimental, in which most of the experiments will be conducted in the laboratory using the chemical either purchased or already inside the lab. This experiments is conducted to see whether the crystallization process is affected by the particles in term of quantity, grain size and salt type.

CHAPTER 2

LITERATURE REVIEW

2.1 Paraffin Wax

Paraffin wax deposition is one of the common problems in the pipeline especially when the pipe is deep below the sea level (Johnsen S.G et al., 2011). As the temperature of the sea level is very low, which is nearly about 4C, the fluid flowing through the pipe is easily cooled down. For the fluid that contains a certain amount of paraffin dissolved, the decrease in temperature may cause them to crystallize when the temperature falls below the Wax Appearance Temperature (WAT) and deposited at the pipeline wall (Couto G. H., 2006). The deposition of the paraffin wax crystal will narrow the pipeline diameter thus making the fluid harder to flow through it. This also can happen in the platform pipeline and also inside the well tubing especially during well testing such as build-up test.

In the oil and gas industry, the crude oil containing salt will be treated using a tools called desalter that can effectively remove most of the salt contained in the crude oil before it enter the oil refinery. This is important as the salt can cause serious corrosion problems to the equipment especially refinery as it is operating under high pressure and temperature. However, this equipment usually installed on the mainland which means that the crude oil containing the salt will be transported through the pipeline from the platform.

There are two ways on how the salt is mixed with the crude oil which are through emulsification with salt solution and direct contact with the salt particles (Voorhees, 1946). During production, the crude oil is sometimes produced along with water that can reduce the amount of salt emulsion with crude oil. When the brine is moving along side with crude oil, it will wash out the salt emulsion that is contained in the crude oil earlier. This will remove the amount of emulsion significantly. However, the salt particles is very hard to remove due to the existence of thin oil layer that encapsulates the salt crystal. This oil layer protects the salt in crystal form by preventing the water from contacting the salt.

2.2 Wax crystallisation

In the most crude oil, there are several types of primary hydrocarbon wax such as paraffin wax (C18-C36) and naphthenic hydrocarbons (C30-c60). These wax can exist in different states depending on the temperature and pressure as each of them have their own chemical properties. Under specific conditions, these wax will crystallised or form a solid that can cause a lot of problems in the industry. The paraffin wax mostly will crystallised into macrocrystalline wax while the wax from naphthenic hydrocarbon will mostly deposited as microcrystalline wax.

There are two types of crystallisation process which are homogenous crystallisation and heterogeneous crystallisation (Yang J, 2005). The homogenous crystallisation is a process where the nucleus is created through a process called nucleation which can happen either instantaneously or sporadically. The nucleus formed then will acts as a center for crystal deposition. The heterogeneous crystallisation can be induced by adding an external agent or impurity into the substance such as dust or small particles. As the crystallisation condition is fulfilled, the monomer deposition or crystal will starts to grow on these nucleus and the shape or dimensions of the crystal can be determined using an Avrami theory.

2.3 Factors affecting the crystallisation

The paraffin wax crystallisation can be affected by several factors which are temperature, aging and flow velocity. (Wu C.H, 2002). The deposition will not occur as long as the temperature of the fluid is above the WAT. That is why it is important to determine the WAT for the new reservoir fluid so that it is possible to predict the crystallisation process especially during transporting it through the pipelines.

The crystallisation process also depends on the flow rate. The research shows that the deposition rate decreases with increasing in flow rate and proved by Creek et al.(1999) and Singh et al.(2000) using flow loop deposition test where the fluid containing the wax is moved inside a closed loop with different flow rate. The crystallisation also affected by

the aging process because when the experiment is conducted again with zero flow rate, the deposition is still increasing over time. It is also showed that the thermal mass transfer is dominant as the static fluid and the moving fluid have the same deposition rate when it has contact with lower temperature region.

L. Ismail et al shows how the movement of the paraffin wax can affect its crystallisation by measuring the paraffin crystallisation degree with different oscillation and wax content. By gravimetric and volumetric measurement, he stated that the oscillation can promote the growth of the crystal for the paraffin with high wax content while can halted the deposition process if the wax content is low. For the practical applications, the paraffin wax usually exist inside the crude oil and transported together through deep sea pipelines thus it is important that the petroleum wax, which is consist of c18-c90 to be monitored regularly to prevent any clogging within the pipelines. (Srivastava et al., 1993)

Couto G. H et al. speculated that by transporting both reservoir fluid and water through the pipelines, it can reduce the deposition of the paraffin wax by using the basis that the water will wet the pipelines wall and reduce the deposition. From their observation, when the crude oil that have high amount of paraffin have a contact with the cold pipe wall, the deposition can occurs at the pipe wall surface which will eventually reducing the diameter of the pipe. Hsu et. al found out that with the present of water, the deposition rate of the paraffin wax decreases at significant amount. He conducted the experiments by pumping the water and waxy oil together in high pressure flow loop under turbulent flow conditions.

According to Brown et al., the deposition process of paraffin occurs through 2 mechanisms, which are shear dispersion and molecular diffusion. From the observation of the paraffin deposition in the pipeline, most of the wax deposited at the wall of the pipe, which showing that the natural direction of shear dispersion is actually from the pipe wall to the middle of the pipe. The deposition that occurs at high shear rate is observed to be hard and brittle while the deposit at low shear rate is soft and pliable.

2.4 Avrami theory

The changing in phase from liquid to solid for the paraffin wax can be determined using Avrami theory by measuring the volume of the crystal over the total crystal formed with the respect of time. The Avrami is using several assumptions which are the nucleation of crystal is totally random, the crystal is formed whether instantaneously or increasing with temperature, and the crystal is consist of different dimensions. The formula for the Avrami theory is shown as:

$$1 - X = e^{-Kt^{\wedge}n} \qquad \text{(Equation 1)}$$

X is the fraction of the crystallized materials, K is the growth rate and n is the Avrami exponent. This exponent is very sensitive to crystallisation temperature, as the values are changing to respect of temperature. The exponent is a representation of crystal structure and the nucleation process. For example, n=1 represent that the crystal is growing in rod-like structure while n=3 or n=4 corresponds to spherulitic growth from sporadic or instantaneous nucleation (Sharples, A., 1966). For the crystallisation initiated by the foreign particles, the nucleation is assumed to be sporadic. In order to determine the growth rate and Avrami exponent based on the experimental data, the equation 1 is changed into logarithmic equation which shows below:

$$\log[-\ln(1 - X)] = \log K + n \log(t) \qquad \text{(Equation 2)}$$

The equation above represent the straight line that relates -ln (1-X) in Y-axis with the log (t) as X axis, and log K as Y-intercept. The fraction of the crystallized materials, X is done by gravimetric method, which is the amount of crystal formed over different time. These set of data will then regressed into straight lines which is represented by equation 1 thus allowing the value of K and n to be determined. (L. Ismail., 2008).

2.5 Measurement tools

Brown et al. (1993) stated that most of the deposition experiments are done using two common apparatus which is cold finger and deposition loop. He stated that the deposition rate is not possible to be measured using cold finger as the total amount of deposition is only available at the end of the test. Thus, this apparatus is not suitable to be used in determining the effect of water salinity to the deposition rate. Ismail L. (2007) is using a new apparatus to study the effect of wax content on the crystallisation process. He proposed that the external motion or energy applied to the paraffin liquid will somehow affect its crystallisation process. The apparatus is built by attaching the test tube containing the paraffin wax into the motor with adjustable speed and frequency. Wu et al. (2002) is using cold disk to study the effect of flow rate and temperature on the crystallisation process. By keeping the temperature of the cold disk constant, the speed of the impeller will represent the flow rate of the paraffin wax as it is rotating with increasing speed. The amount of crystal deposited at the cold disk will be in the function of flow rate with constant time.

The crystal or wax deposit is studied using a J-tube with a mercury to determine the changes in the density of the fluid. As the fluid turns into solid or crystal, the density will change depending on the structural integrity of the crystals. This can acts as an early indication to see whether the crystal formed have a strong structure or not. Another tools to calculate the deposition process is by using an equipment called Differential Scanning Calorimetry (DSC). This equipment have a sensor that can capture the value of heat dissipated by the fluid. As we already know, the liquid needs to liberate a certain amount of heat in order to turn into solid form which is called the heat of fusion. The equipment is capturing how much the energy is removed by the molecules in order for it to turn into crystal. The liquid wax that needs to liberate a higher amount of heat energy to turn into wax deposits means that the growth rate is slower assuming the heat dissipation rate is constant throughout the experiment.

CHAPTER 3

METHODOLOGY

3.1 Research Methodology

This project is consist mainly of experimental work with some calculations to determine the kinetics of the crystallisation process occurred during the experiments. The experiment is done in the batch mode to simulate the continuous process of wax crystallisation.

3.2 Experiments Set up
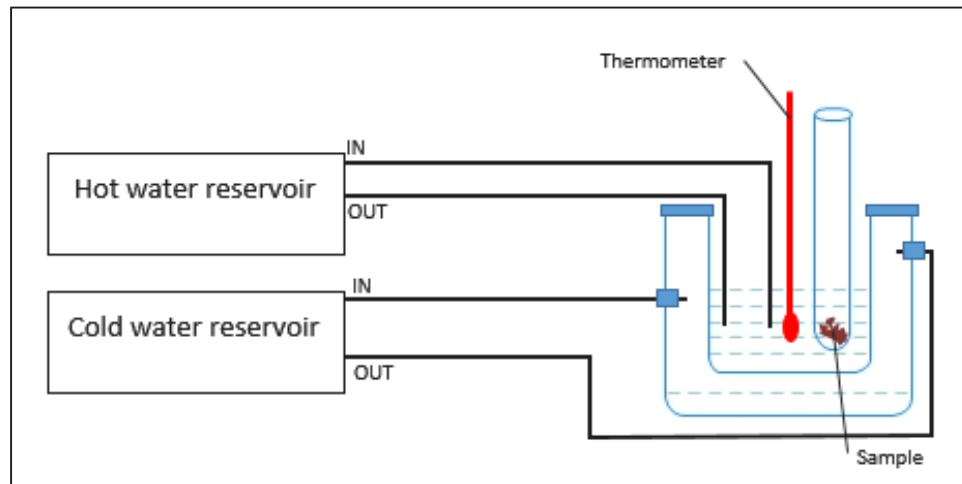
Figure 1: Experiment set up for wax deposition

The experiment is set up as shown in figure above. The water bath temperature is controlled by the machine to be kept slightly above the Wax Appearance Temperature. During cooling down, the constant cooling is achieved by pumping the cold water to cool the water bath. The temperature drop will cause the waxy oil sample to crystallise.

The experiment is done in batch mode as it is easier to control and the fact that the fluid is easily reproducible to simulate the continuous experiments. The experiments is also done to study the crystallisation based only on the temperature effect as this project is used to simulate the deposition of static waxy fluid which is encountered in the real field operations such as during shut-in well, maintenance and technical failure.

3.3 Procedures

3.3.1 Objective 1: To study the effect of different salt content to crystallisation kinetics

In order to study the effect of different amount of salt on the crystallisation process, the experiment is done by mixing the paraffin wax with different amount of salt crystal. For this purposes, the sodium chloride is sprayed directly into the powdered paraffin wax to simulate the salt crystal entrapped inside the crude oil or wax. The test tube will have the fixed amount of powdered paraffin wax which is grounded beforehand to speed up the melting process and allow the salt to mix easily during melting process.

Amount of salt (grams)	Percentage of salt (%)
0.14	1
0.26	2
0.4	3

Table 1: The amount of salt with its corresponding percentage with paraffin wax.

Steps:

1. The salt is weighted according to the table above.
2. The paraffin wax of 5g in mass with 10ml of diesel as a model oil is put into the three test tube.
3. All the test tube will be put inside the water bath until all the solid turns into liquid. Then, the salt measured earlier is splashed into the test tube before returned into the water bath.
4. After all the paraffin wax melts completely again, the test tube is taken out and the water bath is cold down by a cold water regulated by chiller with temperature at 10C and the timer is started.
5. After 2 minutes interval, the liquid wax will be taken out through gravimetric method and weighted.
6. The liquid wax and deposit then recombined and reheated under water bath to allow it melted completely again.
7. Steps 4 is repeated but with additional 2 minutes.
8. Steps 4, 5 and 6 is repeated until all the liquid turns into solid.

3.3.2 Objective 2: To study the effect of salt type to crystallisation kinetics.

This experiment is done in order to identify the effect of salt type to the crystallisation kinetics. Based on several research, the crystallisation is induced by adding a foreign agent into the sample such as dust particles. The significance of this objectives is that we will be able to identify whether the crystallisation process is dependent on the salt type or not. For this experiment, there will be 2 types of salt used, which are sodium chloride (NaCl) and calcium chloride ($CaCl_2$).

The reason why these two types of salt is used is because they are commonly produced along with the crude oil. For this experiment, the size is kept within a certain range of particles size using a sand sieve to make sure that the size is not affecting the end result of this experiments.

Steps:

1. A sodium chloride and calcium chloride is weighted first to make sure both of them have the same mass before each of them is added into their respective test tubes.
2. The paraffin wax of 5g in mass with 10ml of diesel as a model oil is put into the two test tube.
3. Then, both of the test tube will be put inside the water bath until all the solid turns into liquid. Then, the salt is splashed into its respective test tube.
4. After all the paraffin wax melts completely again, the test tube is taken out and the water bath is cold down by a cold water regulated by chiller with temperature at 10C and the timer is started.
5. After 2 minutes interval, the liquid wax will be taken out through gravimetric method weighted.
6. The liquid wax and deposit is recombined and reheated using the same water bath until it becomes liquid again.
7. Steps 4 is repeated but with additional 2 minutes.
8. Steps 3, 4 and 5 is repeated until all the liquid turns into solid.

3.3.3 Objective 3: To study the effect of grain size to the crystallisation process

This experiment is conducted to determine the relationship of the grain size with the growth rate and dimensions of the crystal formed. This is important as some crude oil is producing along with the sand and salt from the formation with different grain size. As these particles can act as the nucleus for the waxy crude oil to crystallise, this objective is required to determine the properties of the crystal formed by the assistance of these different grain size particles.

The experiment is conducted by using two group of grain size which are 0.425mm and 0.6mm. The relatively big grain size is chosen so that it can be visible by naked eye.

Steps:

1. The 0.425mm and 0.6mm sand is weighted first to make sure both of them have the same mass.
2. The paraffin wax of 5g in mass with 10ml of diesel as a model oil is put into the two test tube.
3. Then, both of the test tube will be put inside the water bath until all the solid turns into liquid. Then, the salt is splashed into its respective test tube.
4. After all the paraffin wax melts completely again, the test tube is taken out and the water bath is cold down by a cold water regulated by chiller with temperature at 10C and the timer is started.
5. After 2 minutes interval, the liquid wax will be taken out through gravimetric method weighted.
6. The liquid wax and deposit is recombined and reheated using the same water bath until it becomes liquid again.
7. Steps 4 is repeated but with additional 2 minutes.
8. Steps 3, 4 and 5 is repeated until all the liquid turns into solid.

3.4 Calculations on Crystallisation Kinetics

From the experiment, the time taken for the experiment will be constantly increasing with 2 minutes interval for each time step. After each interval of time, the liquid paraffin will be separated from the sample using gravimetric method and the crystallized wax will stay in the test tube. The volume of the collected liquid paraffin will be measured.

$$X = \frac{volume\ of\ wax\ crystallized}{\text{Total crystallized wax}} = \left(\frac{total\ wax\ volume - volume\ of\ collected\ wax}{\text{Total crystallized wax}}\right)$$

The data recorded will show that the percentage of deposit to be increasing over time until all the liquid inside the sample turns into solid after some time. For the sample with different salt properties like the one that will be conducted in this project, it is predicted that the value of deposits over time will be quite different as shown in figure below.
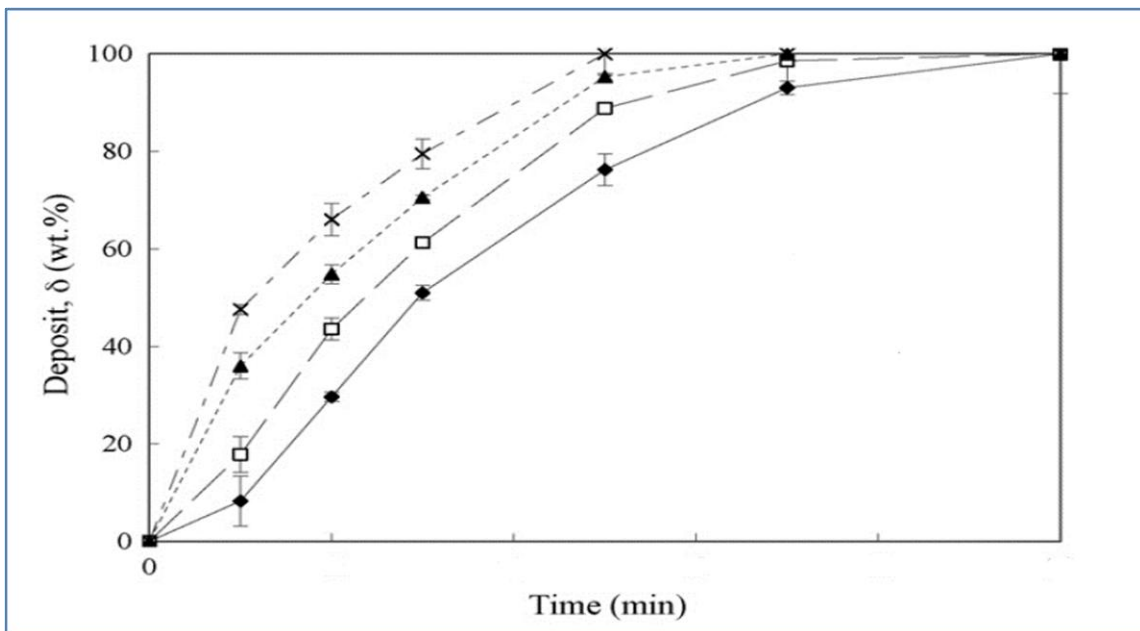
Figure 2: The percentage of wax deposited vs. time

Time taken (min)	Deposits fraction (%)	log (- ln (1-X))	log (time)
x	m	-	-
y	n	-	-
z	100	-	-

Table 2: Example of data obtained by the experiment

Table 2: The recorded and calculated data for wax deposits fractions with its corresponding time.

From the data of time taken with its corresponding wax deposit fractions, we will calculate the values of log (- ln (1-X)) and log (time) and plot them under Cartesian graph. The data set that is plotted then regressed into a straight line which can be represent by the equation as shown below. In the equation, the log K represent the y-intercept while the n represent the slope of the line.

$$\log[-\ln(1-X)] = \log K + n \log (t)$$

Thus, from the equation above, it will be possible to determine the value of K which is the growth rate of the crystal and Avrami exponent, n that represents the dimensions of crystal growth.

3.5 Summary of methodology

A fixed amount of paraffin wax is added into each test tube

The different amount of NaCl is added into the test tube after the wax is melted completely.

NaCl and $CaCl_2$ is added into their respective test tube with the same amount and same range of grain size.

The sand is separated into 0.425mm and 0.6mm grain size using sieves before added into their respective test tube.

The test tube is put into the water bath to let the paraffin wax to melt and stirred.

The test tube with the water bath is put into the chill water to simulate the cooling for 2 minutes interval. Then, the liquid paraffin is separated gravimetrically and weighted.

The steps above is repeated but with additional 2 minutes on top of the previous time. Thus, the time will be increasing at constant time interval until sample turns completely into solid which means the deposit fraction turns 100%.

The deposit fraction is denoted by X. The X is in the function of time.

Using Avrami theory, the K and n is determined by plotting the values of $\log(-\ln(1-X))$ versus $\log(\text{time})$

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Wax Deposition vs. Time

The experiment is conducted according to the methodology mentioned above.

4.1.1 To study the effect of different salt content to crystallisation kinetics

The salt used is Sodium Chloride (NaCI) with different volume. The salt is sprayed into the test tube after all the paraffin is melted due to the heat from water bath at 56C. The weight of the deposit is calculated by subtracting the total mass by the mass of the liquid paraffin separated using gravimetric method for every interval.

The data for the experiment can be seen in the table below.

Time	Weight liquid (g)	Deposit weight fraction	Deposit %
0	13.77	0.000	0.0
2	13.24	0.038	3.8
4	9.25	0.328	32.8
6	5.61	0.593	59.3
8	2.85	0.793	79.3
10	0.49	0.964	96.4

Table 3: Data obtained from sample with 1% NaCI

Time	Weight liquid (g)	Deposit weight fraction	Deposit %
0	12.9	0.00	0.0
2	12.06	0.07	6.5
4	7.95	0.38	38.4
6	3.97	0.69	69.2
8	1.28	0.90	90.1
10	0	1.00	100.0

Table 4: Data obtained from sample with 2% NaCI

Time	Weight liquid (g)	Deposit weight fraction	Deposit %
0	13.1	0.00	0.0
2	12.21	0.07	6.8
4	8.21	0.37	37.3
6	3.8	0.71	71.0
8	0.29	0.98	97.8
10	0	1.00	100.0

Table 5: Data obtained from sample with 3% NaCI

The plot of the weight percent vs. time can be seen in the figure below.

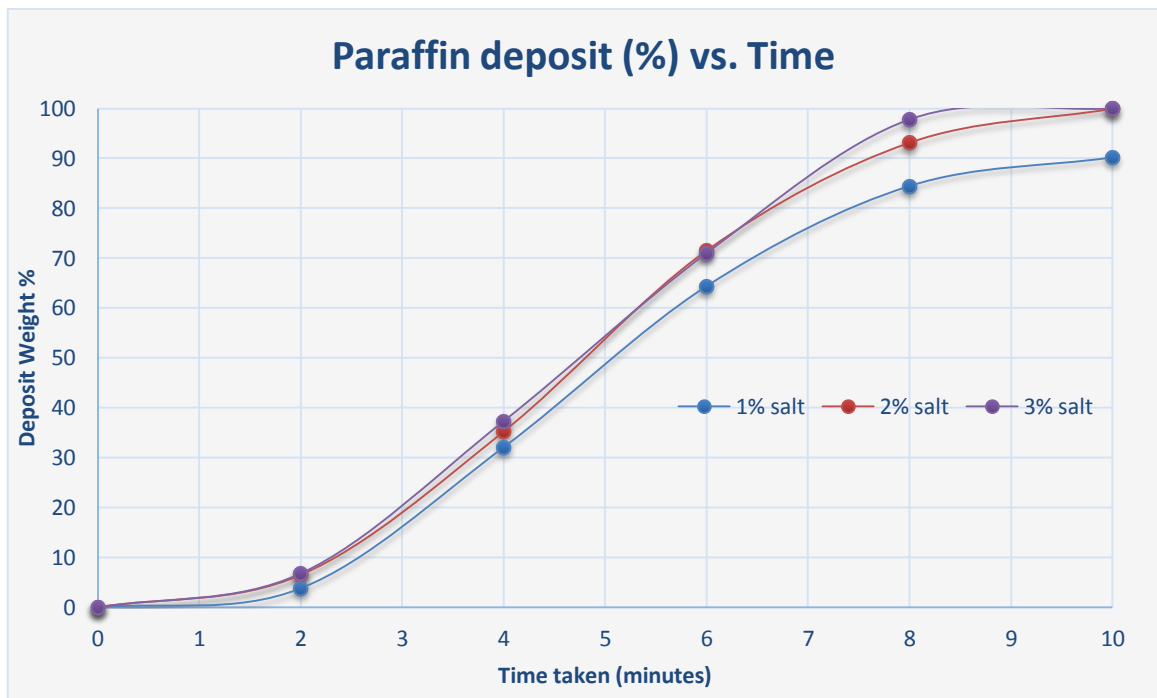*Figure 3: The percentage of paraffin weight deposit vs. time for different salt concentration*

From the plot above, we can see that the amount of deposition increases with increasing in salt particles. This is consistent with our early hypothesis that the crystallisation rate is faster as the amount of particles increases in the system. However, from the plot, we can

see that the deposit for the oil sample with 2% salt have higher deposit in the 6th minutes compared to oil sample with 3% salt. This is due to the differences in time for the sporadic nucleation to occur. It is theorized that the sporadic nucleation will take longer to occur in the sample with higher amount of particles. This is due to the differences in energy needed for the crystallisation. The energy needed for the particles to deposit onto the surface of the solid particles (sand particles) will be lower compared to the process of creating new solid phase from liquid phase. This can be seen in the sudden increases in the wax deposition for the oil sample with 3% salt in the 8th minutes due to late sporadic nucleation that occurs in 6th to 8th minutes compared to the oil sample with 2% salt particles which probably occurs in the 4th to 6th minutes.

4.1.2 To study the effect of different salt type to crystallisation kinetics

For this purposes, the experiment is done by putting two different kind of salt into the samples as explained in the methodology section. The salt used are Sodium Chloride (NaCI) and Calcium Chloride ($CaCI_2$). The result for the paraffin deposited vs. time can be seen in the table 6 and 7 below.

$CaCI_2$:

Time	Weight liquid (g)	Deposit weight fraction	Deposit %
0	13.09	0.00	0.0
2	12.12	0.07	7.4
4	9.74	0.26	25.6
6	4.5	0.66	65.6
8	0.6	0.95	95.4
10	0	1.00	100.0

Table 6: Data obtained from sample with $CaCI_2$

NaCI:

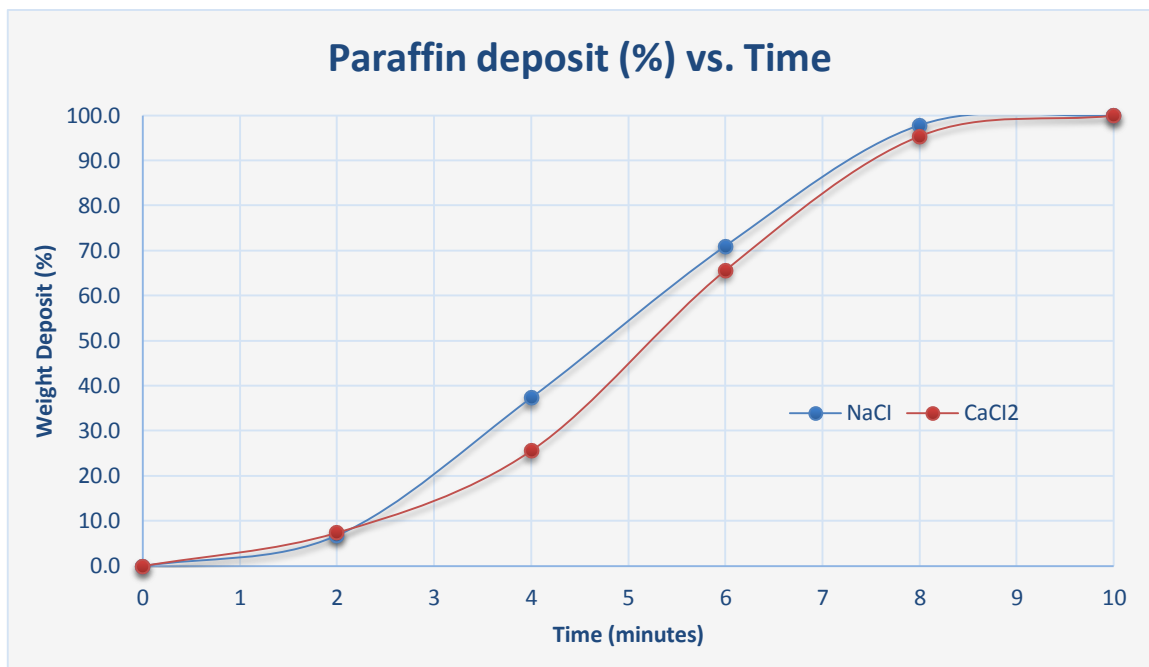| Time	Weight liquid (g)	Deposit weight fraction	Deposit %
0	0	0.00	0.0
2	12.21	0.07	6.8
4	8.21	0.37	37.3
6	3.8	0.71	71.0
8	0.29	0.98	97.8
10	0	1.00	100.0

Table 7: Data obtained from sample with NaCI

Figure 4: The percentage of paraffin weight deposit vs. time for different salt type

From the figure 4, we can see that the paraffin deposit for $CaCI_2$ shows slightly different curve pattern compared to NaCI. This observation contradict with our early hypothesis that the deposition rate and process should be same with each other. This is because the crystallisation process is dependent on the physical properties of the particles rather than chemical. This may be due to the error in the measurement for the $CaCI_2$ as it has hygroscopic properties (absorb moisture from air). This means that during measurement, some of the salt turns into liquid and causing some particles to stick together. This problem can caused some uncertainty in the grain size of the salt added into the test tube which

may affect the crystallisation kinetics. The highest error tends to occur in the 4th minutes. This is due to the method of experiment which is done in the batch mode. As the liquid collected in the 2nd minutes reading and deposit is re-mixed into the test tube to repeat for the next timesteps, this causes the $CaCl_2$ particles to stick to each other due to the salt properties. The existence of the crystal growth from the sporadic nucleation causes the amount of wax deposit to be nearer to each other at the end of the crystallisation process despite having high differences in the beginning.

4.1.3 To study the effects of particle size on nucleation process.

For this objectives, the particles used is sand with different grain size. The sand is divided into two distinctive groups of grain size by using mesh filter which is 0.0425mm and 0.06mm. The sand is used for this objectives due to its inert properties compared to salt as salt has a tendency to react with moisture in the air and compromised the grain shape during filtration. The experiment is conducted and the result for the paraffin deposited vs. time can be seen in the table 8 and 9 below.

Time (minutes)	Weight liquid (g)	Deposit weight fraction	Deposit %
0	13.12	0.00	0.0
2	12.11	0.07	7.5
4	8.78	0.33	32.9
6	4.45	0.66	66.0
8	0.52	0.96	96.0
10	0	1.00	100.0

Table 8: Data obtained from sample with sand grain size = 0.425mm

Time (minutes)	Weight liquid (g)	Deposit weight fraction	Deposit %
0	13.08	0.00	0.0
2	11.97	0.09	8.6
4	9	0.31	31.2
6	4.32	0.67	67.0
8	0.71	0.95	94.6
10	0	1.00	100.0

Table 9: Data obtained from sample with sand grain size =0.6mm
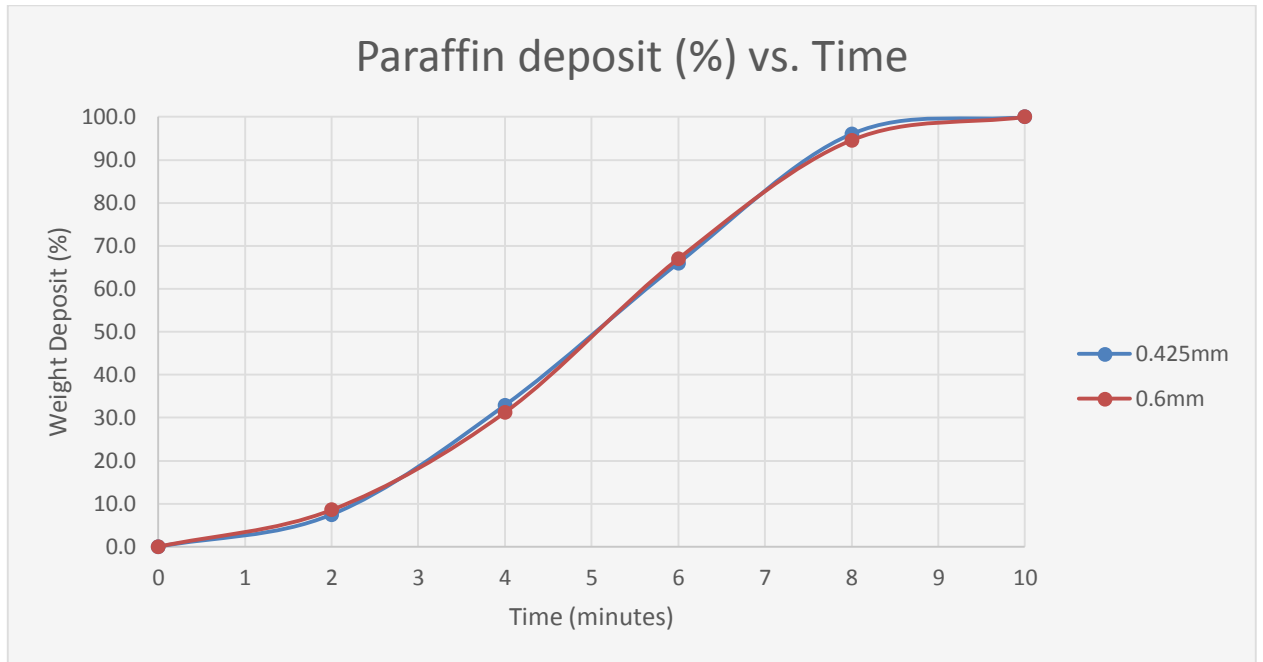
Figure 5: The percentage of paraffin weight deposit vs. time for different grain size

From the figure 5 above, we can see that the crystallisation process between both samples are quite similar. However, when we observe it carefully, the sample with sand of 0.6mm grain size shows faster crystallisation growth in the beginning compared to the sample with 0.425mm grain size. This is probably due to the higher surface area covered by bigger diameter particles which allows more crystal to deposit on its surface.

At 2nd minutes until 4th minutes, the deposition shows lower rate compared to 0.425mm sample. This is due to some of the shape with bigger particles to drop to the bottom of sample due to gravity. As the particles is not evenly distributed for the sample with 0.6mm compared with sample of 0.425mm sand, the sporadic nucleation took shorter time to occur. This can be seen from the 4th minutes until 6th minutes when the deposition rate for the 0.6mm sample becomes faster compared to 0.425mm sample despite having less deposition in the 4th minutes. However, the deposition in the 0.425mm sample starts to have their own sporadic nucleation in the 4th to 6th minutes which resulting faster deposition in the 8th minutes reading. However, in order to determine its growth rate and dimension of growth, the Avrami analysis is required.

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4.2 Avrami calculation

4.2.1 Avrami calculation for samples with different salt concentration

In order to determine the growth rate (K) and the Avrami exponent (n), the Avrami equation is applied to the data. By plotting Avrami term, -ln (1-X) vs. time in logarithmic graph, the K and n can be determined.

$$\log[-\ln(1-X)] = \log K + n \log (t)$$

From the equation above, we can determine growth rate from the y-intercept and the Avrami exponent from the slope of the straight line represented by the data sets. The plot for the equation is shown in the figure below.
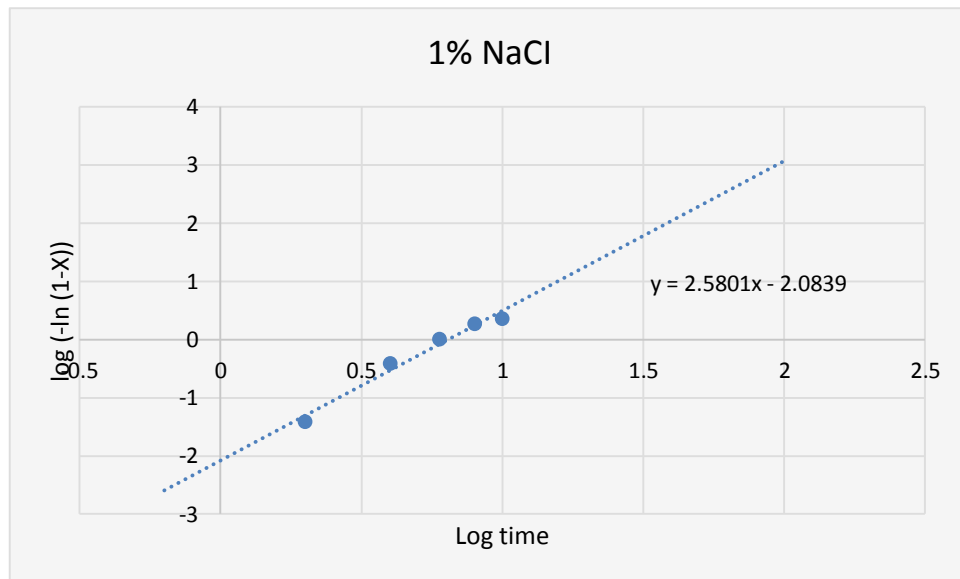
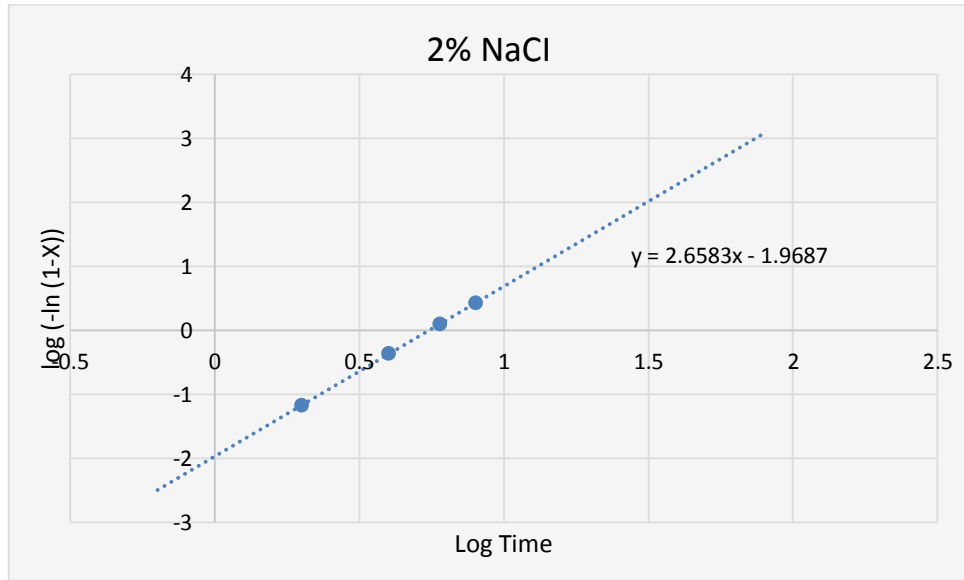*Figure 6: Avrami plot on 1% salt amount*
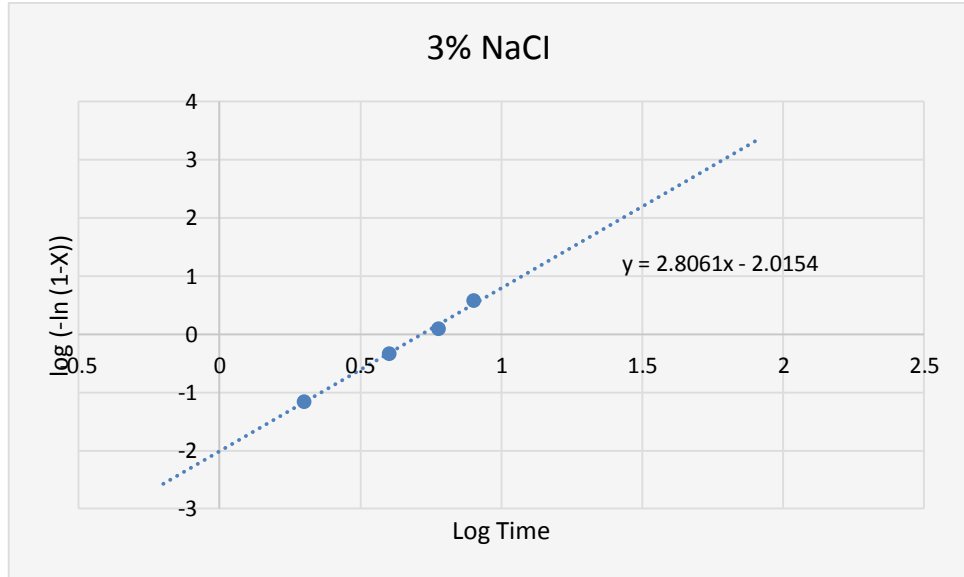
Figure 7: Avrami plot on 2% salt amount

Figure 8: Avrami plot on 3% salt amount

From the equation of the straight line created by the data, we can determine the growth rate, K and the Avrami exponent, n.

Salt content (%)	Growth rate, K	Avrami exponent, n
1	0.008243279	2.5801
2	0.010747316	2.6583
3	0.009651615	2.8061

Table 10: Growth rate, K and Avrami exponent, n calculated for sample with different salt amount

From the table 10, we can see that the growth rate for both samples is almost identical to each other with Avrami exponent to be increases as the salt content increases. The Avrami exponent determine the nature of crystal growth and dimension of the crystal deposit. As the exponent calculated is about +-2, we can conclude that the crystal formed by all the samples have the same dimensions.

The exponents shows increasing in value as the number of particles increases. This is due to the higher amount of deposit formed by the foreign nucleus compared to other sample. As the number of particles increases, the distribution of particles in the sample is broader, thus slowing down the sporadic nucleation from taking place during crystallisation. The dimension of growth from self-generating nucleus through sporadic nucleation is mostly 1 dimensional compared to dimension of crystal growth from the foreign particles which is in 2 dimensional.

4.2.2 Avrami calculation for samples with different salt type

The method of calculation is the same as above using Avrami equation. The data is taken from the samples with NaCI and $CaCI_2$ under same procedure. The plot of Avrami term calculated using those data is shown in the figure below.
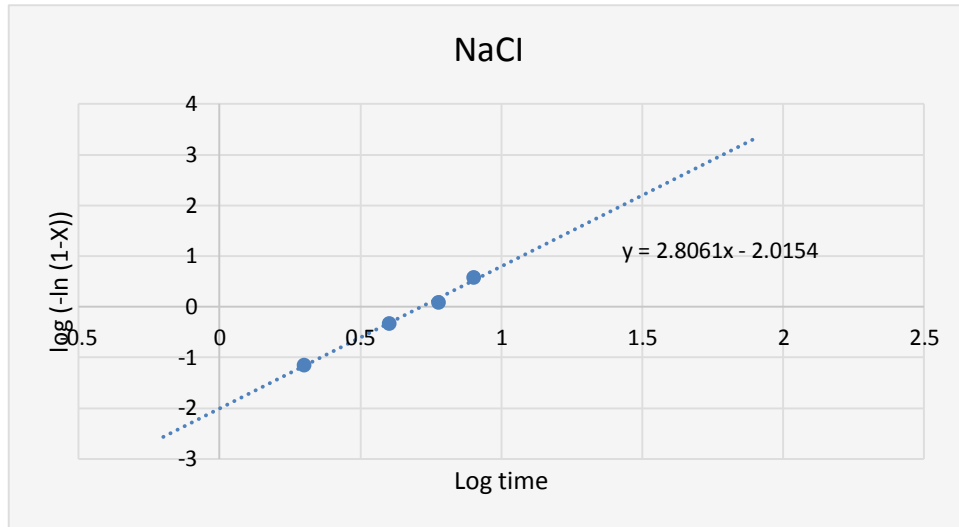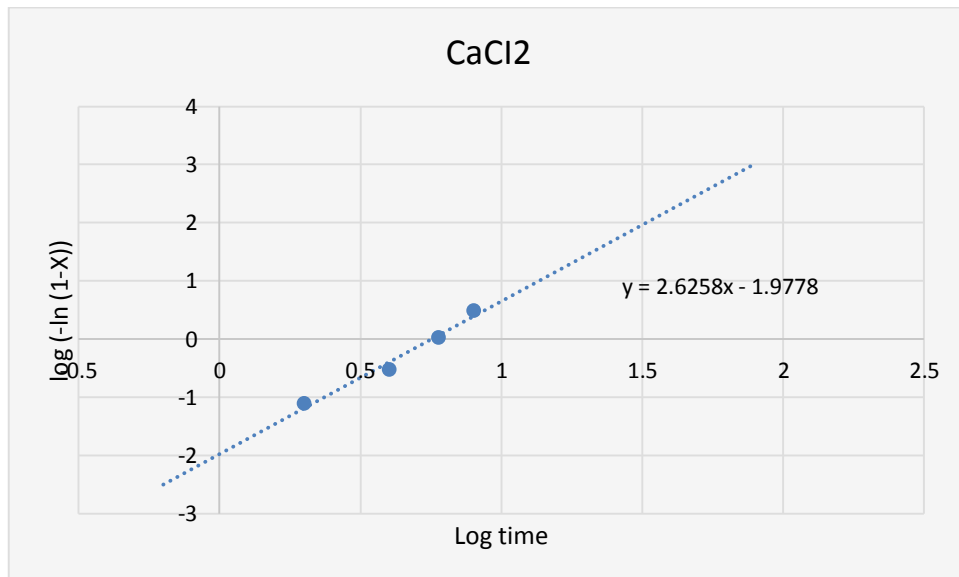

Figure 9: Avrami plot on samples with NaCI

Figure 10: Avrami plot on sample with CaCI2

From the equation of straight line representing the data set, we can determine the growth rate, K and the Avrami exponent, n.

Salt type	Growth rate, K	Avrami exponent, n
NaCI	0.009652	2.8061
CaCI$_2$	0.010524	2.6258

Table 11: Growth rate, K and Avrami exponent, n calculated for sample with different salt type

From the result above in table 11, we can conclude that the sample with CaCI$_2$ have faster crystal growth rate. However, the differences is not significant. Based on the Avrami exponent, both of the samples shows the Avrami exponent to be around 2, which indicates that the dimensions of the crystal growth formed by both samples are also nearly identical to each other. However, as salt particles is not soluble in oil, the growth rate and Avrami exponent is predicted to be the same for both sample. The error or differences in the data calculated is maybe due to the CaCI$_2$ as it has hygroscopic properties (absorb moisture from the air). This will cause the particles to stick to each other and some of it will melted once they exposed to the air causing some error in the results obtained.

The higher Avrami exponent for the CaCI$_2$ is due to the nature of the particles. As they tends to stick to each other rather than moving independently with each particles in the sample, the distribution of the particles is not as good as the sample with NaCI. The sample with good distribution of particles will takes longer to undergo sporadic nucleation as the deposition process prioritize the foreign particles for the deposition due to lower energy barrier. This causes the deposit that grow from the foreign particles to be more in the NaCI sample compared to CaCI$_2$ thus explaining the higher Avrami exponent.

4.2.3 Avrami calculations for sample with salt of different grain size.

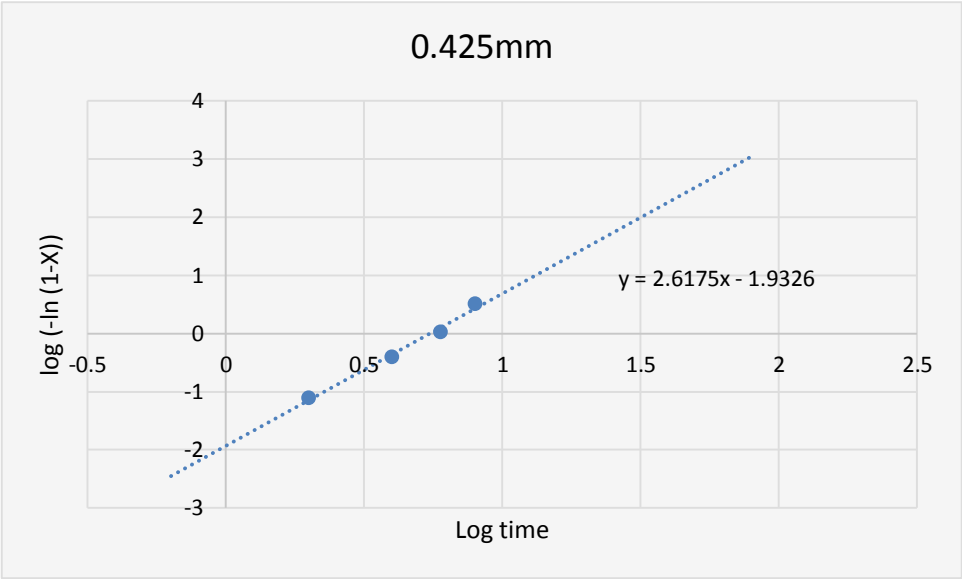The method of calculation using the Avrami formula is the same with the other two objectives.

Figure 11: Avrami plot on sample with salt of 0.425mm grain size
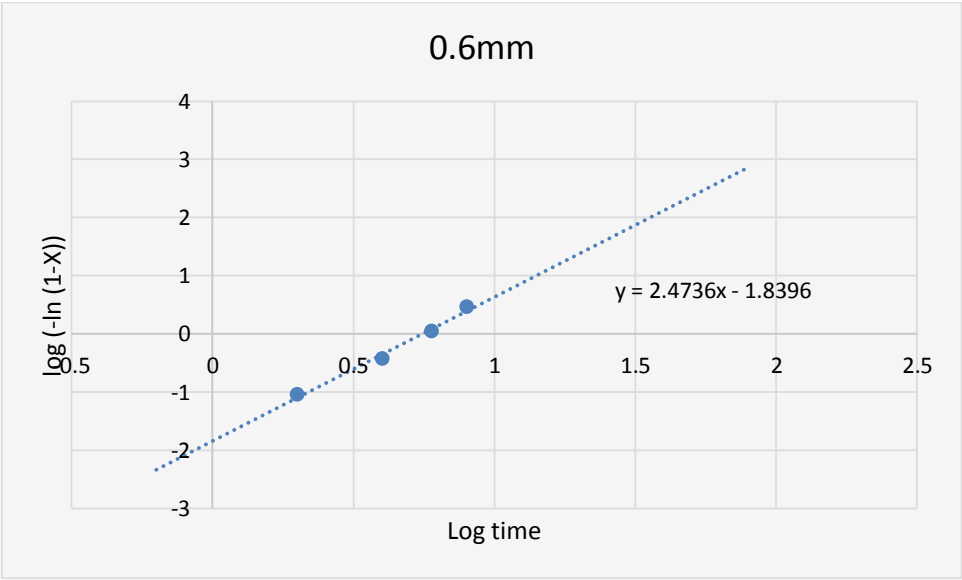

Figure 12: Avrami plot on sample with salt of 0.6mm grain size

From the plot, we can see that the slope and y-intercept is almost the same which represent the Avrami exponent, n and log K, where the K represent the growth rate of the crystal from the sample.

Sand size	Growth rate, K	Avrami exponent, n
0.425mm	0.011679	2.6175
0.6mm	0.014468	2.4736

Table 12: Growth rate, K and Avrami exponent, n calculated for sample with different grain size

The table 12 shows that the sample with smaller grain size has lower growth rate compared to bigger grain size. This is due to the bigger surface area of the particles. As the monomer of the crystal will grow on the particles surface and increases over time, having bigger surface area will speed up the process. However, as the grain size is not that different from each other, the differences in growth rate between those two samples are low. The selection of the grain size is chosen to be not that different between each other in order to investigate the sensitivity of the Avrami exponent.

From the table, the Avrami exponent increases with increasing in grain size. This is due to the differences in the weight of the particles. As 0.425mm sand particles is technically lighter compared to 0.6mm diameter sand particles, the distribution of 0.425mm sand is better compared to 0.6mm. Thus, the sporadic nucleation takes longer to occur in the oil sample with 0.425mm sand. This caused higher percentage of crystal formed by the sand nucleus in the 0.425mm sample compared to 0.6mm sample thus explaining the higher Avrami exponent.

CHAPTER 5

5.1 Conclusion

From the experiment and the Avrami analysis, it is shown that the properties of the crystal changes due to the particles shape and amount. In the simple term, this happen due to increasing in surface area of the particles thus giving the monomer of the crystal to deposit onto it, creating the growth with the particles acting as a center or nucleus.

The Avrami is important to determine the growth rate as the data of deposit vs. time is not constant. This is due to the several mechanism such as secondary nucleation which happen when the sample is cooling down causes abrupt increases in the deposition rate after some time. However, this fluctuating deposition rate can be represented by Avrami growth rate, K which represent the total rate divided by the time taken for it to fully crystallised. Thus, Avrami growth rate, K will represent the average growth rate of the crystal which makes it easier to be analysed.

The Avrami exponent also important as it represent the dimension of the crystal growth. Thus, theoretically, increasing in Avrami exponent will increase the strength of the crystal, thus in this case, the value is not that different with each other. As the value of the Avrami exponent is ranging from 2 to 3, the crystal is predicted to grow in both 1 dimensional (rod) and 2 dimensional (platelets) direction. From the experiment, it is shown that the Avrami exponents tends to be dependent on the particles distribution in the sample.

5.2 Recommendation

The result of the experiment can be improved by using a more sophisticated set up. The thermocouple with computer software is recommended as it can record the temperature accurately during cooling down. Besides, the experiment set-up used for this project is open and conducted in batch mode. This may cause some error in the results obtained due to the heat loss to surroundings. The experiment also can be expanded by considering the dynamic flow of the waxy crude oil.

Besides, it is also important to check the reliability and accuracy of the Avrami using another method or equipment such as Differential Scanning Calorimetry (DSC). This is to determine whether the Avrami method is sensitive to the properties of the oil such as oil composition. Although the Avrami prediction is consistent with the hypothesis, it is essential that the reliability of Avrami calculation to be established using another equipment to confirm the results obtained to be good representative of the sample used.

Besides, the growth dimension of the crystal also need to be verified using a microscope to determine the accuracy of the Avrami. This is important to establish the boundary or the limitation of the Avrami method. As the Avrami is technically faster and cheaper method to investigate the crystallisation kinetics, more experiments need to be conducted with different parameter in order to investigate the potential of the Avrami theory in the industry.

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