ผลของสภาวะการตกผลึกต่อการกระจายอัตราการเติบโตของผลึกน้ำตาลทราย ในสารละลายที่ใช้น้ำเป็นตัวทำละลาย

นางสาวศรีสุดา พฤกษา

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
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THE EFFECT OF CRYSTALLIZATION CONDITIONS ON THE GROWTH RATE DISTRIBUTION OF SUCROSE CRYSTALS FROM AQUEOUS SOLUTIONS

Miss Srisuda Puagsa

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Engineering in Chemical Engineering

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วัตถุประสงค์ของงานวิจัยนี้คือเพื่อให้เข้าใจถึงผลของสภาวะต่าง ๆ ที่ใช้ในการตกผลึกต่อการแจกแจงและการกระจายอัตราการเติบโตของนิวคลีไอ (nuclei) ของผลึกน้ำตาลทราย และตัวล่อผลึก การทดลองแบ่งออกเป็น 3 ส่วนคือ ส่วนที่หนึ่งศึกษาการกระจายอัตราการเติบโต (GRD) ของผลึกนิวคลีไอ (nuclei) ของน้ำตาลทรายในสารละลายน้ำตาลบริสุทธิ์ที่ขึ้นกับอุณหภูมิ อัตราการไหล และความอิ่มตัวยิ่งยวด ส่วนที่สองศึกษาการกระจายอัตราการเติบโต (GRD) ของผลึกนิวคลีไอ (nuclei) ของน้ำตาลทรายในสารละลายน้ำตาลที่ไม่บริสุทธิ์ที่ขึ้นกับความอิ่มตัวยิ่งยวด ชนิดของสิ่งเจือปน และอัตราส่วนของสิ่งเจือปนต่อน้ำ และในส่วนที่สามศึกษาการกระจายอัตราการเติบโต (GRD) ของตัวล่อผลึกบริสุทธิ์ที่ไม่ผ่านการบด และตัวล่อผลึกบริสุทธิ์และไม่บริสุทธิ์ที่ผ่านการบดในสารละลายน้ำตาลบริสุทธิ์ที่ขึ้นกับอุณหภูมิ ความอิ่มตัวยิ่งยวดและชนิดของตัวล่อผลึก

การทดลองได้ออกแบบโดยใช้การวิเคราะห์ความแปรปรวน (ANOVA) เพื่อศึกษาผลของทั้ง 3 ปัจจัย ที่มีต่อตัวแปรตาม 2 ตัว โดยพิจารณาจากค่าเฉลี่ยและค่าสัมประสิทธิ์ความแปรปรวนของการแจกแจงอัตราการเติบโตของผลึกน้ำตาล ตัวแปรแต่ละตัวในทุกการทดลองจะแบ่งออกเป็น 2 ค่าดังนี้ อัตราการไหลแบ่งได้เป็น หยุดนิ่ง และ 40 มล./วินาที อุณหภูมิของการทดลองส่วนที่ 1 และ 3 คือ 25°C และ 40°C และส่วนที่ 2 คือ 20°C และ 25°C ค่าความอิ่มตัวยิ่งยวด ($\Delta T = T - T^*$) จะมีค่าเป็น 10°C และ 5°C สารเจือปนที่ใช้ในการทดลองส่วนที่สองมี 4 ชนิดคือ กลูโคลส และฟรุคโตส ที่มีอัตราส่วนของสิ่งเจือปนต่อน้ำเท่ากับ 0.25 และ 0.5 โซเดียมคลอไรด์ และโพแทสเซียมคลอไรด์ ที่มีอัตราส่วนของสิ่งเจือปนต่อน้ำเท่ากับ 0.2 และ 0.4 ตัวล่อผลึกที่ใช้ศึกษาในการทดลองส่วนที่สาม มีขนาดอยู่ในช่วง 106–150 ไมครอน ทุกการทดลองได้ทำการศึกษาในโฟโตไมโครสโกปิกเซลล์ (Photomicroscopic Cell) และผลึกนิวคลีไอ (nuclei) ได้มาจากวิธีที่เรียกว่า Contact Nucleation ผลึกเหล่านี้จะถูกเลือกแบบสุ่มอย่างน้อย 30 ผลึก เพื่อวัดอัตราการเติบโตและหาการกระจายการเจริญเติบโต (GRD) จากการทดลองพบว่าผลึกน้ำตาลมีการเติบโตด้วยกลไกการเติบโตที่ไม่ขึ้นกับขนาด และแสดงให้เห็นถึงการเกิดการกระจายอัตราการเติบโต (GRD)

ผลจากการวิเคราะห์ด้วยสถิติ พบว่าค่าอัตราการเติบโตเฉลี่ยมีค่าอยู่ระหว่าง 0.113–5.12×10^{-6} มม./วินาที 0.131–1.19×10^{-6} มม./วินาที และ 0.872–10.54×10^{-6} มม./วินาที และสัมประสิทธิ์ความแปรปรวน (C.V.) มีค่าระหว่าง 0.546–0.995, 0.305–0.679 และ 0.20–0.873 สำหรับการทดลองที่ 1 2 และ 3 ตามลำดับ ค่าเฉลี่ยที่คำนวณได้แสดงถึงความเร็วของอัตราการเติบโต และ C.V แสดงถึงการกระจายอัตราการเติบโต ผลจากการวิเคราะห์ด้วย ANOVA ต่อค่าเฉลี่ย พบว่าอุณหภูมิ ความอิ่มตัวยิ่งยวด และชนิดของสิ่งเจือปนมีอิทธิพลมากต่อค่าอัตราการเติบโตเฉลี่ย ในขณะที่อัตราการไหลและชนิดของตัวล่อผลึกมีอิทธิพลน้อยกว่า ผลจากการวิเคราะห์ด้วย ANOVA ต่อค่า C.V. พบว่าในการทดลองส่วนที่หนึ่งไม่มีตัวแปรใดเลยที่มีนัยสำคัญต่อค่า C.V. หมายความว่าการกระจายขนาดมีค่าคงที่ไม่ขึ้นกับตัวแปรใดเลย ในการทดลองส่วนที่สองพบว่าความอิ่มตัวยิ่งยวด ชนิดของสิ่งเจือปน และปฏิสัมพันธ์ของทั้งสามตัวแปรมีอิทธิพลเพียงเล็กน้อยต่อค่า C.V. หมายความว่าการกระจายขนาดมีสาเหตุมาจากปัจจัยดังที่กล่าวมาแล้วข้างต้น ในการทดลองส่วนที่สามพบว่าความอิ่มตัวยิ่งยวด และชนิดของตัวล่อผลึกมีผลเพียงเล็กน้อยต่อค่า C.V. ดังนั้นจึงมีผลเพียงเล็กน้อยต่อค่า GRD ด้วย

สาขาวิชา วิศวกรรมเคมี ลายมือชื่อนักศึกษา _____

ปีการศึกษา 2547 ลายมือชื่ออาจารย์ที่ปรึกษา _____

SRISUDA PUAGSA : THE EFFECT OF CRYSTALLIZATION CONDITIONS ON THE GROWTH RATE DISTRIBUTION OF SUCROSE CRYSTALS FROM AQUEOUS SOLUTIONS. THESIS ADVISOR : ASST. PROF. ADRIAN FLOOD, Ph.D. 124 PP. ISBN 974–533–357–3

CRYSTALLIZATION/GROWTH RATE DISTRIBUTION/GRD/SUCROSE

The objective of this study was to understand the effect of processing conditions on the growth rate distribution, and growth rate dispersion of sucrose nuclei and seed crystals. The experimental was separated into three parts; these involve determination of the growth rate dispersion of sucrose nuclei in pure aqueous sucrose solution as a function of temperature, flow rate and supersaturation; the growth rate dispersion of sucrose nuclei in impure stagnant sucrose solution as a function of supersaturation, type of impurity, and impurity/water ratio; and the growth rate dispersion of uncrushed pure seeds and crushed pure and impure seed crystals of sucrose in pure stagnant sucrose solution as a function of temperature, supersaturation and type of seed crystal.

The experiments used Analysis of Variance (ANOVA) designs, to study the effect of three factors on the response of two parameters, the mean and the coefficient of variation (C.V.) of the crystal growth rate distribution. Each factor of all sections was explored at two levels; stagnant and 40 mL/min for flow rate; temperatures were 25°C and 40°C for the first and the third section, and 20°C and 25°C for the second section; the supersaturation ($\Delta T = T–T^*$) had a high limit of 10°C and a low limit of 5°C. In the second section, there were four types of impurities used – glucose and fructose with impurity/water ratios of 0.25 and 0.5; sodium chloride and potassium

chloride with impurity/water ratios of 0.2 and 0.4. The seed crystals studied in the third section were in the size range between 106μm and 150μm. All experiments are investigated in the photomicroscopic cell, and nuclei were generated by contact nucleation. Contact nuclei were selected randomly, at least 30 nuclei, and their growth rate measured to determine a growth rate distribution. The crystal grew by a size independent growth mechanism, but display significant growth rate dispersion.

From the statistical results, the major considerations are the mean growth rate and coefficient of variation of the growth rate distribution; these parameters varied in the ranges between $0.113–5.12\times10^{-6}$ mm/s, $0.131–1.19\times10^{-6}$ mm/s and $0.872–10.54\times10^{-6}$ mm/s for growth rate, in the three experimental sections; and between 0.546–0.995, 0.305–0.679 and 0.20–0.873 for the C.V. in sections 1, 2, and 3 respectively. The mean growth rate is an average value of the speed of growth, and the C.V. shows how much the crystal growth rate is dispersed. The ANOVA results show that temperature, supersaturation and impurities are strong influences on the mean growth rate, however, flow and seed type are less significant effects. With the ANOVA results on C.V., all factors of the first section do not influence the C.V., that is, the dispersion is independent of all factors. However, in the second part, supersaturation, impurities and the interaction of all factors have a small significant effect on C.V., that is, the magnitude of growth rate dispersion can be affected by these factors in impure solutions. In the third section, supersaturation level and seed type have very small effects on the magnitude of the C.V., and therefore affect the level of GRD.

School of Chemical Engineering Student's Signature _____

Academic Year 2004 Advisor's Signature _____

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Nomenclature

A and B	complex temperature–dependent constants
A_s	surface area of the crystal
a_i	*i*the area for the *i*th face of a crystal bounded by n faces
BCF	Burton–Cabrera–Frank theory
BMG	crushed impure seed crystals
BMP	crushed pure seed crystals
C and *c*	concentration (mass of solute per mass of solvent or solution, or mole or mass of solute per volume of solution),
C^*or c^*	saturation concentration (g sucrose/100 g solution)
C_i	inlet solution concentration
c_i	solute concentration in the solution at the crystal–solution interface
C_o,	outlet solution concentration
ΔC or Δc	different in concentration
CV	coefficient of variation
g_i	surface free energy per unit area of the *i*th face
I/W	impurity/water ratio
k_d	coefficient of mass transfer by diffusion
k_r	rate constant for the surface reaction or integration process
K_G	overall crystal growth coefficient
L	characteristic length or the growth enlargement
L_s	size of seed

Nomenclature (Cont.)

L_p	size of product crystals
$L_{16\%}$	16% of size from a cumulative mass distribution curve
$L_{50\%}$ (or L_M)	50% or median size from a cumulative mass distribution curve
$L_{84\%}$,	84% of size from a cumulative mass distribution curve
ΔL	growth enlargement
m	mass of solid deposited in time t
M	mass of solid
min	minimum
M_p	product crystal yield
M_s	initial mass of seed
n	population density
N	number of crystals
N_s	number of seeds
N_p	number of product crystals
Q_i	volumetric feed rate
Q_o,	volumetric discharge rate
R	crystal growth rate
S	supersaturation ratio
t	time
T	temperature
T^*	solid–liquid equilibrium temperature
ΔT	supercooling

UCP	uncrushed pure seed crystals

Greek Symbols

α	volume shape factor
σ	relative supersaturation
ρ_c	crystal density

Chapter 1

Introduction

1.1 Significance of the Problem

In crystallization processes, the formation of nuclei and the size of the crystals should be controlled, due to the fact that uniform size and crystal shape make the final product more attractive and easier to flow and handle (packaging). Therefore the time and amount of seeding is important, as is temperature control, agitation rates, and time of the withdrawal of the crystals, to obtain the desired size and uniformity of crystals.

There is a summary of sucrose crystal growth in Ullmann's Encycopedia of Industrial Chemistry 6th vol. 34, (2003) that discusses the factors that influence rate of crystallization. For example, the work proposed by D. Schliephake and B. Ekelhof in 1983 suggested that the parameters that influence the crystallization rate of sucrose are purity of solution, temperature and supersaturation. Another example was presented by Vaccari, Mantovani, Squoldino, Aquilano and Rubbo in 1986, about the effect of impurities on the rate of crystallization, which typically cause a decrease in the rate; such impurities are high molecular weight substances (such as carbohydrate polymers), species causing color in the juice, and other sugars such as raffinose and kestose. They proposed that a raffinose concentration of more than 1% could reduce the crystallization rate of sucrose, and result in the formation of needle–shaped crystals.

The first time that growth rate dispersion was recognized as a serious problem in crystallization was in the study of White and Wright (1971). The phenomenon of growth rate dispersion (GRD) has a pronounced effect on the size distribution of crystals in an industrial crystallizer. The mechanism of growth rate dispersion is not completely understood, but it is extremely important for the product size distribution, and must be recognized as an important factor in the analysis of crystallization processes. The prediction and control of growth rate dispersion during crystallization is important if a product with a narrow crystal size distribution (CSD) is required. Growth rate dispersion can occur because of many factors that may not have a clearly understood mechanism: for example, Janse and de Jong (1976) found that fracture pieces in NaCl crystals grew very slowly or not at all, where other contact nuclei grew at a higher rate.

As most crystallization processes are not carried out in pure solutions, the effects of impurities on the kinetics of crystal growth are important. In particular, the growth and shape of crystals are apparently affected by the impurities present in the solution. It is well known that sucrose crystals can have various shapes due to different combination of forms. Occurrences of particular forms depend on the conditions of nucleation and growth. This can be confirmed by the work of Monomaga, Niehorster, Henning, and Ulrich (1996) that presented the effect of impurity on solubility, growth behaviour, and shape of sucrose crystals.

Details of the nucleation of crystals are also very important for product quality: in particular the competition between nucleation and growth will determine the product size distribution and texture of the product. In many food industries, the quality and texture of the product are very important; one important variable

determining these parameters is considered to be the temperature at which nucleation takes place. For example a very large amount of nucleation is required in crystallization of sugar confectionary, where sucrose and corn syrup are mixed and cooked to the appropriate temperature to meet the desired water content of the final product. In other processes few nuclei are desired, as in the production of white sugar. In some cases crystallization is undesired, as an amorphous product is required, as in the production of hard candies.

1.2 Research Objective

The objective of this work is to understand and model the effect of processing conditions on the growth rate distribution, and growth rate dispersion of sucrose crystals formed as contact nuclei. This will involve determining growth rate dispersion of sucrose contact nuclei as function of the main parameters known to affect crystal growth rates in pure solutions, namely temperature, flow rate and supersaturation. The effect of impurities on the crystal growth rate dispersion of sucrose will be studied by experiments involving contact nucleation when impurities present in raw sugar syrups (glucose, fructose, NaCl, and KCl) are present, with the parameters crystallization temperature and supersaturation also varied. The effect of the type of crystal initiating the crystallization will be investigated by observation of the growth rate dispersion of uncrushed and crushed pure seed crystals, and crushed impure seed crystals of sucrose in pure stagnant sucrose solutions, allowing a comparison between growth rate distributions of contact nuclei and various types of seed crystal.

1.3 Scope and Limitations

The experiment will be separated into three parts. The first part involves a study of growth rate dispersion of contact nuclei in aqueous sucrose solution; the experiments use four different saturated concentration temperatures, (30, 35, 45 and 50 °C), at two different operating temperatures, (25°C and 40°C). This results in two supersaturation levels, ΔT = 5°C and ΔT = 10°C. The experiments also use two different flow rates (0 ml/min and 40 ml/min) to investigate whether GRD is more significant under diffusion controlled or surface integration controlled growth.

To investigate the effect of impurities on growth rate dispersion, contact nuclei grown in stagnant impure solutions are studied. There are four impurities used in this work; glucose, fructose, sodium chloride and potassium chloride. The saturated concentration for the three component mixtures (sucrose/water/impurity) is estimated following the ternary diagrams proposed by Kelly (1954) that are valid for 30°C. As is typical for studies on the effect of impurities on crystal growth, the impurity concentration is presented as a ratio of impurity mass/water mass in the solution. The low and high level of the impurity/water ratios for glucose and fructose are 0.25 and 0.5. For NaCl and KCl low and high level of impurity/water ratios are 0.2 and 0.4. Different levels were required for the carbohydrate and salt impurities because the invariant point (the point on the phase diagram where the stable crystal form changes from sucrose to the impurity) is at lower levels of salt than carbohydrates. The operating temperature for these experiments are 20°C and 25°C, and the levels of the supersaturation are ΔT=5°C and ΔT=10°C. These were chosen because the phase diagram (and therefore the saturation temperature) was only known at 30°C.

The third section is a study of growth rate dispersion of three different types of seed crystals – uncrushed pure seeds, crushed pure seed, and crushed impure seeds, in order to compare these results to GRD where contact nuclei initiated the crystallization. The conditions for these experiments are stagnant pure solutions of sucrose at four different saturated concentration temperatures, (30, 35, 45 and 50°C) as used in the first part. The experiment is operated at two different levels of crystallization temperature, 25°C and 40°C, and two different levels of the supersaturation – ΔT=5°C and ΔT=10°C.

1.4 Expected Usefulness

1.4.1 The mechanisms involved in crystallization, such as nucleation and growth would be better understood, leading to, in particular, a better understanding of crystal growth rate dispersion.

1.4.2 The study of the effect of processing conditions, such as solution flow rate, temperature, supersaturation, solution purity and type of seed crystals, on nucleation, growth and growth rate dispersion, would give more accurate information on the effect of processing conditions on the crystal nucleation and growth of sucrose.

Chapter 2

Literature Review

2.1 Sucrose

Sugar is one of the largest commodity chemicals in the world. Worldwide production in 1999/2000 was over 130 million tons per year. The largest sugar exporters are Brazil, the European Union, Australia, and Thailand (United States Department of Agriculture, Foreign Agricultural Service, 2004). Information from the Department of Customs of Thailand, quoted by the Office of Agricultural Economics of Thailand (2004), shows that in 2003, Thailand exported 2.52 million tons of sugar, which had a value of 20.8 billion baht in 2003.

Because sugar is used mostly as a food product, it must be produced at extremely high purities, and raw sugar crystals are typically produced at greater than 99.0 percent purity, and refined sugar crystals at 99.98 percent purity. Sugar crystallization has been extensively studied and there is now a good deal of knowledge on the system.

Overall, cane and beet can be considered as a mixture of water, sugar (sucrose), water insolubles (fiber), and impurities, which they include all the other water soluble species, e.g. salts, and reducing sugars. The major soluble impurities are given in Table 2.1.

Table 2.1: Compositions (%) of major components in a typical raw juice. (Wheyman: 1993, cited in Jetoo: 2000).

	Sucrose	88	
	Ash (inorganics)	4 (see below for details)	
	Reducing sugars	4 (mainly fructose and glucose)	
	Other organics	4 (see below for details)	
Ash components		Other Organic components	
K and Na	1.60	Aconitic acid	1.30
Ca	0.20	Malic and Citric acids	0.60
Mg	0.17	Protein	0.50
Al	0.05	Starch	0.03 – 0.20
Cl	0.26	Dextran	0.00 – 1.00
SO_4	0.67	Others (amino acids,…)	trace
P	0.07		

In processing, the fiber can be removed by mechanical means and the water by evaporation. Some impurities are removed via precipitation with lime, and by adsorption onto activated carbon, however crystallization remains the preferred means of separating sugar from the major impurities. As the sugar crystal is extremely selective as to what it builds into its lattice, theoretically absolutely pure crystals can

be produced by crystallization. In practice however there is a significant carry–over of impurity with the adhering liquor film and often there is some included mother liquor within the crystals.

2.1.1 Chemistry of Sucrose

The technical terms for cane and beet sugar is sucrose, or in some parts of the world saccharose. Sucrose is a natural product of green plants, which combine carbon dioxide, water and the energy of the sun in storing energy. The combination makes sucrose a member of the carbohydrate family of organic compounds. Sucrose is a main component of the food chain and is one of the most plentiful carbohydrates found in nature.

The sucrose molecule is composed of twelve atoms of carbon, twenty–two atoms of hydrogen, and eleven atoms of oxygen; it is written in chemical shorthand as $C_{12}H_{22}O_{11}$. The molecular weight of sucrose is 342.30. Its chemical structure and crystal morphology are shown in Figures 2.1 and 2.2, respectively. Sucrose is a disaccharide composed of one molecule of glucose (or dextrose) and one molecule of fructose (or levulose) linked by a glycosidic bond. Since glucose is a major component of blood and fructose is a component in many fruits, these two sugars are also called blood and fruit sugar, respectively. The International Union of Pure and Applied Chemistry (IUPAC) gives the following name for sucrose:

α–D–glucopyranosyl–β–D–fructofuranoside

Sucrose crystallizes into an anhydrous crystal under all processing conditions. Sucrose belongs to the monoclinic system of crystals (three axes of unequal lengths,

two axes at right angles, the third is inclined at 103.5° for sucrose). The crystals formed can show a large number of pairs of faces.

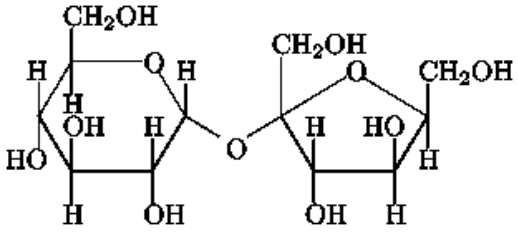


Figure 2.1 Chemical structure of sucrose molecule.

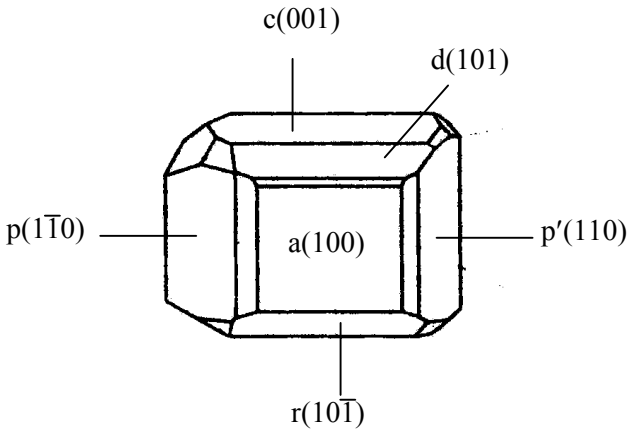


Figure 2.2 Sucrose crystal showing the eight most important faces.

The sucrose molecule can be split into one molecule of glucose and one molecule of fructose by a reaction commonly called inversion. The mixture of glucose and fructose obtained is called invert sugar. This reaction is a simple irreversible hydrolysis reaction which can be accelerate d with increasing acidity and temperature. For example, a pure sucrose solution can invert about 5000 times faster

at 90°C than at 20°C, and the reaction can proceed more quickly as the pH decreases. The reaction can also be catalyzed by enzymes present in the juice due to bacterial contamination. The reaction is very important in the sugar processing industry, as it is the major cause of sugar deterioration. The process mainly operates at high temperature, and inversion to glucose and fructose both decreases the process yield, and produces impurities that inhibit crystal growth.

2.1.2 Physical Properties of Sucrose

Sucrose is very stable in its crystalline form, and in general, it is used as a solid. Pure sucrose is colorless, odorless, and sweet tasting. The crystalline form of sucrose is monoclinic. It has melting temperature between 160°C and 186°C and the temperature for extraction is dependent on the solvent of crystallization, and purity of the solution. The specific gravity of single sucrose crystals is 1.588, but for a large grouping of crystals the specific gravity will vary somewhat depending on the average crystal size and size distribution, by around 0.08 specific gravity units. For most products the bulk density is between 48 and 54 pounds per cubic foot (about 0.9 metric tons per cubic meter).

2.1.2.1 Solubility of Sucrose

The solubility of sucrose is the sucrose concentration in a saturated solution, a solution in equilibrium with the solid state of sucrose. Sucrose can be dissolved in polar solvents such as water and alcohol, but sucrose does not dissolve significantly in non–polar solvents such as ether and benzene. There are many research papers which study the sucrose solubility in water, because it is an important matter in the production process, and it is important to define the supersaturation or driving force for growth. The saturation point, or solubility of

sucrose in water, can be determined by equations or numerous tables at various temperatures and conditions. For example, an equation to determine saturation concentration of sucrose (C^*) as percent by weight in water, determined by Vavrinecz (1955) is:

$$C^* = 64.47 + 0.10336T + 1.424 \times 10^{-3}T^2 - 6.02 \times 10^{-6}T^3 \qquad (2.1)$$

and the equation proposed by D.F. Charles (1995) is:

$$C^* = 64.397 + 0.07251T + 0.0020569T^2 - 9.035\times10^{-6}T^3 \qquad (2.2)$$

where C^* is saturation concentration (g sucrose/100 g solution) and T is temperature in degree Celsius. The equations are valid in a range of temperatures from 0 to 86°C and –13°C to 100°C for the first and the second equation, respectively. The equations are plotted in Figure 2.3: the equations give similar results for the solubility values, but there are noticeable differences over the temperature range 5 to 70 °C. The experimental data for sucrose solubility are a little scattered, so it is difficult to state with confidence which equation is better. A plot based on the experimental data is shown in Figure 2.4. This plot also shows the metastable limits for nucleation of sucrose crystals.

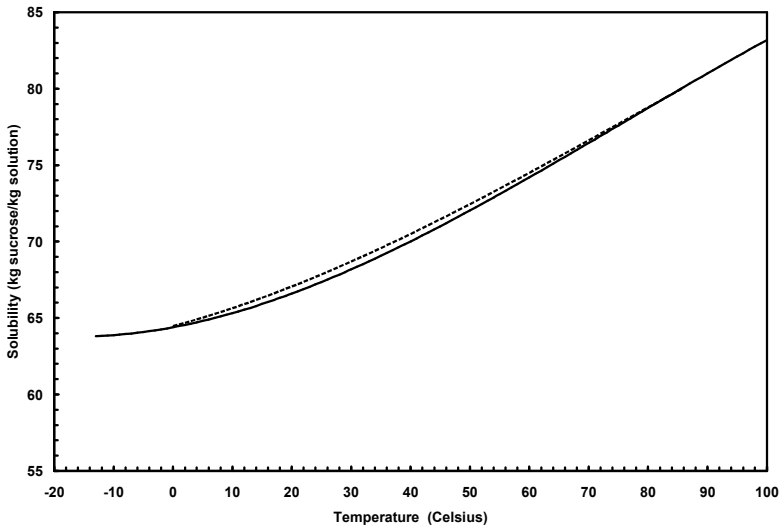


Figure 2.3 Sucrose solubility via the Vavrinecz equation (- - -) and the Charles equation (—).

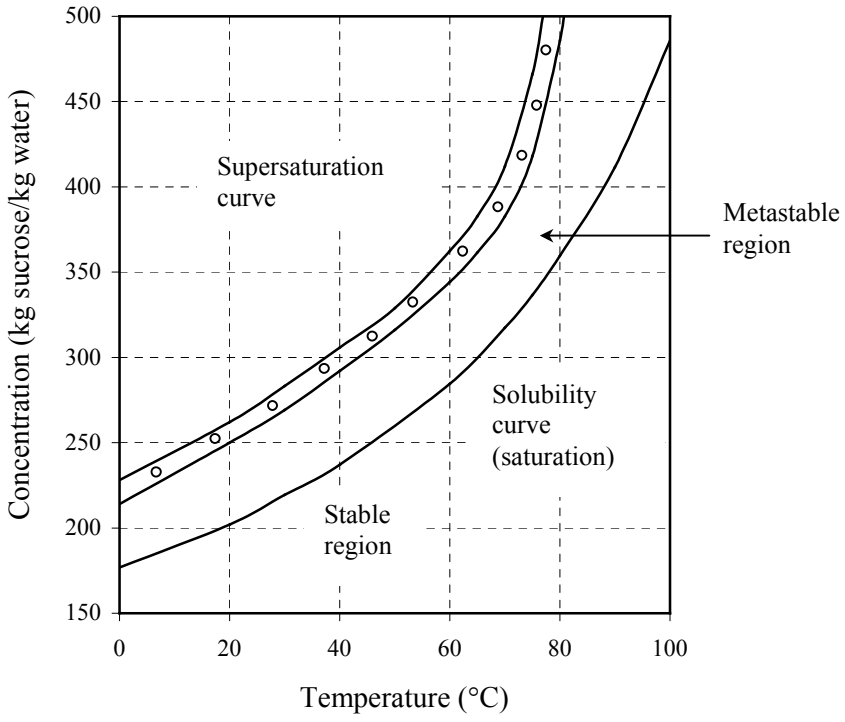


Figure 2.4 Solubility curve for sucrose in water. (Earle, 1983).

The sucrose molecule can easily form a significant number of hydrogen bonds with water molecules, and therefore sucrose is highly soluble in water. The sucrose solubility is dependent on temperature and the amount and type of other dissolved molecules (impurities, non–sugars). If there is a very small amount of impurities, it will not significantly affect the sucrose solubility. For many non–sugars which remain in sugar juices after their purification, the impurities will increase solubility.

Because sugar has a very high solubility in water, and solutions range from only 10 to 30 % water content, the solutions are very viscous. This is a significant constraint in processing. Having prepared sugar crystals by crystallization, it is necessary to separate them from the mother liquor. This is carried out in high speed centrifuges. For efficient separation it is necessary for the crystals to be large and of reasonably uniform size. The size and size distribution of the material is also important in the later flow of the crystalline product for bulk handling.

2.1.2.2 Viscosity

The viscosity is an important functionality measurement of any fluid. For sucrose solutions, as the solids content increases, the viscosity increases also, although it is not a linear function of temperature. As temperature increases, the viscosity of a saturated sucrose solution will increase rapidly due to the increase of solubility with temperature. In general the viscosity will also increase with an increase in the impurity levels in sucrose solutions. Thus it can be said that viscosity is affected by solid content, temperature and impurities.

2.1.3 Crystallization of Sucrose

Raw juice from the sugar milling process is crystallized in a combination of seeded (typically batch) vacuum pan crystallizers and cooling crystallizers. Sucrose will decompose (caramelise) at high temperatures, above 70–80°C, so evaporative crystallization is carried out under vacuum, typically at about 65°C. Since the crystallization is faster, and the vacuum required is less at higher temperatures, the highest practical operating temperature is used.

2.2 Crystallization

"Crystallization is the formation of structured solid particles within a homogeneous phase. It is the process of arranging atoms or molecules that are in a fluid or solution state into an ordered solid state" (Boyle, 2003). Weber has summarized the significance of crystallization to industrial processing with the following comment: "Crystallization processes represent a significant separation and purification technique in the chemical, pharmaceutical, petrochemical and food industries. Crystallization is one of the several means by which a metastable supersaturated solution can reach a stable lower energy state by reduction of solute concentration" (Weber, 1991 quoted in Berry, 1995). The general processes by which substances crystallize are similar for molecules of both microscopic (salt and small organics) and macroscopic (proteins, DNA and RNA) dimensions (Berry, 1995). Crystals may occur as solute is transferred from the vapor to be solid particles, as in snow; as solidification from a liquid melt, as in the manufacture of large single crystals; or as crystallization from liquid solution. Crystallization from solution is important industrially because a variety of material are marketed in crystalline form,

including food products such as sucrose and salt, pharmaceutical products, and commodity chemicals such as ammonium sulfate and sodium nitrate.

2.2.1 Supersaturation

Crystallization processes can take place only in supersaturated, or supercooled, phases. The rate of crystallization is often determined by the degree of supersaturation, the driving force for crystallization, which has been commonly expressed either as the difference in concentration between the supersaturated and saturated solutions

$$\Delta C = C - C^* . \text{ or } \quad \Delta c = c - c^* \tag{2.3}$$

or as supersaturation (S), or relative supersaturation (σ)

$$S = \frac{C}{C^*} = \frac{c}{c^*} \text{ or } \sigma = \frac{C - C^*}{C^*} = S - 1 \tag{2.4}$$

where C and c is concentration (mass of solute per mass of solvent or solution, or mole or mass of solute per volume of solution), S is the supersaturation ratio, σ is the relative supersaturation and an asterisk (*) denotes the condition at saturation. Another expression for supersaturation is the supercooling, that can be written as

$$\Delta T = T^* - T \tag{2.5}$$

where ΔT is the supercooling, T^* is the solid–liquid equilibrium temperature and T is a temperature that is less than T^*.

2.2.2 Phase Diagram for Crystallization

There are four zones on a phase diagram for crystallization, as shown in Figure 2.5. The first zone is below the equilibrium concentration between the liquid phase and the solid phase. This zone, called the unsaturated or undersaturated region, is the zone in which any crystals present in the solution will dissolve until the saturation point is reached.

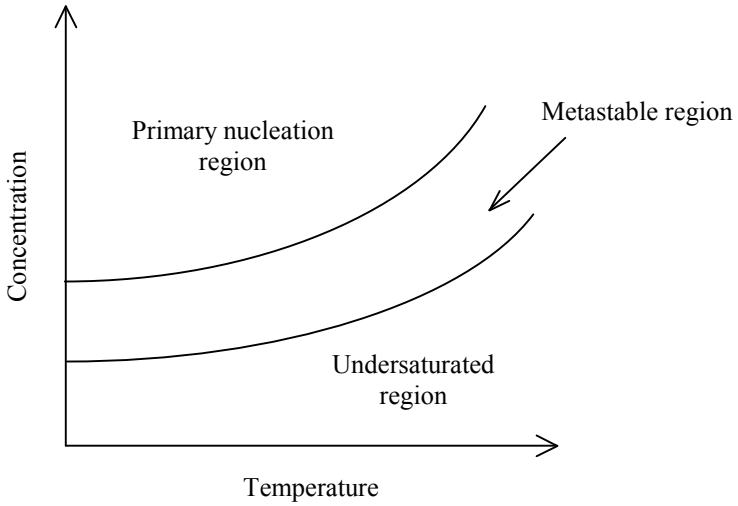


Figure 2.5 Supersaturation curves for crystallization.

The second zone is called the metastable region. This zone lies in the region just above the undersaturated zone. Here the solution is supersaturated, but the driving force is not enough to form nuclei or new crystals. If there are some crystals already present in the solution, they will grow in size so that the concentration is reduced to the equilibrium point, however no nuclei can be formed in a finite length of time. If there are not any crystals present in the solution then the solution will remain

at the supersaturated state as before, and not reach equilibrium. The reason for this is that the formation of nuclei requires larger energies than crystal growth on already present crystals.

The third zone is where new crystals form only if other crystals are present. This region is called the zone of secondary nucleation. The addition of seed crystals will induce the formation of nuclei crystals (at very small size). The fourth zone is where nuclei will form even when other crystals are not present: this region is called the primary nucleation region. Crystallizers are rarely run here due to the high concentrations in this region, and because primary nucleation produces very large numbers of nuclei, which greatly reduces the mean particle size of the product.

2.2.3 Solubility

For the process of crystallization, the solubility is a very important value because it determines the value of the supersaturation of the solution, which in turn partly determines the value of crystallization rate. The solubility often increases significantly with the temperature, which is demonstrated at higher temperature, commonly used in industrial crystallization, by the high viscosity of mother liquors and high dry solids content. However there are also other systems where the saturation concentration remains approximately constant or decreases with increasing temperature. Figure 2.6 illustrates the solubility of some anhydrates such as KNO_3, KCl, NaCl, and $NaNO_3$ (Mersmann, 2001).

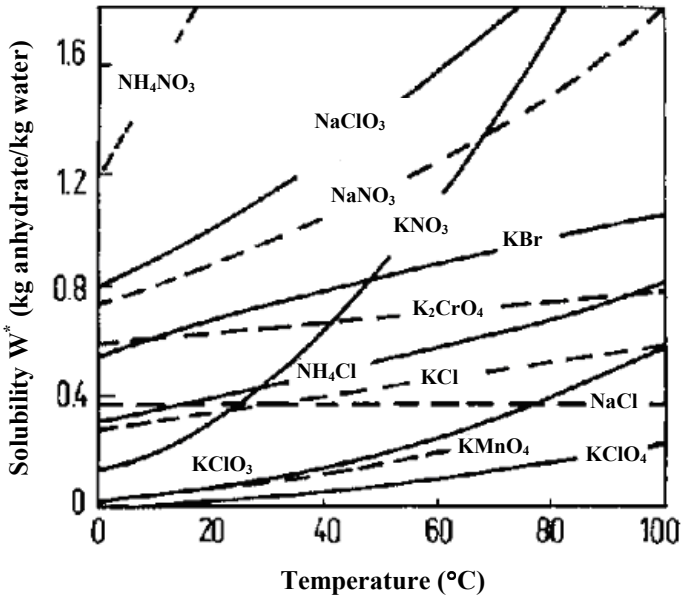


Figure 2.6 Solubility curves for several anhydrates. (Mersmann, 2001).

2.2.4 Nucleation

The condition of supersaturation or supercooling alone is not sufficient cause for a system to begin to crystallize. The creation of a new solid phase initially requires the appearance of minute clusters of building units (atoms or molecules) in the volume of the supersaturated fluid phase (solution, vapor, or melt); this was initially postulated by Gibbs. Similarly, before crystals can develop to macroscopic sizes, there must exist in the solution a number of minute solid entities, nuclei or seeds, which act as centers of crystallization. Nucleation may occur spontaneously or it may be induced artificially.

Experiments in the early 1900's showed that nucleation can often be induced by agitation, mechanical shock, friction, and extreme pressures within solutions and melts. For many years there have also been studies about the uncertain

effects of external influences, such as electric and magnetic fields, spark discharges, ultra–violet light, χ–ray, γ–ray, sonic and ultrasonic irradiation on nucleation, but none of these methods show any significant application in large–scale crystallization practice (Mullin 2001).

Crystallization from solution involves two steps; nucleation and crystal growth. Nucleation is the formation of new crystals, called nuclei. The growth of nuclei into macroscopic sized particles is called crystal growth. Nucleation in both batch and continuous crystallizers can occur by either primary or secondary mechanisms as shown in Figure 2.7.

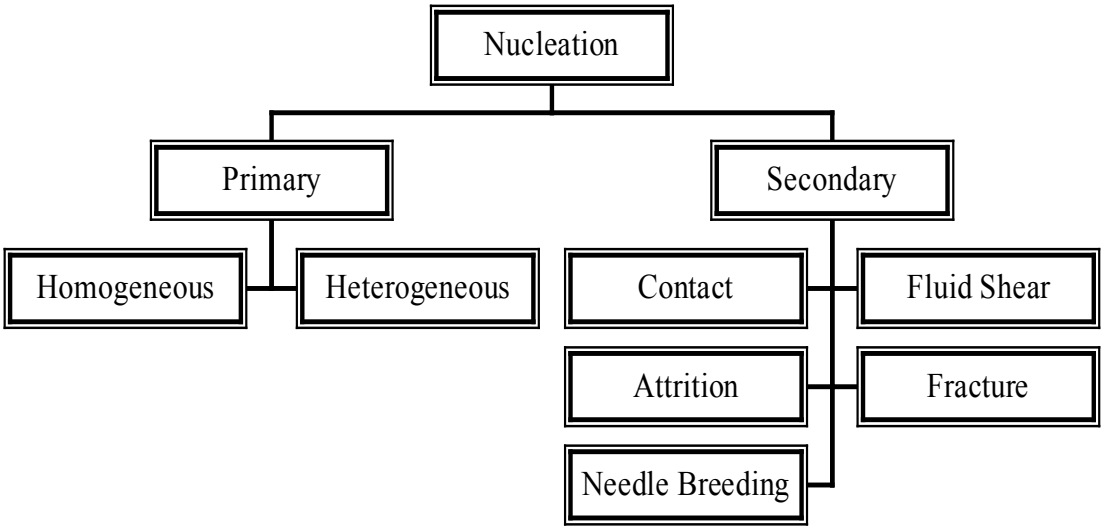


Figure 2.7 Nucleation Mechanisms (Randolph and Larson, 1988).

2.2.3.1 Primary Nucleation

Primary nucleation is the nucleation mechanism where nuclei are produced in the absence of solute crystals. Nucleation from a single–phase system

is an example of primary nucleation. It can be either homogeneous or heterogeneous. Homogeneous or spontaneous nucleation of a species takes place in solutions containing neither solid foreign particles, nor other crystals of the species. This mechanism requires the largest driving force, because there are no nucleation sites in the solution. It is normally accepted that true homogeneous nucleation is not a common event. For example, unknown seed such as dust or impurities might be seeded unknowingly into the supersaturation solution, so that it contains the active particles or heteronuclei. In the laboratory, the solution prepared might contain $>10^6$ solid particles per cm^3 of sizes <1 μm. In heterogeneous nucleation foreign particles are used as substrate for nuclei. These particles act as nucleation sites, so lower driving forces are required. The presence of suitable foreign bodies, or sympathetic surfaces, can induce nucleation at an amount of supercooling lower than those required for homogeneous nucleation.

2.2.3.2 Secondary Nucleation

Secondary nucleation is the nucleation mechanism where suspended solute particles are required to induce the formation of nuclei. It can be separated into:

1. Contacting or touching crystals with other surfaces, or other crystals, to obtain contact nucleation. This results in removing part of an absorbed layer from the surface of a parent crystal, followed by the piece of absorbed layer becoming a contact nuclei by rearrangement to reduce its' surface area.

2. Nucleation by fluid shear results when the relative velocity between fluid and crystal is large enough to remove the absorbed layer. If the cluster is sufficiently large, nuclei can be obtained.

3. Fracture nucleation occurs in the systems having high mechanical stresses or brittle crystals, where crystals fracture to produce nuclei from the fragments.

4. Attrition nucleation results from crystal–crystal interaction at high suspension densities as well as from crystal-apparatus contacts. It looks like nucleation by fracture but visible damage to the parent crystal is usually very slight and is quickly repaired. The mechanism involves fracture of very small sections of the corners and edges of parent crystals.

5. Needle breeding is the breakage of needle-like crystals to form new crystals. Reducing the agitation and suspension density can reduce this phenomenon.

2.2.5 Crystal Growth

After the formation of nuclei, the nuclei begin to grow larger through the addition of solute molecules to the crystal lattice, a process called crystal growth. The mechanism of crystal growth from solution refers to the transportation of solute from bulk solution to the crystal surface (diffusion) and then the orientation of the molecules into the crystal lattice. Thus, the crystal growth in a supersaturated solution is dependent on two successive processes, the diffusion of solute molecule from the bulk solution to the crystal surface and the accommodation of the solute molecules into the crystal lattice (Chen and Chou, 1993). The growth rate of a crystal is defined as the change of a linear size with respect to time (e.g. in μm/min units), with size usually taken as the volume equivalent size, i.e. the diameter of a sphere with the same volume as the crystal. This measure of size is convenient for models using mass balances.

The growth of crystals from nuclei is strongly influenced by diffusion and convection effects. As with nucleation, increased supersaturation results in increased growth rates whether the crystal growth is controlled by diffusion or surface integration. Again, this may be a function of the rate at which molecules reach the growing surface of the crystals, or the rate at which they can integrate into the lattice. The growth of crystals in a supersaturated solution is very complex process that has not been fully understood up to now. The reason for this is that supersaturated solutions are composed of a variety of units, such as atoms, molecules, ions, hydrated solute molecules, dimers, trimers, polymers, clusters, etc. and can have an uncertain structure. Little is known about the various species and the structure.

Cessation of growth of crystals can occur for many of reasons. The most important is the decrease in concentration of the crystallizing solute to the point that the solid and solution phases reach exchange equilibrium, which results in discontinued crystal growth. However some crystals reach a certain size beyond which growth does no proceed irrespective or solute concentration. This may be a result either of cumulative lattice strain effects or poisoning of the growth surface. Poisoning of growing faces occurs when foreign or damaged molecules are incorporated into the growing crystal face resulting in successive defects, which interrupt the crystal lattice. A schematic diagram of crystal growth is shown in Figure 2.8.

According to Periodic Bond Chain theory (Boistelle and Astier, 1988 qute in Berry, 1995), three different types of growth faces exist: flat faces, stepped faces, and kinked faces. The three face types are described in Figure 2.9.

1. The flat face (F) or ledge, which requires two–dimensional nucleation (the formation of growing layers of molecules) in order to induce growth. These faces grow the slowest, due to the mechanism of growth.

2. Stepped faces (S) grow as columns of molecules, which require only one–dimensional nucleation, and thus have intermediate growth rates. Stepped faces typically occur as a result of a crystallographic screw axis causing spiral growth patterns to occur at the surface of the crystal.

3. Kinked faces (K) are growth sites, which do not require nucleation to promote further growth, and therefore grow faster than the other face types.

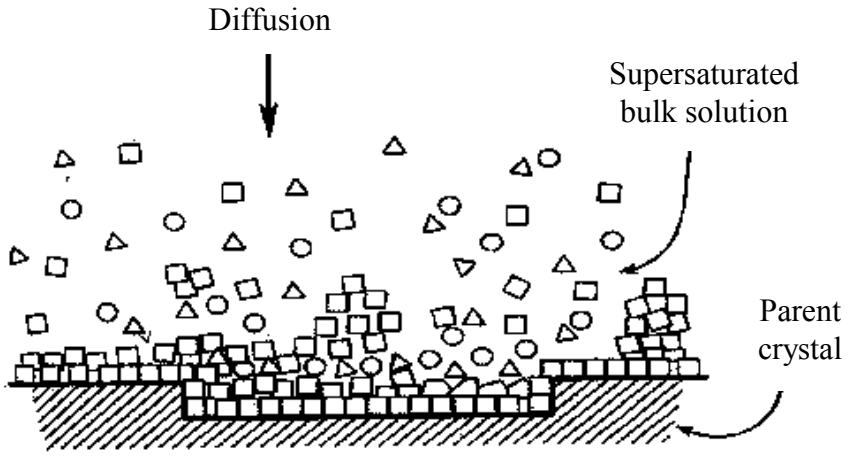


Figure 2.8 Absorbed layer of solute on the surface of a growing crystal. (Randolph and Larson, 1988).

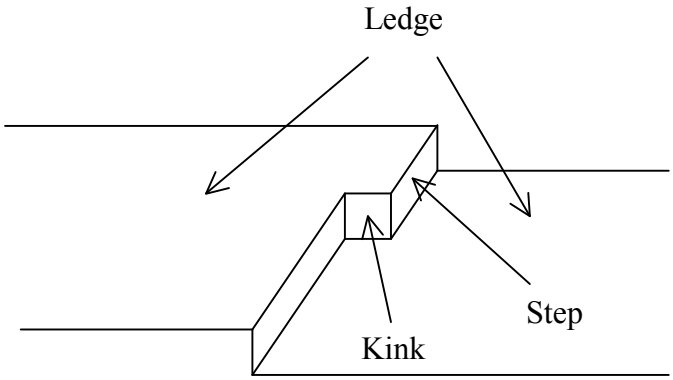


Figure 2.9 Surface growth sites.

2.2.4.1 Growth theories classified by Garside

Garside (1984) categorizes growth theories as continuous growth, surface nucleation, and continuous step growth. The growth model applicable for a particular crystal grown from a solvent depends on the crystal surface roughness which relates to intermolecular bonds in the crystal, in the liquid phase, and at the interface. The continuous growth model assumes a rough surface (on a molecular level), as shown in Figure 2.10–(a), where the growth unit will integrate at a site of the lowest energy for its orientation.

Surface nucleation growth is controlled by the frequency of formation of two–dimensional nuclei on a relatively smooth surface of a growing crystal. This means that surface nucleation is the controlling step. The mechanism of birth and spread is shown in Figure 2.10–(b). The term birth and spread model was named and described by O'Hara and Reid in 1973. After the birth of the surface nuclei there is a subsequent spread of solute molecules around the nucleus.

The model used most for crystal growth, and the one that is most often applicable, is a form of the continuous–step model, suitable for growth of extremely smooth crystal surfaces. The form that is preferred is the Burton–Caberra–Frank (BCF) model first described in 1951. This model incorporates the idea of a self–perpetuating kink ledge, and leads to concept of growth around a screw dislocation as show in Figure 2.10–(c). The addition of a growth unit not only fills a kink site but also creates another, which is favorable to growth. Screw dislocations have been found on etched surfaces of crystals.

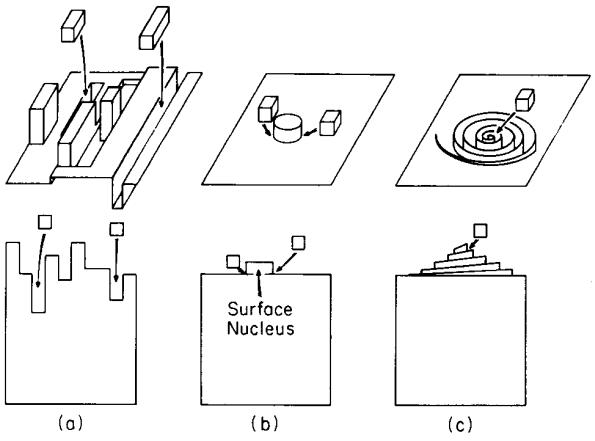


Figure 2.10 Crystal growth model (a) Continuous growth; (b) Birth and Spread; (c) Dislocation (BCF). (Randolph and Larson, 1988).

2.2.4.2 Crystal Growth Theories Classified by Mullin

The mechanisms of crystal growth are classified into categories and discussed in the following section. The surface energy theories are based on the concept that a growing crystal assumes the shape that will give it a minimum surface

energy, and therefore a minimum total energy for its size. Diffusion theories assume that solute is deposited continuously onto the crystal face at the rate of diffusion, a rate that is proportional to the concentration gradient between the surface and the bulk solution. The adsorption layer theories suggested by Volmer (Volmer, 1939; quoted in Mullin, 2001) assume that crystal growth is a discontinuous process, taking place by adsorption, layer by layer, on the crystal surface.

1. Surface energy theories

Gibbs, in 1878, proposed that the growth of a crystal should be such that the total free energy of the crystal in equilibrium with its surroundings at constant temperature and pressure would be a minimum for a given volume. If the volume free energy per unit volume is assumed to be constant throughout the crystal, then it can be expressed as:

$$\sum_{1}^{n} a_i g_i = \min \tag{2.6}$$

where a_i is the area for the ith face of a crystal bounded by n faces, and g_i the surface free energy per unit area of the ith face.

Wulff later suggested that the crystal faces would grow at rates proportional to their respective surface energies in which he showed that the equilibrium shape of a crystal is related to the free energies of the faces. Because there is little quantitative evidence to support the surface energy theories of crystal growth, there is no general acceptance of these theories. However, they still continue to attract attention, but their main defect is their failure to explain the well–known

effects of supersaturation and solution movement on the crystal growth rate (Mullin, 2001).

2. Adsorption layer theories

The first suggestion for a crystal growth mechanism, based on the existence of an adsorbed layer of solute atoms or molecules on a crystal face, was by Volmer in a series of papers in the 1930s. The theory is based on thermodynamic considerations. When the arriving units of the crystallizing substance are at the crystal face they are not immediately integrated into the lattice, but they will lose one degree of freedom and then they are free to migrate over the crystal face by surface diffusion. At the interface, there will be a loosely adsorbed layer of integrating units, and a dynamic equilibrium is established between this layer and the bulk solution. The adsorption layer, that is sometimes called the third phase, plays an important role in crystal growth and secondary nucleation. Atoms, ions or molecules will link into the lattice in positions where the attractive forces are greatest, i.e. at the active centers and under ideal conditions this step–wise build–up will continue until the entire face is completed. Before the crystal face can continue to grow, or before a further layer can start, a centre of crystallization must come into existence on the facial surface. With the Gibbs–Volmer theory, it is suggested that a monolayer island nucleus, which is often referred to as a two–dimensional nucleus, is created.

The Kossel model of a growing crystal face visualizes that an apparently flat crystal surface is made up of a moving layer of steps of monatomic height, which may contain one or more kinks. In addition, there will be loosely adsorbed growth units on the crystal surface and vacancies in the surfaces and steps. Growth units are most easily incorporated into the crystal at a kink; the kinks move

along the step and the face is eventually completed. This means that a crystal should grow fastest when its faces are entirely covered with kinks. However, it is impossible that the number of kinks would remain at high value for any length of time and it is well known that broken crystal surfaces rapidly heal and then proceed to grow at a much slower rate. Many crystal faces, however, readily grow at quite fast rates at relatively low supersaturation, far below those needed to induce surface nucleation. An example is iodine crystals, which can grow from the vapour at 1 percent supersaturation at rates some 10^{1000} times greater than predicted by classical theory (Volmer and Schultz, 1931 quoted in Mullin 2001). Mullin (2001) has concluded that the Kossel model, and its dependence on surface nucleation, is unreasonable for growth at moderate to low supersaturation.

With the concept of Frank (Frank 1949, quoted in Mullin 2001), few crystals ever grow in the ideal layer–by–layer fashion without some imperfection occurring in the pattern. This result was considered to be the answer to the above dilemma. Most crystals contain dislocations, which cause steps to be formed on the faces and promote growth. Therefore, the screw dislocation is considered to be important for crystal growth, since it removes the need for surface nucleation. It is apparent that a completely smooth face never appears under conditions of spiral growth; the surface is covered with kinks, and surface nucleation is not necessary.

Burton, Cabrera and Frank developed a kinetic theory of growth in which the curvature of the spiral near its origin was related to the spacing of successive turns and the level of supersaturation. The growth rate at any supersaturation can be calculated by assuming that surface diffusion is an essential

step in the process and by the application of Boltzmann statistics to predict kink populations. The Burton–Cabrera–Frank (BCF) relationship may be written as;

$$R = A\sigma^2 \tanh\left(B/\sigma\right) \tag{2.7}$$

where R is the crystal growth rate. The supersaturation $\sigma = S - 1$, where $S = c/c^*$. A and B are complex temperature-dependent constants which include parameters depending on step spacings. At low supersaturations the BCF equation approximates to $R \propto \sigma^2$, but at high supersaturations it predicts $R \propto \sigma$.

The BCF theory was derived for crystal growth from the vapour; and while it should also apply to growth from solutions and melts, it is difficult to quantify the relationships because of the more complex nature of the systems. For example, viscosities are higher and diffusivity is lower in solutions than in vapours (Mullin, 2001).

3. Diffusion–reaction theories

The origin of the diffusion theories is the work of Noyes and Whitney (Noyes and Whitney 1897, quoted in Mullin 2001). They considered the face of a growing crystal at which there was the deposition of solid that was essentially a diffusional process. They also assumed that crystallization was the reverse of dissolution, and that these processes have the rate governed by the difference between the concentration at the solid surface and in the bulk of the solution. Mullin (2001), however, has suggested that the concept of film diffusion alone is not sufficient to explain the mechanism of crystal growth, and crystallization

is not necessarily the reverse of the dissolution. In general, a substance dissolves at a faster rate than it crystallizes under the same relative driving force.

Another important study was made by Miers in 1904; he determined the solution concentrations near the faces of crystals of sodium chlorate growing in aqueous solution. He showed that the solution in contact with a growing crystal face is not saturated but supersaturated.

A modification of the diffusion theory of crystal growth was made by Berthoud and Valeton (Berthoud, 1912; and Valeton, 1924, quoted in Mullin, 2001). They suggested that there were two steps in the mass deposition process; a diffusion process and a first order reaction. The first step, diffusion, is the transportation of solute molecules from the bulk of the fluid phase to the solid surface. The following step, a first order reaction, is the arrangement of the solute molecules into the crystal lattice. These two stages occurred under the influence of different concentration driving forces, that can be expressed by the equations;

$$\frac{dm}{dt} = k_d \mathrm{A}\left(c - c_i\right) \qquad \text{(diffusion)} \tag{2.8}$$

and

$$\frac{dm}{dt} = k_r \mathrm{A}\left(c_i - c^*\right) \qquad \text{(reaction)} \tag{2.9}$$

where k_d is a coefficient of mass transfer by diffusion; k_r is a rate constant for the surface reaction or integration process and c_i is solute concentration in the solution at the crystal–solution interface.

These two equations are not easy to use in practice because the interfacial concentrations are difficult to measure. Thus for convenience, the c_i term is usually cut off, and the overall concentration driving force ($c - c^*$) is considered, which is quite easily measured. The general equation for crystallization can be written as;

$$\frac{dm}{dt} = K_G \mathrm{A}(c - c*)^g \tag{2.10}$$

where K_G is an overall crystal growth coefficient. The exponent g is usually referred to as order of the overall crystal growth process. In crystallization work, it is applied to a concentration difference that has no fundamental significance and cannot give any indication of the number of elementary species involved in the growth process.

4. Birth and spread models

There are others names for the birth and spread (B+S) model, such as the nuclei above nuclei (NAN) model, and poly nuclear growth. These models suggest that growth develops from surface nucleation, which can occur at the edges, corners and on the faces of a crystal. In addition, surface nuclei can develop on the monolayer nuclei as they spread across the crystal face.

2.3 Growth-Rate Dispersion

Growth rate dispersion (GRD), sometimes also called size dispersion, is a phenomenon that crystals of the same size grown under apparently identical conditions have different growth rates. GRD is a significant factor in the control of crystal size distribution (CSD) in batch crystallizers. GRD is an important

phenomenon in industrial crystallization due to the importance of a narrow product size distribution.

GRD was first identified as a phenomenon that had a serious bearing in crystallizer performance by White and Wright (1971). They studied crystallization of sucrose in a batch crystallizer and observed that the standard deviation of an initially narrow size distribution of crystals increase as time progresses. This meant that the crystals in their crystallizer were not growing at the same rate. Now, this phenomenon is a generally accepted behaviour in all crystallizers.

The initial studies of GRD focused on defining and clarifying how GRD appeared in the crystallization system. The main problem of the studies was the question of whether the growth rates of crystals fluctuated randomly, the random fluctuation (RF) model (Randolph and White; 1977) or whether they were constant for each crystal, the constant crystal growth (CCG) model (Ramanarayanan, 1982), where the growth rates of all the crystals in a system could be fit by a probability density distribution.

Studies assuming the CCG model have shown how the growth rate distribution of crystals in a mixed–suspension, mixed-product removal (MSMPR) crystallizer can be derived from the product size and vice versa distribution. After these studies, GRD researchers have virtually given up the concept of the RF model of GRD in favor of an intrinsic growth–rate (IGR) model. The IGR model assumes that a crystal's growth rate does not fluctuate randomly but it is intrinsic to each crystal in the system and may change as system parameters change. At any time during the crystallization process, the growth rate of the crystals in the crystallizer system can be expressed as a growth rate distribution.

Growth rate dispersion stems mainly from different interferences with the surface integration kinetics on different crystals. Random surface adsorption or physical incorporation of impurity species, leading to the development of different crystallographic faces, but there is evidence to suggest that the prime causes could be the varying degrees of lattice strain and deformation in individual crystals and their dislocation structure (Ristic, Sherwood and Shripathi, 1991; Jones et al., 2000). Lattice strain can be caused by mechanical stresses imparted to crystals in a crystallizer by fluid shear, or physical contact with other crystals, the agitator or other internal parts of the equipment. The less ductile the crystals the more likely they are not to be prone to growth rate dispersion.

2.3.1 Crystal Size Distributions from Crystallizers

Montillon and Badger (1927) were one of the earliest to study the crystal size distribution from industrial crystallizers; in particular they investigated $Na_2SO_4 \cdot 10H_2O$ and $MgSO_4 \cdot 7H_2O$ in a continuous crystallizer. Two years later, McCabe (1929) analyzed the problem of crystal size distribution (CSD) and develop the ΔL law. The assumptions used for this law are:

1. All crystals have the same shape
2. They grow invariantly, i.e. the growth rate is independent of crystal size
3. Supersaturation is constant throughout the crystallizer
4. No nucleation occurs
5. No size classification occurs in the crystallizer
6. The relative velocity between crystals and liquor remains constant.

The mass of one crystal of a chosen characteristic size L is given by $\alpha\rho_c L^3$, where α is the volume shape factor and ρ_c is the crystal density. The number of crystals, dN, of size L in as mass dM is thus

$$dN = \frac{dM}{\alpha\rho_c L_p^3} \tag{2.11}$$

Assuming no nucleation, the number of seeds dN_s of size L_s is equal to the number of product crystals dN_p of size L_p, i.e.

$$\frac{dM_s}{\alpha\rho_c L_s^3} = \frac{dM_p}{\alpha\rho_c L_p^3} = \frac{dM_p}{\alpha\rho_c (L_s + \Delta L)^3} \tag{2.12}$$

where ΔL is the growth enlargement. Therefore

$$dM_p = \left(\frac{L_s + \Delta L}{L_s}\right)^3 dM_s \tag{2.13}$$

$$M_p = \int_0^{M_s} \left(1 + \frac{\Delta L}{L_s}\right)^3 dM_s \tag{2.14}$$

where M_p is the product crystal yield obtained from an initial mass of seed, M_s.

There were some limitations of the ΔL law that were suggested by McCabe. The ideal conditions assumed in the derivation are unlikely to be attained in a real crystallizer. For examples, temperature and supersaturation gradients are unavoidable; invariant growth is comparatively rare; different crystal faces usually grow at different rates and may be dependent on solution velocity, in which large crystals may grow faster than small; and so on. However the ΔL law still provides an

interesting, if oversimplified, approach to the development of a crystal size distribution (CSD).

Crystal size distributions (CSD) may be conveniently classified by the median size and the coefficient of variation (C.V.). The C.V., which quantifies the size spread, is a statistical property related to the standard deviation of a Gaussian or normal distribution and is normally expressed as a percentage by

$$C.V. = 100\left(\frac{L_{84\%} - L_{16\%}}{2L_{50\%}}\right) \tag{2.15}$$

The values of $L_{84\%}$, $L_{50\%}$ (or L_{M}) and $L_{16\%}$ may be obtained from a cumulative mass distribution curve. The higher the C.V. the broader the spread; C.V. equal to zero denotes a monosized distribution. For a Gaussian distribution, the C.V. is 52%, but the product from mixed suspension–mixed product removal (MSMPR) crystallizer, which generally conforms more closely to a gamma function distribution, has a C.V. of ~50%.

There are many cases in which a narrowly–sized crop of seeds can be grown in a batch cryatallizer operated with low supersaturation and gentle agitation such that the final crop has a narrow CSD populated mainly by the original seed rather than second generation nucleated crystals. Batch sugar pans are the outstanding example of such systems. In such cases the final width of the CSD is significant and can only be explained assuming some size dispersion mechanism. The technique suggested by White and Wright describes the details of measurement of size dispersion in batch processes. Broadfoot and White incorporated a size dispersion effect together with mass and population balances in the design and simulation of

continuous staged sugar pans. However their technique utilizes the moment transformation that depends on the assumption of mixed product removal and thus is not useful for simulating classified recycle processes.

In continuous mixed discharge crystallizers the variation of residence times usually overrides growth rate variations and the theoretical-predicted wide CSD is produced. However, if a narrow CSD is to be produced in a continuous process, e.g. with a staged, classified fines recycle configuration, the phenomenon of size dispersion due to growth rate should be included in the process description to correctly model the amount of staging and/or classification necessary to produce an acceptably narrow distribution.

2.3.2 Influence of Temperature on Crystal Growth

The rate of crystallization increases rapidly with an increase in temperature for an equal supersaturation. Foster (Foster, 1959 quoted in Chen and Chou, 1993) investigated the rate of sucrose crystal growth from Queensland molasses. He shows that a steady increase in crystallization rate as supersaturation was increased at each temperature and with increasing temperature in the higher supersaturation ranges the crystallization become more rapid. The effect of temperature on crystal growth rate showed that as the rate of integration increases more rapidly with temperature than does the rate of diffusion. In addition crystal growth rates tend to become diffusion controlled at high temperature and integration controlled at low temperature. A study by Smyth (1967) showed that above 40°C sucrose crystallization is controlled by diffusion, and Rumford and Bain (Rumford and Bain 1960 quoted in Mullin 2001) showed the same trend but for sodium chloride that is controlled by diffusion at temperatures above 50°C.

Controlling nucleation of sucrose in many foods is important for product quality and texture. The onset of nucleation is dependent on composition and processing conditions. The temperature at which nucleation takes place is an especially important parameter because as temperature decreases for a given concentration, the driving force for crystallization increases due to the decreasing solubility curve. In the system of the mixture of sucrose and corn syrup, when temperature becomes sufficiently low, molecular mobility becomes important and the onset of nucleation is delayed despite the increasing crystallization driving force due to decrease in mass transfer rates. Mullin and Leci (1969) showed the effect of temperature on nuclei formation in the citric acid water system and clearly showed the relationship between number of nuclei formed at any temperature and the viscosity of the solution at that temperature. A dramatic increase in viscosity was observed as temperature decreased and this led to a maximum in the number of nuclei formed (Mullin and Leci, (1969) quoted in Wesner, Jonathan, Hartel and Day, 2002).

2.3.3 Effect of Impurity on Crystal Growth

As most crystallization processes are not carried out in pure solutions, the effects of impurities on the kinetics of crystal growth are important. In particular, the growth and shape of crystals are apparently affected by present impurities. Any substance other than the material being crystallized can be considered an impurity, so even the solvent from which the crystals are grown is in the strictest sense an impurity, and it is well known that a change of solvent frequently results in a change of the crystal habit. The growth of succinic acid crystals from water and isopropanol solutions is an example that was reported by Davey, Mullin and Whiting (1982). They studied effect of solvent on the growth of the (010) and (001) faces and their

results showed that both faces growth faster in water than in isopropanol resulted in a succinic acid habit modification from platelets to needles.

The presence of impurities in a system can have a deep effect on the growth of a crystal. Some impurities can suppress growth entirely; some may enhance growth, while others may exert a highly selective effect, acting only on certain crystallographic faces and thus modifying the crystal habit. It is well known that sucrose crystals can have various shapes due to different combinations of forms. The occurrence of particular forms depends on the conditions of nucleation and growth. The study of Momonaga, Niehörster, Henning and Urich (1996) investigated the effect of impurities on the solubility, growth behaviour and shape of sucrose crystals. The impurities used in their experiment were glucose, fructose, maltose, and ethanol. The results showed that solubility of sucrose decreased with increasing impurity concentration. Adding impurities can decrease the mean growth rate of sucrose, with the exception of ethanol. Ethanol added will reduce viscosity of the solution resulting in an increased growth rate. There is a little shape change for each impurity, c–direction was changed by glucose and maltose and b–direction was changed by fructose and ethanol.

In general, all impurities tend to impede the crystallization rate of sucrose. Different added impurities have different effects, and it follows that impure solutions of different origins vary in their crystal growth rates at a given purity. The rate of crystallization, then, depends not only on the degree of concentration of impurities, but also on the detailed composition of the impurities. Bliznakov (Bliznakov 1965 quoted in Mullin 2001) studied lead nitrate growth in the presence of increasing amounts of methelene blue, and showed a reversed effect at the low

impurity level of approximately 5 mg/L. That is, at small amount of impurity the growth rate of lead nitrate increased until about 5 mg/L of methelene blue, where the growth rate decreased.

Impurities can influence crystal growth rates in many ways. The properties or the equilibrium saturation concentration, and hence the supersaturation, of the solution can be changed (structural and otherwise). The impurities can change the characteristics of the adsorption layer at the crystal–solution interface and influence the integration of growth units. They may be built into the crystal, especially if there is some degree of lattice similarity. The adsorption of an impurity at a kink site would depend on the similarity of the molecular structure of the impurity with respect to the lattice pattern at the kink on a particular surface. The different faces of a crystal have different surface regimes and different plane lattice patterns so that there is a different probability for adsorption of an impurity on the various surfaces of a sucrose crystal (Smyth, 1966).

The presence of impurities in a system can affect nucleation behaviour very considerably. For example, the presence of small amounts of colloidal substances such as gelatin can suppress nucleation in aqueous solution, and certain surface–active agents also exert a strong inhibiting effect. Traces of foreign ions, especially Cr^{3+} and Fe^{3+}, can have a similar action on inorganic salts. The study of Mullin, Chakraborty and Mehta (1970) studied nucleation of ammonium sulphate aqueous solution with five impurities, Cr, Fe, Al, Ni and Na. Their results showed a certain patterns of behaviour that the higher the charge on the cation the more powerful the inhibiting effect, e.g. $Cr^{3+} > Fe^{3+} > Al^{3+} > Ni^{2+} > Na^{+}$. Furthermore there

often appears to be a threshold concentration of impurity above which the inhibiting effect may actually reduce.

The study of Giulietti et al. (1999) about the effect of additives (solvents, ionic substances and surfactants) on crystallization of copper sulphate pentahydrate shows that the habit of crystals was changed, and the overall growth rate was reduced. The work of Wang et al. (2000) on sucrose crystallization indicates that glucose molecules adsorbed onto the surface of the (110) face causing the growth of this face to stop. The growth of the faces $(0\bar{1}1)$ and (111) was reduced when fructose was added. They suggested that the results obtained, including the formation of a sawtooth–like roughening, may come from adsorption of fructose on these faces.

Botsaris, Denk and Chua (1972 quoted in Mullin 2001) have made a suggestion for the action of impurities; if the impurity suppresses primary nucleation, secondary nucleation can occur if the uptake of impurity by the growing crystals is significant; the seed crystal creates an impurity concentration gradient about itself; the concentration of impurity near the crystal surface becomes lower than that in the bulk solution; and if it is reduced low enough, nucleation can occur. Another suggestion is proposed by Sarig and Mullin (1980): They proposed that certain impurities could enhance secondary nucleation by adsorbing at defects on existing crystal surfaces and by initiating crack propagation, making the crystals inclined to disintegration. On the other hand Kubota, Ito, and Shimuzu (Kubota, Ito, and Shimuzu 1986 quoted in Mullin 2001) have interpreted the effects of ionic impurities on contact secondary nucleation by a random nucleation model.

The effects of soluble impurities may be caused by changing the equilibrium solubility or the solution structure, by adsorption or chemisorption on

nuclei or heteronuclei, by chemical reaction or complex formation in the solution, and so on. The effects of insoluble impurities are also unpredictable.

2.3.4 Effect of Crystal Perfection on Crystal Growth

An investigation of Lacmann and Tanneberger (1995) on single crystal growth of potassium alum shows that the surface quality can affect the face–specific growth rate. In particular, they showed that the mean growth rate of (111) faces on hurt crystals can grow faster than unhurt ones. This result was also apparent for the (100) faces. This study also quoted the work of Offermann and Ulrich (1983), and Ulrich and Offermann (1985), that implied that the perfection of different crystal will be different, and this will result in different growth rates.

2.3.5 Techniques Used to Study Crystal Growth

2.3.5.1 Batch Crystallizer

The crystalline products such as fine chemicals, pharmaceuticals, dyestuffs, and other specialty chemicals, can be produced in small and medium amounts, so that in many real processes it is more suitable to use batch crystallizers than the continuous crystallizers. Batch crystallizers are often seeded with a narrow size distribution of solute crystals. The supersaturation in batch crystallizers is not constant, that is, they operate in an unsteady state condition, and thus the crystal size distribution (CSD) and other product quality in batch crystallizers can be affected by the initial condition and the retention time in the crystallizers. There are wide varieties of batch size selection depending on the crystal size expected and the sample used.

Laboratory batch crystallizers are simple equipment that requires less apparatus and solvent, and are also simple to operate, usually at constant

temperature and pressure. In batch crystallizers the supersaturation can be achieved by evaporation, cooling, salting out and combinations of these procedures. Figure 2.11 shows a batch crystallizer where the evaporation is used to reach the supersaturation.

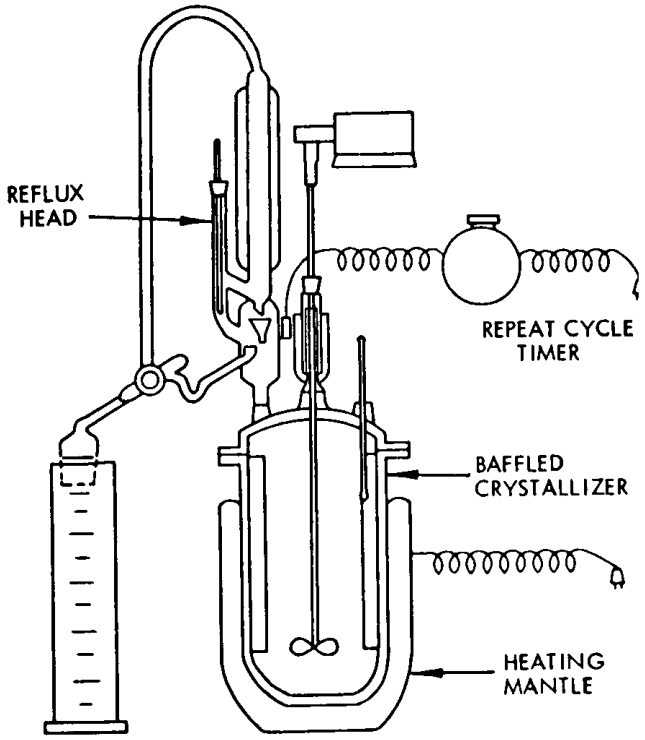


Figure 2.11 Evaporative batch equipment (Randolph and Larson, 1988).

2.3.5.2 Mixed–Suspension, Mixed–Product–Removal (MSMPR)

The continuous mixed–suspension, mixed–product–removal (MSMPR) crystallizer, shown in Figure 2.12, is analogous to the continuous stirred–tank reactor (CSTR). This type of crystallizer is consists of an inlet tube, outlet tube, baffles, and stirrer. This type of crystallizer is often used for study in the laboratory,

and also in real processes. The reasons for its selection are that it is easy to use and gives a relatively uniform particle size if perfectly mixed. There is no product output returned to the crystallizer, so that the liquid in the crystallizer has got the same concentration as in the product output. Another advantage of using this type of crystallizer is the variety in choice of the equipment sizes, that is appropriate for both experimental studies and industry. Moreover, a MSMPR used in the laboratory can operate with conditions similar to industrial use, and it is also possible to use plant liquors in experiments.

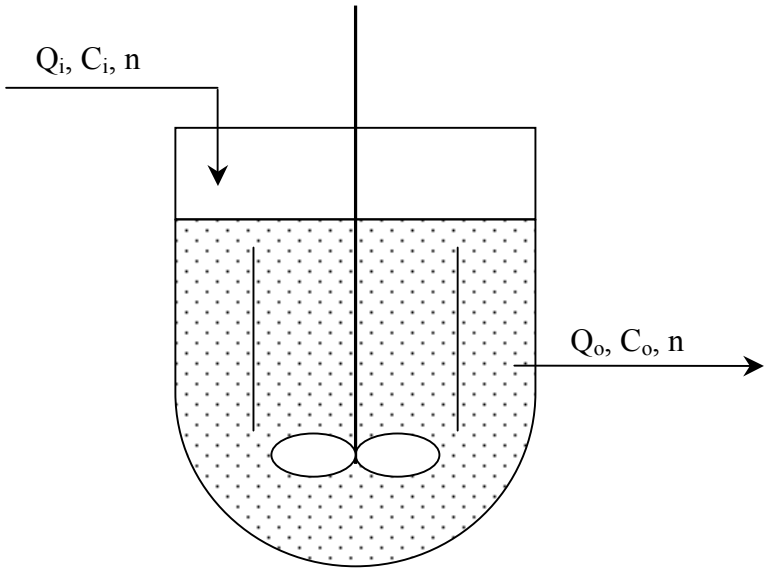


Figure 2.12 Schematic representation of MSMPR crystallizer.

2.3.5.3 Photographic Nucleation Studies

The photographic nucleation study technique was developed by Garside and Larson (1978), and is often used to determine the growth of individual nuclei or crystals. The equipment they used is called the secondary nucleus cell, or

photomicroscopic cell, nucleation and growth cell, or small cell. The main components of this cell are the upper chamber and the lower chamber that are separated by glass or clear acrylic at which crystals can be back–lit and photographed through an optical microscope. Thus the number and size of growing nuclei can be observed and photographed or videotaped. The upper chamber is filled with the solution and the lower one used to circulate constant temperature water. This technique has been used to study growth rate dispersion and the effect of any processing conditions on the growth rate in variety of materials, such as sucrose, fructose, $NaNO_3$, citric acid monohydrate. Figure 2.13 is the equipment set used by Garside and Larson (1978).

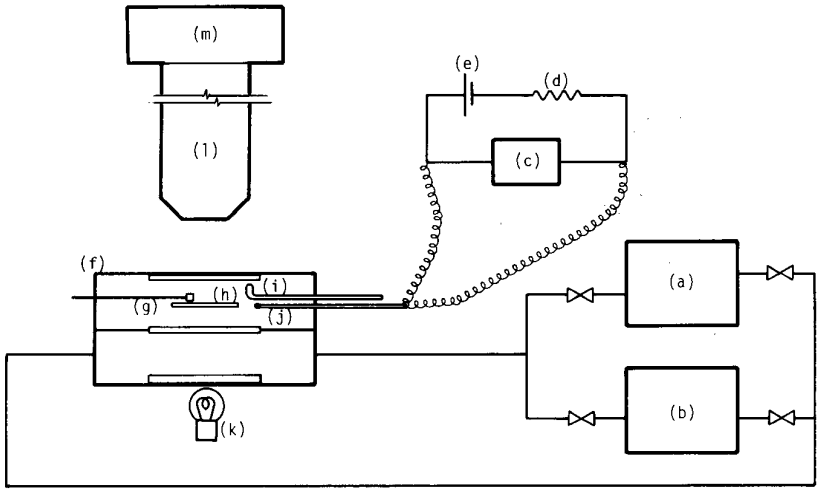


Figure 2.13 Secondary nucleus cell (a), (b) saturation chambers; (c) voltmeter; (d) resistance; (e) battery; (f) cell; (g) crystal holder; (h) contact surface; (i) crystal contactor; (j) thermistor; (l) microscope; (m) camera (Randolph and Larson (1988)).

2.3.5.4 Contact Nucleation Method

In industrial crystallizers, the primary source of nuclei produced is contact nucleation where a small number of nuclei are generated, compared to other mechanisms, such as fracture or attrition. Contact nucleation in the crystallizer is because of the contact between crystals and the agitator, pump, flow lines or other crystals. However, in every contact there may be also some fracture and usually some attrition occurring. Power (1963), Strickland–Constable (1968), Clontz and McCabe (1971) proposed that contact nucleation is the main source of secondary nuclei. Strickland–Constable (1968) showed that by sliding a growing crystal along the bottom of a beaker, nucleation was induced and then new crystals appeared on the bottom of the beaker. Three years later Clontz and McCabe (Clontz and McCabe 1971 quoted in Randolph and Larson 1988) confirmed that nuclei could be generated by the contact nucleation mechanism. They showed that low energy contacts normal to the surface of a growing crystal produced a number of new crystals after a short growth period, as in the previous study. In 1987, Shimizu et al. (1987) studied the growth rate of potassium alum secondary nuclei. They generated nuclei by contact between crystal and glass rod, and after growth these nuclei were observed under a microscope. They found that contact nuclei are irregularly shaped, and of variable size (from a few micrometer up to fifty micrometer), and were apparently broken pieces of the parent crystal. The crystals had significant growth rate dispersion, but the growth rates of individual contact nuclei was not related to their size.

Chapter 3

Research Procedure

The experiment will be separated into three parts. The first part is a study of the growth rate distribution of nuclei in pure aqueous sucrose solutions. The second part is a study of the growth rate distribution of sucrose secondary nuclei in impure solutions. The third part is a study of the growth rate distribution of crushed pure and impure seeds, and uncrushed pure seed crystals in pure aqueous sucrose solutions.

3.1 Chemicals

The chemicals used in this study are:

1. Refined sugar (Commercial grade (~99.8%), Mitrphol, Thailand)
2. Mineral sugar (Commercial grade, Mitrphol, Thailand)
3. Glucose (ACS–grade, Italmar (Thailand))
4. Fructose (ACS–grade, Italmar (Thailand))
5. Sodium chloride (ACS–grade, Italmar (Thailand))
6. Potassium chloride (ACS–grade, Italmar (Thailand))
7. Distilled water (Environmental Engineering Laboratory, F5, SUT, Thailand)

For experiments involving nuclei and seed crystals in pure solution, the chemical used as a solute is commercial food grade white sugar (sucrose) produced by Mitr Phol (~99.8 % purity) and distilled water obtained from the Environmental

Engineering laboratory, SUT, as a solvent. The saturated concentration of pure solution is calculated using an equation proposed by Vavrinecz (1955) as follows:

$$C^* = 64.447 + 0.10336T + 1.424 \times 10^{-3}T^2 - 6.02 \times 10^{-6}T^3 \qquad (3.1)$$

where C^* is the saturation concentration (g sucrose/100 g solution) and T is temperature in degree Celsius. The equation is valid in a range of temperatures from –13 to 100°C. This equation is widely accepted as very accurate for pure aqueous solutions of sugar.

For impure solutions, fructose, glucose, potassium chloride and sodium chloride are used as impurities. Solubility for various impurity/water ratios will be predicted following the three–component ternary diagrams proposed by Kelly (1954), valid for 30°C.

Sucrose or sugar is a common food ingredient. It is used primarily to satisfy the natural human desire for sweetness. In most of its forms, it is a very pure food ingredient. It is also a versatile ingredient and, as a digestible carbohydrate, a nutrient. Sucrose is produced by most plants, but the plants used in commercial operations are sugar beet and sugarcane only. Refined sugar is available in variety of granulations. There is no standard definition of granulation grades, so crystals from different manufacturers may have different mesh size as standard.

Brown sugar is composed of very fine crystals in a thin film of syrup. It is produced in two different ways. For the traditional method, a suspension of sugar crystals in cane syrup selected for its colour and flavour is boiled to produce a sugar cane brown sugar with flavour and colour throughout the crystal: in the other method, cane or beet sugar crystals are coated with a proper molasses. Another name of brown

sugar is soft sugar. This sugar is relatively high in ash and moisture and usually slightly sticky, although an agglomerated, free–flowing form is available. Brown sugars are generally graded by colour with grades ranging from light yellow to dark brown. In this work the commercial grade of natural mineral sugar produced by Mitrphol, is used as impure seed crystals for the third part of experiment – different kind of seed crystals grow in pure solution. Its colour is light brown.

Glucose, a simple sugar monosaccharide is one of the most important carbohydrates and is used for energy in plants and animals. It was formerly known as dextrose. Glucose ($C_6H_{12}O_6$) is a hexose – a monosaccharide containing six carbon atoms. Five of these carbons, plus an oxygen atom, form a loop called a pyranose ring, the most stable form for aldoses. In this ring, each carbon is linked to hydroxide and hydrogen side groups with the exception of the fifth atom which links to a 6^{th} carbon atom outside the ring, forming a CH_2OH group. The two main isomers of glucose are alpha–glucose and beta–glucose. Structurally, they differ in the orientation of the hydroxide group linked to the first carbon in the ring. The alpha form has the hydroxide group below the hydrogen group, the beta form has the hydroxide group above the hydrogen.

Fructose, or levulose, is the form of sugar found in fruit and honey. It is a laevorotatory monosaccharide with the same empirical formula as glucose but with a different structure. Although fructose is a hexose (6 carbon atoms), it can exist as a 5–membered hemiacetal ring (a furanose). All fruit naturally contains a certain amount of fructose (often together with glucose), and it can be extracted and concentrated to make an alternative sugar.

Potassium chloide (KCl) is a metal halilde which is used in medicine, scientific applications, food processing and in judicial execution through lethal injection. It occurs naturally as the miniral Sylvite and in combination with sodium chloride as Sylvinite. In a pure state it is a odourless, white to colourless vitreous crystal. It is a face–centred cubic which cleaves easily in three directions; its physical properties include a density of 1.987 g/cm³, a melting point of 776°C, a boiling (sublimation) point of 1500°C, and a molecular weight of 74.55. It is readily soluble in water and insoluble or only slightly soluble in alcohols.

Sodium chloride, also known as common salt or table salt, is a chemical compound with the formula NaCl. Sodium chloride is the salt most responsible for the salinity of the ocean and of the extracellular fluid of many multicellular organisms. It is commonly used as a flavour enhancer and preservative for food and to de-ice roads. Sodium chloride is essential for life. Humans are unusual among primates in secreting large amounts of salt by sweating.

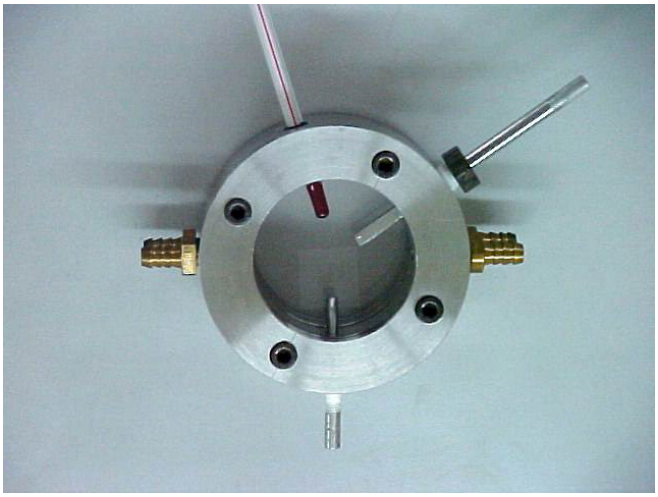
As can be seen by Table 2.1, fructose, glucose (together as invert sugar), potassium chloride, and sodium chloride are among the highest concentration impurities in the raw syrup in sugar processing plants, and are thus suitable compounds for impurity studies.

3.2 Equipments

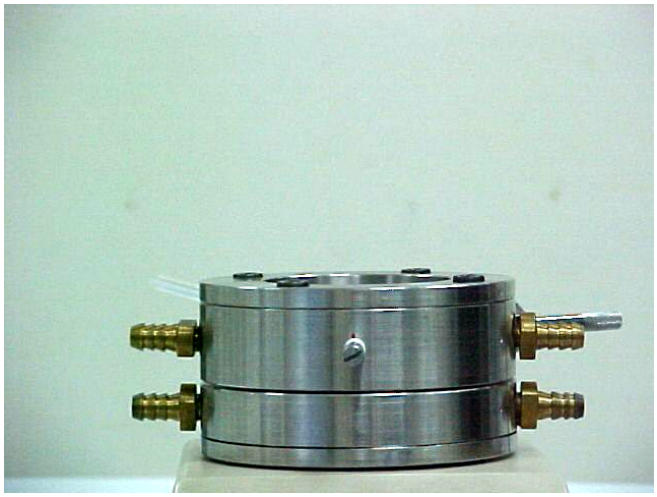
All experiments are investigated in a small cell called the photomicroscopic cell. Figure 3.1 and Figure 3.2 show the photomicroscopic cell and its drawing and assembly, respectively. The cell can be separated into two chambers, the upper and the lower. The volumes of the upper and lower chamber are 76.97 cm^3 and 61.58

cm^3, respectively. Both chambers are separated by transparent acrylic. The top and bottom of the cell are also closed by the transparent acrylic. This material is more durable than glass and does not easily break when flow is applied. The upper chamber is a solution chamber that contains a thermometer with an accuracy of ± 0.25ºC, a glass cover slip holder, movable rod, and solution inlet and outlet. If solution flow is required, a peristaltic pump as shown in figure 3.3, will be used to generate flow. The movable rod is the rod next to the thermometer, where the parent crystal is glued. The fixed rod is a support rod for glass cover slip, opposite to the thermometer. The lower chamber is a water chamber that circulates constant temperature water at a desired value using a constant temperature water bath (Figure 3.4) with an uncertainty of ±0.02°C.

Nuclei and seed crystals are observed during growth using a microscope. They are photographed as the time progresses using a Sony colour video printer connected to the microscope. The microscope and its connection to the colour video printer show in Figure 3.5 and Figure 3.6, respectively.

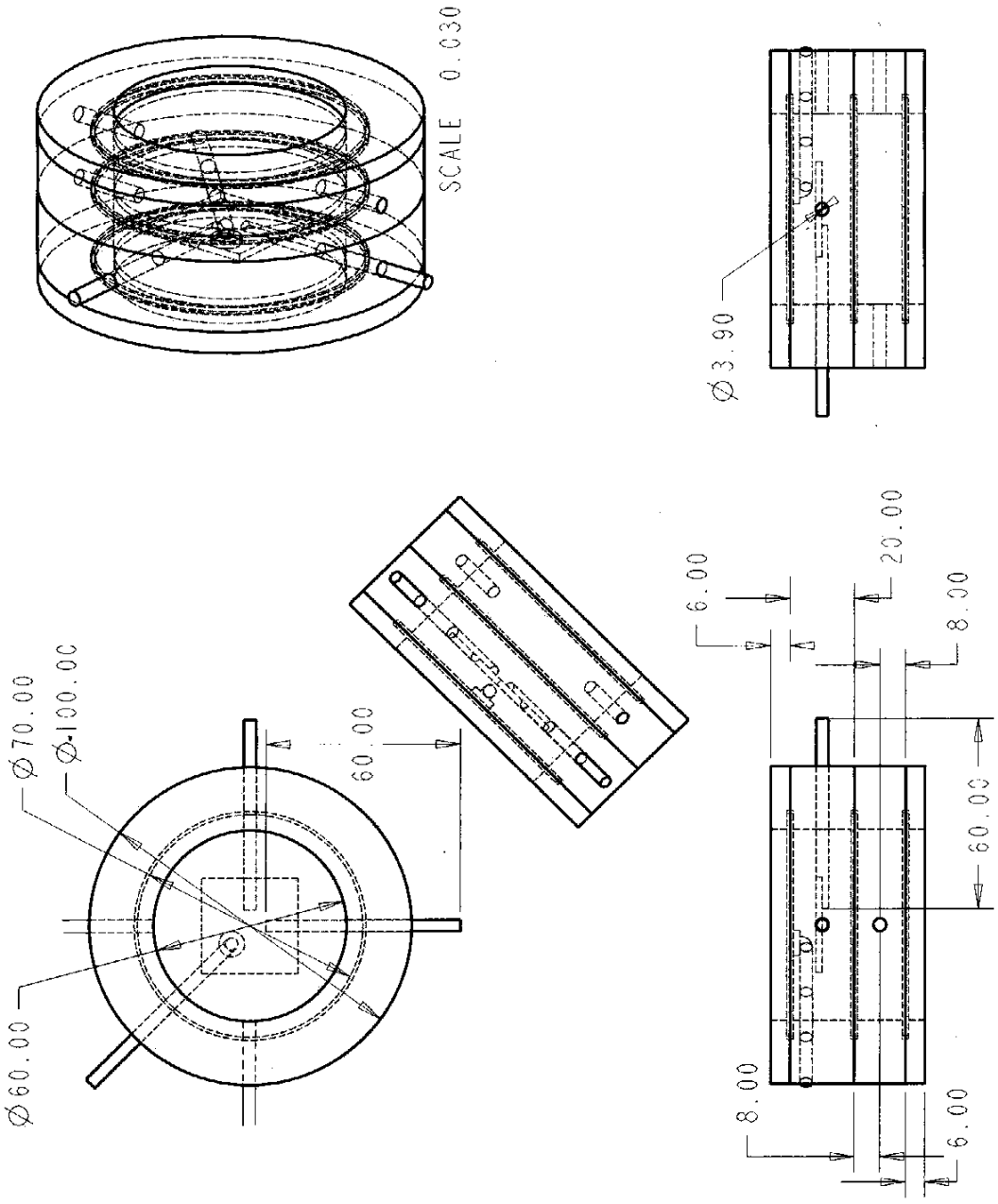


(a)



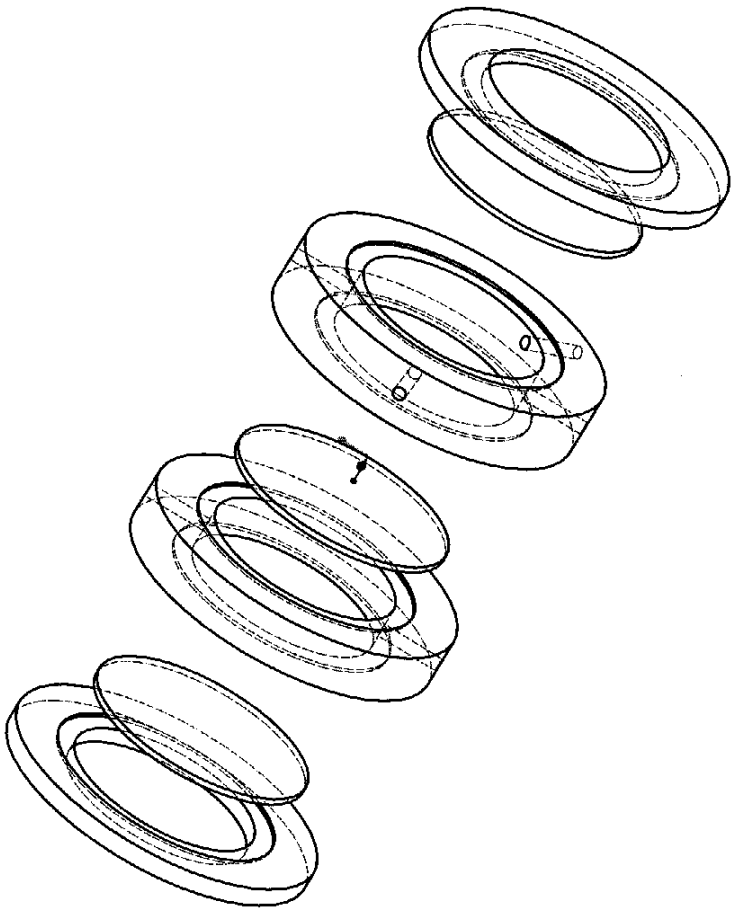
(b)

Figure 3.1. Photomicroscopic cell picture: (a) top view; (b) side view.



(a)

Figure 3.2 (a) Photomicroscopic cell drawing; (b) Top and bottom chambers assembly.



(b)

Figure 3.2 (Cont.) (a) Photomicroscopic cell drawing; (b) Top and bottom chambers assembly.

Figure 3.3 Peristaltic pump.

Figure 3.4 Constant temperature water bath.

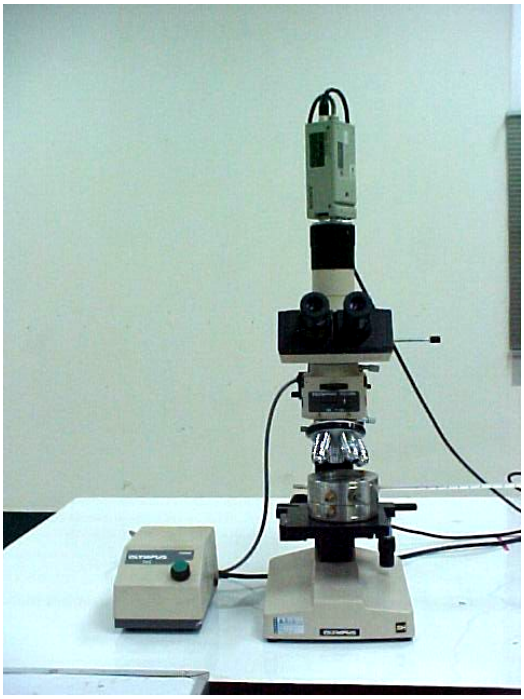


Figure 3.5 Microscope.

Figure 3.6 Crystallization equipment and microscope, connected to colour video printer.

3.3 Procedures

3.3.1 Contact Nucleation in Pure Solution Technique

The chemicals used to study crystal growth rate dispersion of nuclei in pure solution were commercial grade sucrose produced by Mitr–Phol ((~99.8%) Thailand) and distilled water obtained from the Environmental Engineering Laboratory (F5, SUT, Thailand). The saturated concentration of pure solutions was calculated following an equation that was proposed by Vavrinecz (1955):

$$C^* = 64.447 + 0.10336T + 1.424 \times 10^{-3}T^2 - 6.02 \times 10^{-6}T^3 \quad (3.2)$$

The experiment involves three factors, flow rate, temperature and supersaturation, each of which is expected to have some effect on the growth rate distribution of nuclei. Each of these factors will be explored at two levels – a high and low level in an ANOVA experiment. The high level of the solution flow rate – 40mL/min – is required for definite surface integration limited growth, while a stagnant solution gives the lowest possible level of the flow. With temperature, the high level is at 40°C, a temperature at which it is reasonable for the equipment, in that the solution will become very viscous at higher temperatures because of the very high solubility. The low level is set at 25°C, as this approximates room temperature in the laboratory. Since secondary nucleation is required, and primary nuclei may be formed at supersaturations ($\Delta T = T - T^*$) greater than 10°C, the maximum supersaturation is set at the limit of ΔT=10°C. The low level of this value is ΔT=5°C, which is half the range between no growth (ΔT=0°C) and the high limit (ΔT=10°C). The conditions used in this part can be summarized in Table 3.1.

Table 3.1. The experimental conditions used to study growth rate dispersion of nuclei in pure aqueous sucrose solution.

Solution flow rate		Temperature		Supersaturation ($\Delta T = T - T^*$)	
Level		Level		Level	
high	40mL/min	high	40°C	High	10°C
low	stagnant	Low	25°C	Low	5°C

The experiments were performed in a photomicroscopic cell, as shown in Figure 3.1. Nuclei can be generated in the upper chamber using the contact nucleation method that is commonly used to generate nuclei, called contact nuclei. With this method a parent crystal will be glued on a moveable rod that will be slid gently over the glass cover slip for 30 seconds to generate nuclei. Nuclei will be left to grow in the solution and their photograph taken every 40 minutes for 6 hours using a colour video printer equipped to the microscope. Examples of the pictures are shown in figures in the next section.

3.3.2 Contact Nucleation in Impure Solution Technique

In order to study growth rate of nuclei when impurities are present, impurities were added with different levels of impurity/water ratio following the ternary diagrams of Kelly. This study investigated four impurities; they are two types; monosacharides – fructose and glucose, which are commonly found in syrups in sugar mills, and two salts – sodium chloride (NaCl) and potassium chloride (KCl), also common impurities in raw juice in sugar mills. The ternary diagrams for the

systems sucrose–fructose–water, sucrose–glucose–water, sucrose–NaCl–water and sucrose–KCl–water, were proposed by Kelly (1954) are used to predict the solubility data, and are valid for 30°C. For fructose and glucose, the maximum impurity/water ratio is I/W = 0.5, while sodium chloride (NaCl) and potassium chloride (KCl) the maximums are 0.4. These values are inferred to be limit (the maximum point) where only sucrose can crystallize out, rather than having a mixed product. The other level of the impurity/water ratio (I/W) is set halfway between the high limit and without impurity; that is I/W = 0.25 for fructose and glucose, and I/W = 0.2 for sodium chloride (NaCl) and potassium chloride (KCl). The last factor considered in this section is the supersaturation, which is set equal to the previous experiment, (ΔT=5°C and ΔT=10°C). To meet these values, operating temperatures were chosen at 20°C and 25°C. The conditions used in this part can be summarized in Table 3.2.

Table 3.2. The experimental conditions used to study growth rate dispersion of nuclei in the impure stagnant solution with saturation concentration temperature at 30°C.

Temperature		I/W ratio			Supersaturation ($\Delta T = T–T^*$)	
			Fructose and Glucose	NaCl and KCl		
Level		Level			Level	
high	25°C	high	0.50	0.40	High	10°C
low	20°C	Low	0.25	0.20	Low	5°C

The experiment will be performed under stagnant conditions only, in the photomicroscopic cell shown in Figure 3.1. The method used to generate nuclei is the contact nucleation method where nuclei were generated by contacting a parent crystal over the glass cover slip. Over a long period, nuclei would be observed and photographed every 40 minutes for 6 hours. These steps are the same as for the contact nucleation experiments in the pure solution experiment. Examples of the photomicrographs are shown in figures in the next section.

3.3.3 Seed Crystals in Pure Solution Technique

The third part of the thesis is a study of the growth rate distribution of seed crystals in pure solution in comparison to the contact nuclei experiments earlier. As in the first part of the experiment, the concentration of pure solution was calculated following equation 3.2. The conditions of this part are also the same as the first part, except that experiments are only carried out under stagnant conditions, and no nuclei are generated. All seed crystals grow in the stagnant pure solution with the supersaturation levels of $\Delta T=5°C$ and $\Delta T=10°C$. Three different types of seed crystals are used; crushed pure and impure seed, and uncrushed pure seed. The uncrushed seed crystals would be selected from the package of commercial refined sugar and sieved to obtain the size range of 106–150 μm. A narrow seed crystals size distribution is preferred to ignore effect of initial size distribution. These crystals would be checked with a microscope to verify that they are single crystals (not twins), and are good crystals. The good crystals chosen usually have smooth flat faces, sharp edges, no inclusions, no striations, and no obvious dislocations. For crushed seed crystals, the crystals from the package will be ball–milled and sieved to obtain a size range of 106–150 μm, as for the uncrushed seed crystals. Next some of the sieved

crystals would be selected randomly without any checking using a microscope, because imperfect crystals are required. At least 30 seed crystals were glued on a glass cover slip by epoxy glue and left to grow in the photomicroscopic cell filled with pure aqueous sucrose solution. These seeds would be photographed every 40 minutes for 6 hours using a colour video printer equipped to the microscope as used in the nucleation experiment. Examples of the pictures are shown in figure in next section. The conditions used in this part can be summarized in Table 3.3.

Table 3.3. The experimental conditions used to study growth rate dispersion of seed crystals in the impure stagnant solution.

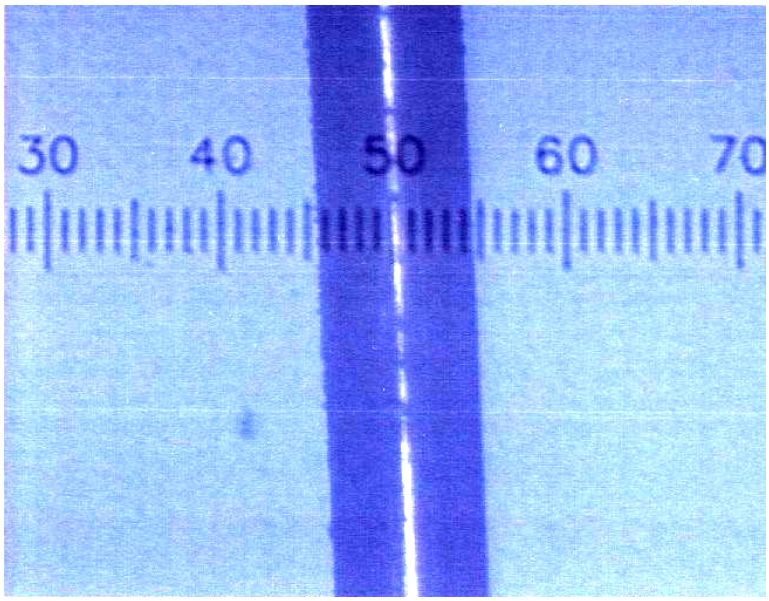
Type of seed crystals	Temperature		Supersaturation ($\Delta T = T - T^*$)	
Uncrushed pure	Level		Level	
Crushed pure	high	40°C	high	10°C
Crushed impure	Low	25°C	low	5°C

3.4 Calibration

In order to obtain the dimension of nuclei and seed crystals exactly, a calibration is required. A reference used for this experiment is a copper wire with a real dimension measured using a digital vernier and micrometer to determine its size. The copper wire was then glued onto the glass cover slip and immersed in the solution at the same conditions as used in the experiment. The reference was magnified by the microscope and photographed by the colour video printer to determine its size as, shown in Figure 3.7 (a) and (b).

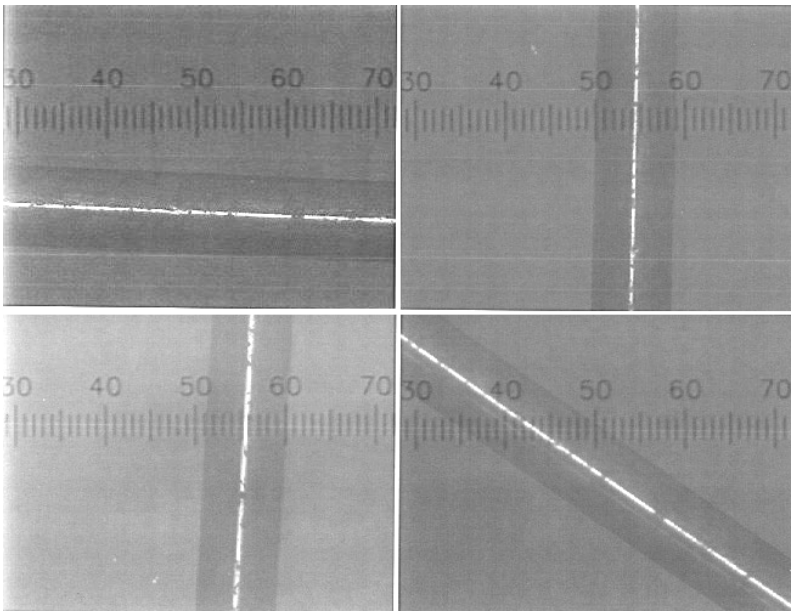
The actual diameter of the copper wire obtained from the digital vernier is 0.24 mm., and from the micrometer is 0.25 mm. The average size of the reference wire is 0.245mm. A ruler – as used to measure nuclei dimension, would measure the size of the wire in the printed micrograph, and the magnified size is 0.875 inch. Thus the analogous dimension is 0.28 mm/inch. This value is used to convert nuclei size obtained from the micrograph to actual size with the unit in millimeter.

For the seed crystal experiments, image analysis software is used to measure the size of the crystals. The picture of the reference wire would be used to measure the diameter using OLYSIAm3 with units of pixels. Four separate pictures gave 66 pixels of reference wire and the real dimension is as before, 0.245 mm. So the analogous dimension is 0.003712 mm./pixel. This value is used to convert size of seed crystals from pixel to millimetre.



(a)

Figure 3.7 Reference wire: (a) for nucleation experiment; (b) for seed crystal experiment.



(b)

Figure 3.7 (Cont.) Reference wire (a) for nucleation experiment; (b) for seed crystal experiment.

3.5 Analysis

In this study, the mean and the coefficient of variation, or the relative size spread, are used to describe the average (or central) growth rate, and the relative uniformity of the growth rate distribution. That is, these terms explain how fast the particles grow, and how much growth rate variation they have relative to the mean growth rate. In addition, the skewness and kurtosis are often used to qualitatively

indicate the shape of the growth rate distribution relative to a normal distribution. The skewness is a measure of the symmetry about the mean and is zero for symmetric distributions. Positive skewness indicates a distribution skewed to the right and negative skewness indicates a skewed to the left of the mean. The log–normal and the gamma distribution are examples of positive skewness. The kurtosis is a measure of the shape of the distribution curve at the extreme ends, relative to the normal distribution. A distribution with positive kurtosis will have a sharper peak but broader tails than a normal distribution. For the normal distribution, the kurtosis is zero.

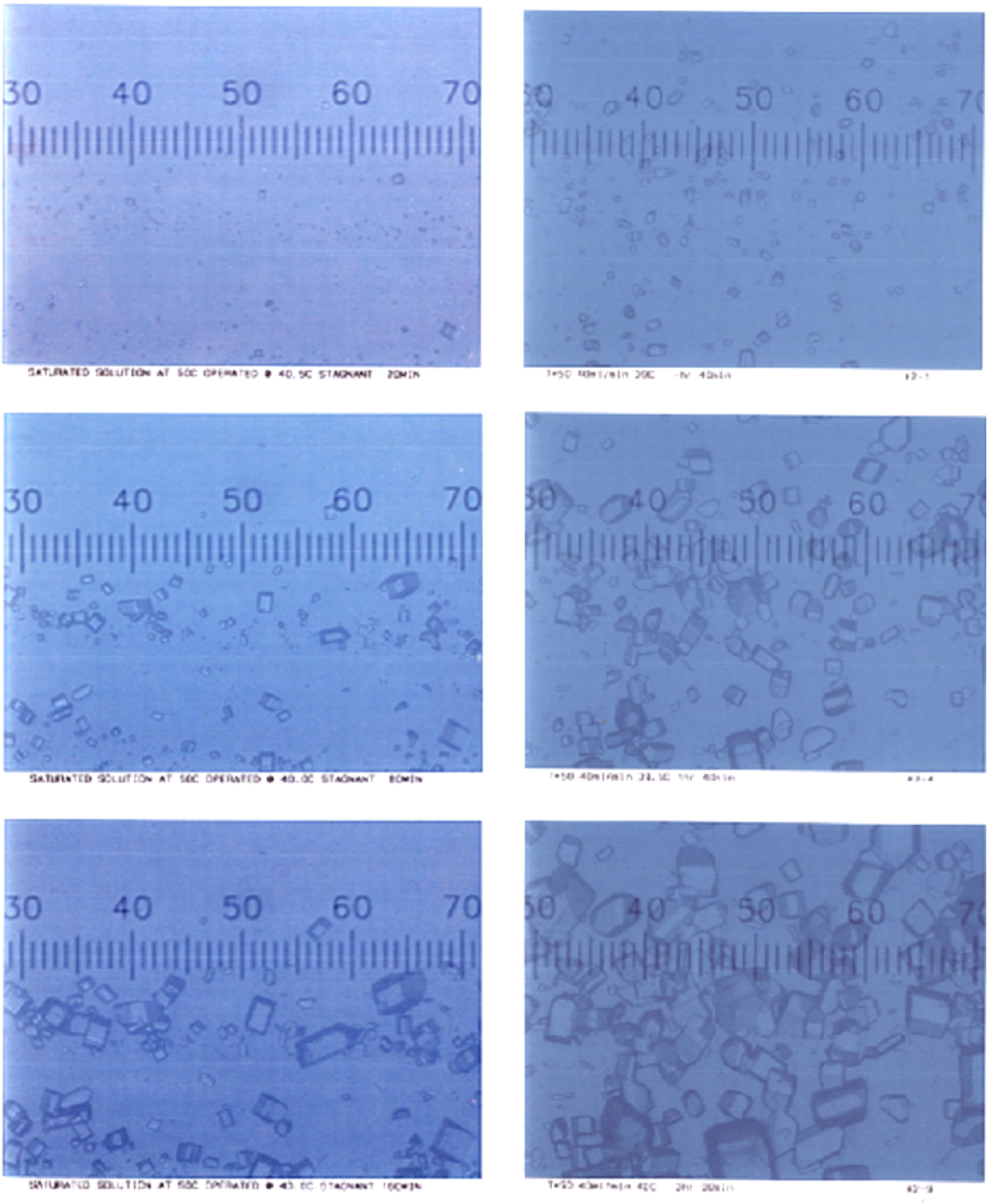
Micrographs obtained from the experiment using a SONY colour video printer showed the growth of nuclei and crystals as the time progressed. Figure 3.8 to 3.11 show examples of nuclei grown in pure and impure solution. For seed crystals grown in pure solution, an example of the results is shown in Figure 3.12.

In the nucleation experiment, nuclei would be selected randomly, at least 30 nuclei, to examine the size by using a ruler with the finest scale of 1/64 inch. Then the size of each individual nucleus (unit: inch) was changed to a characteristic length L with units of millimetre by multiplication by 0.245mm/inch – the square root of product of the width and length:

$$L = \sqrt{L_1 \times L_2} \tag{3.3}$$

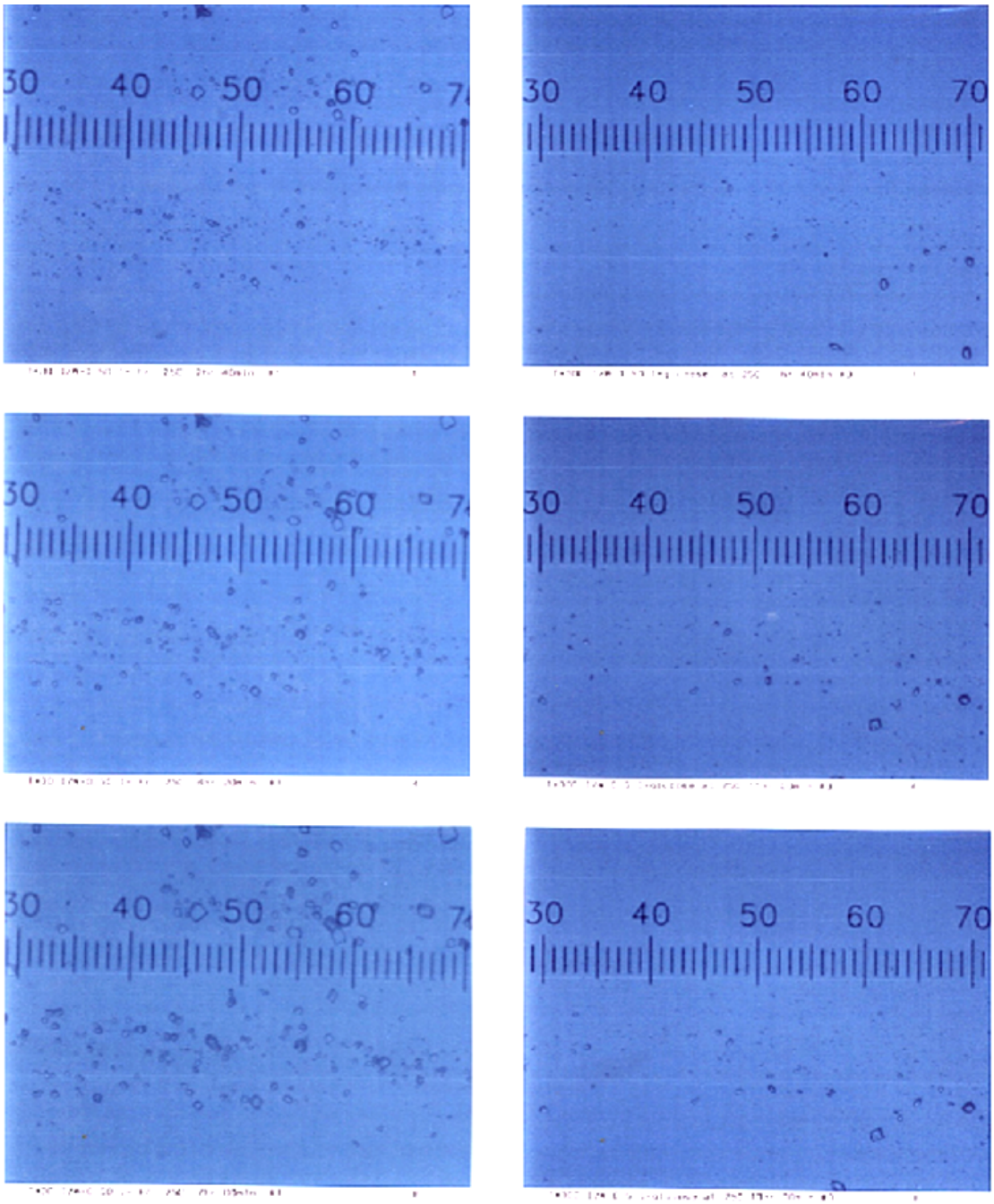
where L_1 and L_2 are two dimensions of the objects – width and length. The characteristic length of nuclei was calculated and plotted as function of time – an example of the plot is shown in Figure 3.13. Microsoft Excel was used for data plotting and linear regression calculations. The slopes of these plots represent the

growth rate of each nucleus. In addition, by using the descriptive statistics command in Excel, the statistical values would be obtained such as mean, standard deviation, and variance, among others.



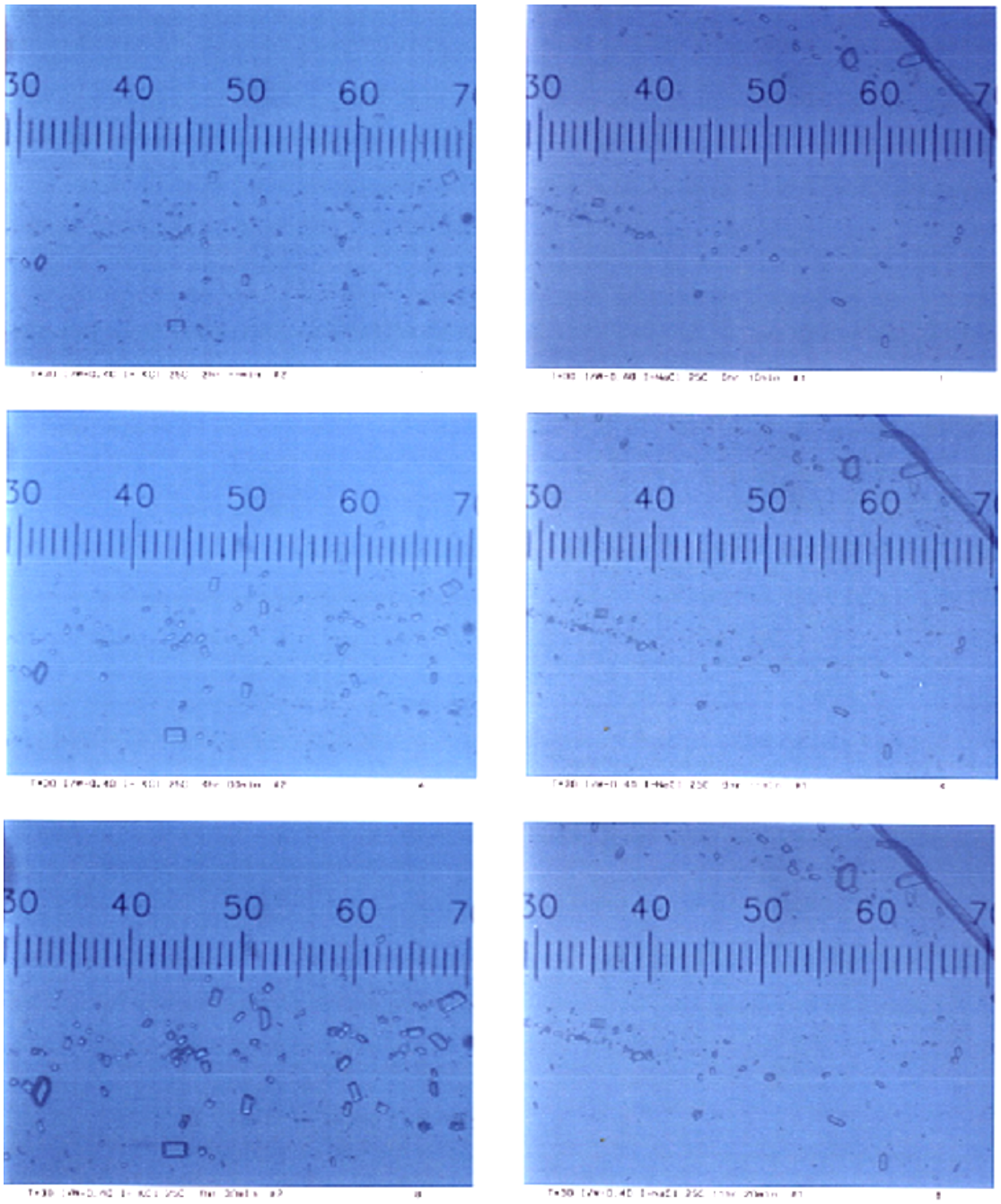
(a) (b)

Figure 3.8 Nuclei obtained from pure–saturated solution at 50ºC (a) stagnant; (b) 40 mL/min and operating temperature 40ºC.



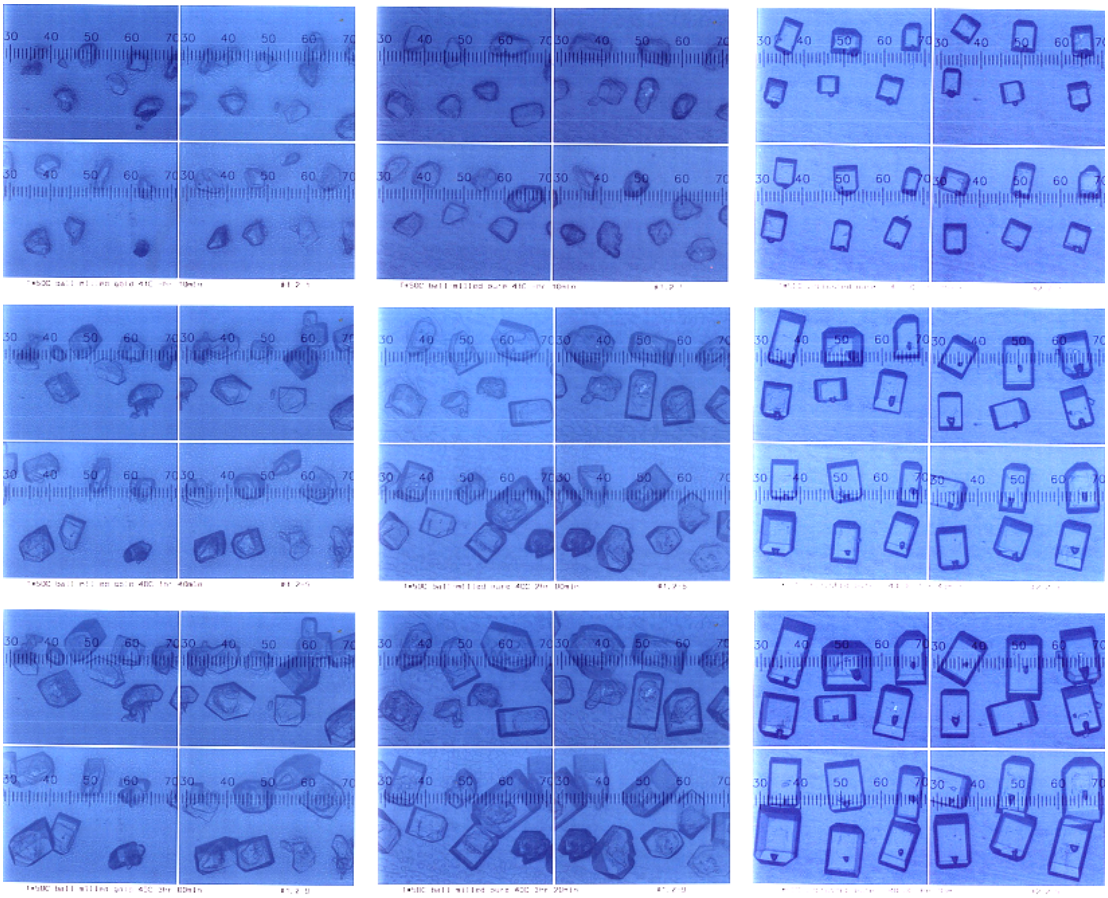
(a) (b)

Figure 3.9 Nuclei obtained from impure–saturated solution at 30ºC with I/W 0.5, stagnant solution at 25ºC and impurity as (a) fructose; (b) glucose.



(a) (b)

Figure 3.10 Nuclei obtained from impure–saturated solution at 30ºC with I/W 0.4, stagnant solution at 25ºC and impurity as (a) KCl; (b) NaCl.



(a) (b) (c)

Figure 3.11 Seed crystals grown in pure sucrose solution at 40ºC and ΔT 10ºC of (a) crushed pure seeds; (b) crushed impure seeds; (c) uncrushed pure seeds.

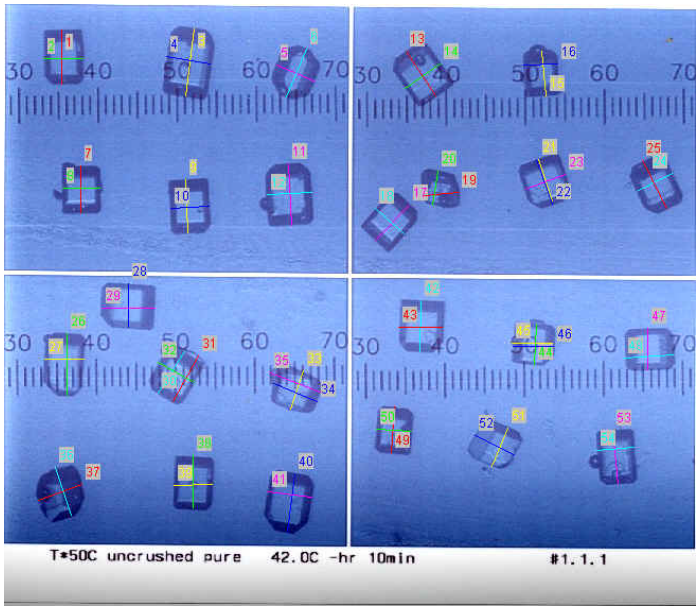


Figure 3.12 Seed crystal measurement using OLYSIAm3.

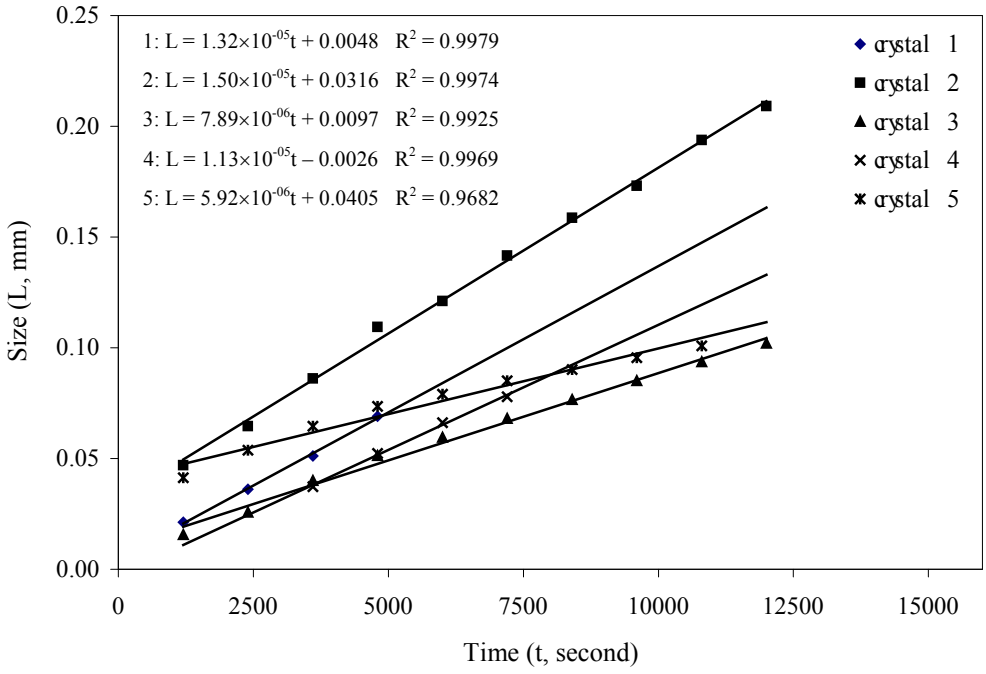


Figure 3.13 Example of size versus time plot for multiple crystals grown in the photomicroscopic cell.

In the seed crystals experiment, the crystals were measured size by using image analysis software named OLYSIAm3. Figure 3.12 shows an example of the micrograph when the software was used; the results obtained were in pixel, and these would be shown in spreadsheet of Microsoft Excel. As previously, the size of crystals would be changed from pixels to a characteristic length in millimeters by multiplication by 0.003712mm/pixel, and then they were plotted with respect to time. By linear regression, the slope of each of the seeds would be obtained, and these slopes are the growth rate for each crystal. These growth rates were applied to the statistical formulas to obtain the statistical values.

Figure 3.13 shows examples of size vs. time plots of individual crystals. The growth rate of each crystal can be represented by the slope in this plot. The variations in slope and intercept of the lines correspond to the growth rate distribution and initial size distribution, respectively. In addition, each individual crystal can grow at different rates but tend to grow at a constant rate. That is, these crystals follow the constant crystal growth model of growth rate dispersion. Further, since the slope of the line is equal to the growth rate, so the plot implies size–independent growth rate also.

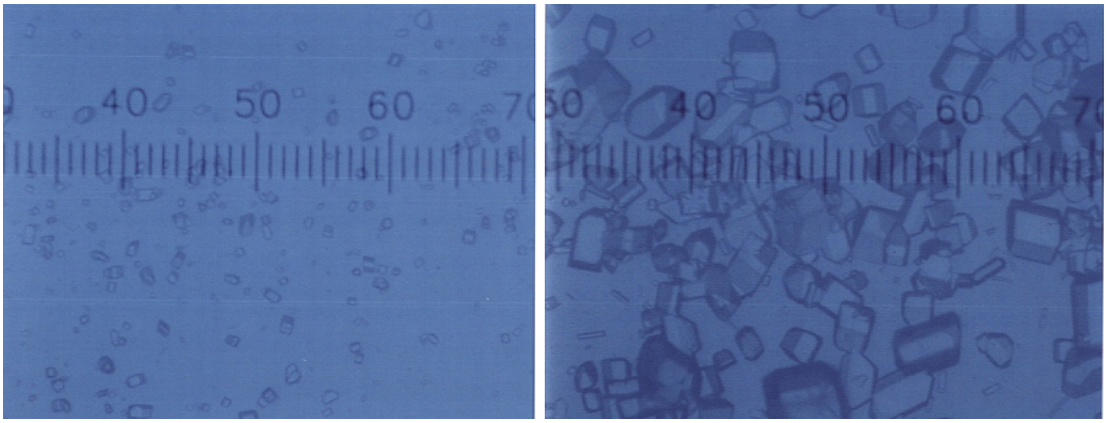
Chapter 4

Results and Discussion

4.1 Results

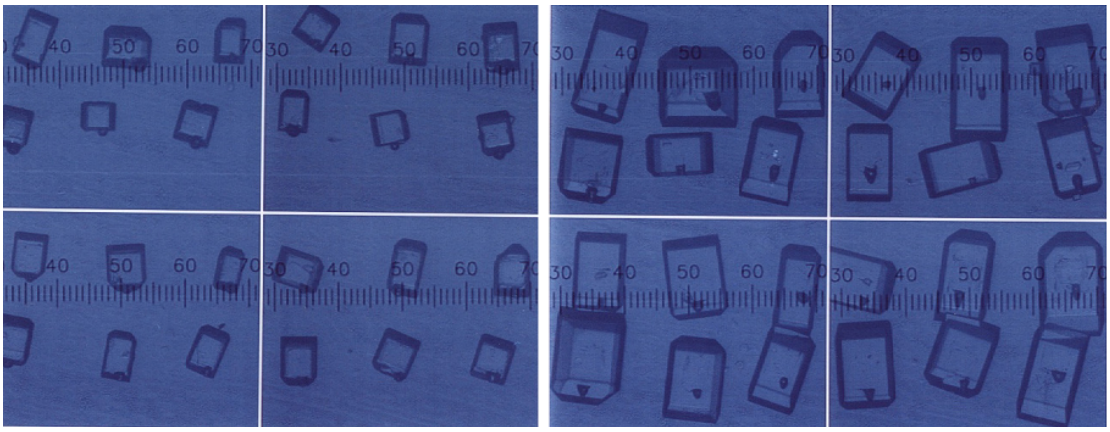
This study is separated into three parts in order to study the effect of processing conditions on the growth of sucrose nuclei and seed crystals. The first part of the experiment studies the effect of three variables – flow rate, supersaturation, and temperature, on the growth of contact nuclei grown in pure sucrose solution. The second part studies the effect of type of impurity, supersaturation, and impurity/water ratio, on the growth of contact nuclei in stagnant sucrose solution. The third part studies the growth of seed crystals in pure solution with effect of type of seeds, the supersaturation and temperature. The pictures below show examples of the growth of nuclei – (Figure 4.1) and the growth of seed crystals – (Figure 4.2), obtained from the beginning of the experiment (a) and at the end of experiment (b). These pictures imply that there are differences in the mean growth rate, where each crystal has its own growth rate, and also that a big crystal does not necessarily grow faster than a small one. The phenomenon that different crystals grow with different rates at the same conditions is called crystal growth rate dispersion. The others parts of the experiment – contact nuclei grown in impure solution, and the use of different kinds of seed crystals grown in pure solution display the same phenomenon – growth rate dispersion. Growth rate dispersion is achieved also where seeds are nearly the same

size initially, but have a different final size. Size dependent crystal growth is not evident in the experiments.



(a) 40 minutes (b) 3 hours

Figure 4.1 Size independent growth of contact nuclei grown in pure sucrose solution at the conditions; solution flow rate 40 mL/min, temperature 40°C and $\Delta T = 10°C$.



(a) 15 minutes (b) 3 hours and 5 minutes

Figure 4.2 Size independent growth of seed crystals; uncrushed pure seed crystals grown in pure sucrose solution at a temperature of 40°C and $\Delta T = 10°C$.

To indicate the different growth rate of each nucleus and each seed, the relationship between size and time is plotted as shown in Figure 4.3. The slope of this plot represents the crystal growth rate. This plot shows variation in slope, that is, there are differences in growth rates of different crystals, which agrees well with the observation from the pictures.

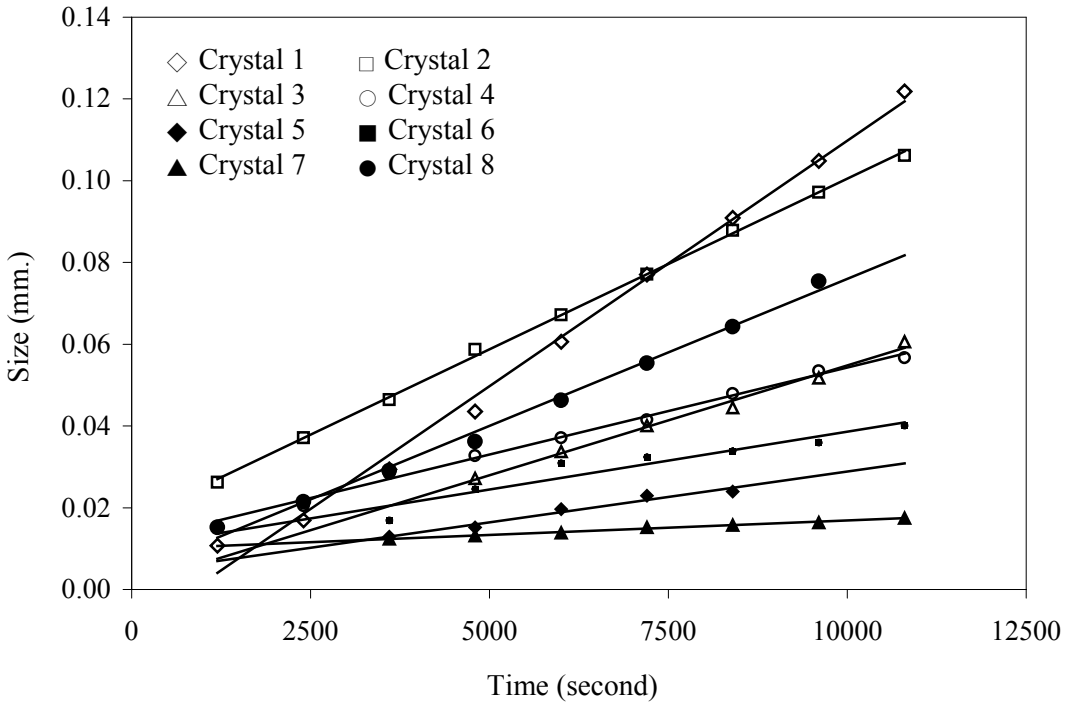
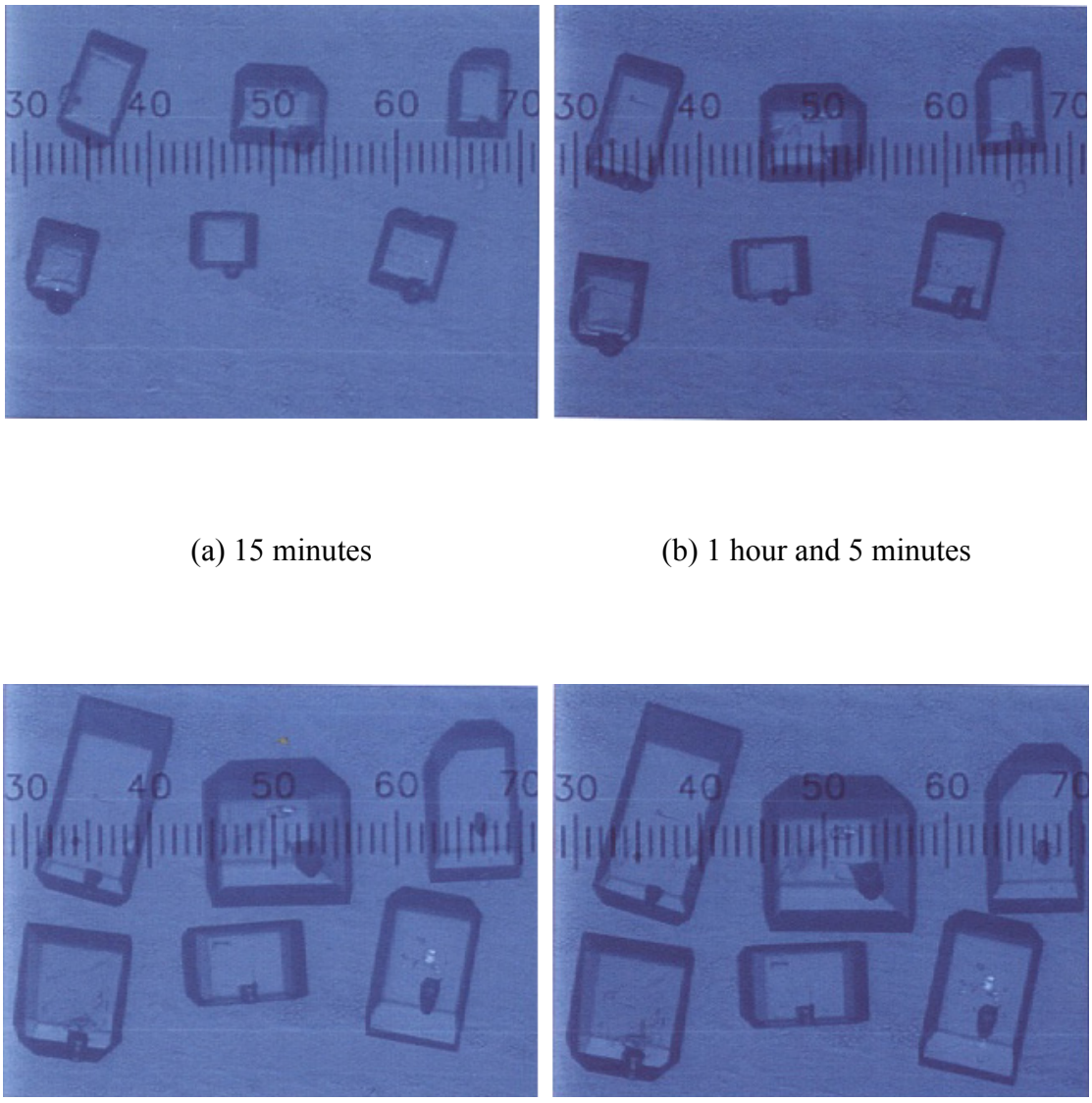


Figure 4.3 An example of the size versus time plot to show size independent growth for nuclei grown in pure sucrose solution at the conditions; solution flow rate 40 mL/min, temperature 40°C and $\Delta T = 10°C$.

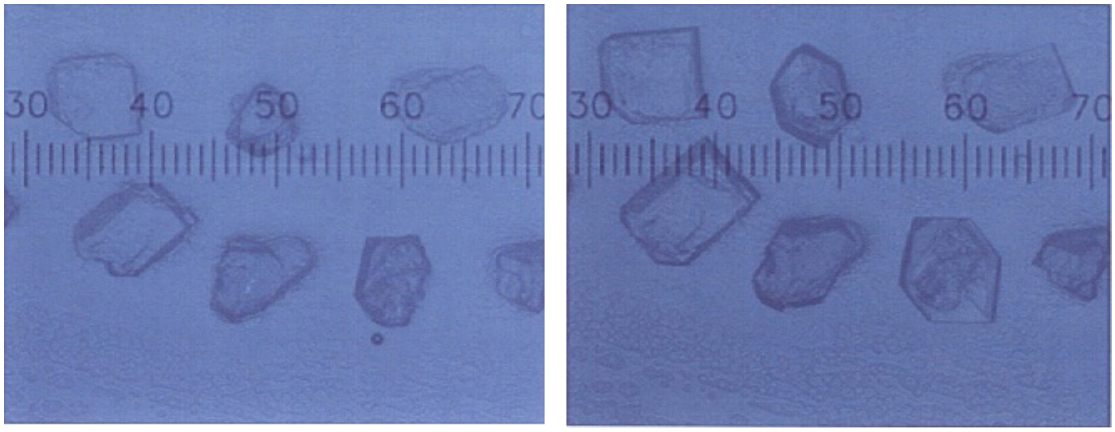
With the third part of experiment – seed crystal grown in pure aqueous sucrose solution, Figures 4.4 and 4.5 shows that each uncrushed seed crystal grows with a different rate even though they are nearly the same size at the beginning, but crushed seed crystals attempt to fix themselves to be the correct shape before additional growth. It can be seen from the diagrams that the rough surface of crushed seeds became a sharp, clean surface before they grow.



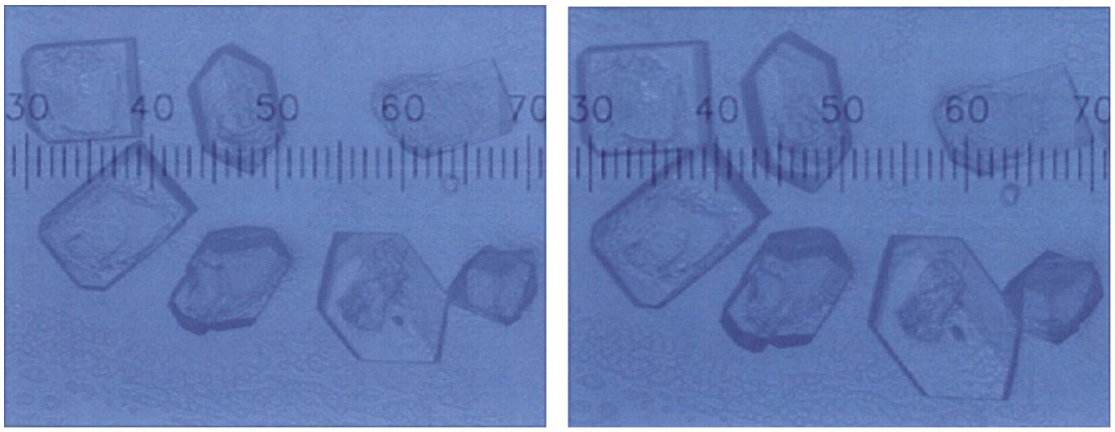
(a) 15 minutes (b) 1 hour and 5 minutes

(c) 2 hours and 45 minutes (d) 3 hours and 5 minutes

Figure 4.4 Growth of uncrushed pure seed crystals in pure sucrose solution at temperature of 40°C and $\Delta T = 10°C$.



(a) 15 minutes (b) 1 hour and 5 minutes



(c) 2 hours and 5 minutes (d) 3 hours and 25 minutes

Figure 4.5 Growth of crushed pure seed crystals in pure sucrose solution at temperature of 40°C and $\Delta T = 10°C$.

4.2 Statistical Analysis

In order to describe the characteristic of the data, statistical measurements were performed to separate data into three main groups – a measure of the location, a measure of the variability, and a measure of the shape of the distribution. The measurements of the average location are the mean, mode and median. The mean, or average of the data is the most commonly used, which implies the central tendency of the measurement. The mean presented here is the arithmetic mean of the growth rate, called the mean growth rate. The median is analogous to the middle of the distribution, where there is half the data below and above this point. In addition, if the ordered data is divided into two equal halves; the middle value is called median. The mode has the largest frequency of the measurement. With the median and the mode shown in Table 4.1–4.5, they represent the median and the mode on the growth rate, respectively.

The common measurements of variability are the standard deviation, variance, and the coefficient of variance (C.V.). The standard deviation indicates how widely the data disperses or scatters from the mean. The variance is the square of the standard deviation, which implies the variation of data or how much size spread there is. In this section, the values represent the standard deviation and the variance on the growth rate, where a higher value represents a wider distribution. The coefficient of variation (C.V.) is dimensionless and is obtained from dividing the standard deviation by the mean. It is the relative size spread, which was developed to describe the relative uniformity. In crystal size distributions it is also used to show how much size variation crystals have relative to the mean size.

Kurtosis and skewness are measures of the shape of the distribution. In addition, they are often used to indicate the shape of the distribution relative to a normal distribution. The kurtosis is the relative degree of curvature near the mode of a frequency curve, as compared with that of a normal distribution of the same variance. In addition, it is a measure of the shape of the distribution curve at the extreme ends, relative to the normal distribution. A distribution with positive kurtosis will have a sharper peak but broader tails than a normal distribution. For the normal distribution, the kurtosis is zero. The skewness is the deviation of the frequency distribution curve from a symmetrical form, or in other words, it is a measure of the symmetry about the mean, and is zero for symmetric distributions, for instance the normal distribution. Positive skewness indicates a distribution skewed to the right and negative skewness indicates a skewed to the left of the mean. The log–normal and the gamma distribution are examples of distributions with positive skewness.

The others statistic values, such as minimum and maximum represent the smallest and the largest value of measurement, that is the highest and the lowest value of measured growth rate in each experiment. Count is the number of data that the statistical formulas are applied (i.e. the number of crystals whose growth rate was measured). The number of measured growth rates in each experiment is different depending on physical characteristics of the seed or nuclei; clear and sharp edged crystals would be measured, while those connected to others would not be measured. Each of them is selected randomly if there were many nuclei, by specifying an arbitrary area where about 30 nuclei are situated. For seed crystals, a number of measured seeds are used depending on how many seeds were glued on the glass cover slip and all of them would be measured if the limitation is not exceeded. The

confidence interval on the mean is the interval estimation that the upper and lower limit covers the mean. The calculation of this value in Table 4.1–4.5 is 90% confident level for the mean at a significance of 10%. Tables 4.1–4.5 show the statistical values, such as mean, mode, median, standard deviation, variance, C.V., 90% confidence level, computed from growth rate distributions of nuclei and seed crystals at different conditions for each experiment.

Table 4.1 is the descriptive statistics for the first part – nucleation in 40mL/min and stagnant pure solution, in which the mean growth rate obtained shows that at the same flow rate and the same degree of supersaturation (ΔT), the higher temperature (40°C) gives higher mean growth rate than at the lower temperature (25°C). It can be concluded that at high temperature a higher kinetic rate would be obtained. Thus in this case it is reasonable that higher temperature produces a higher mean growth rate at equal driving force and flow conditions. When conditions involve the same flow rate and temperature, a high degree of supersaturation (ΔT) gives higher mean growth rate than the low one, because high supersaturation has a high driving force for crystal growth. At the same supersaturation (ΔT) and same temperature at 40°C, the high flow rate (40 mL/min) gives higher mean growth rate than low flow rate (stagnant). At high temperatures the supersaturated solution becomes higher viscosity (due to the higher solubility), and this results in lower mass transfer rates. This will be most significant under stagnant solutions growth, because under high flow the rate of mass transfer is enhanced. Inversely, at the same supersaturation (ΔT) and same temperature at 25°C, the low level of flow rate (stagnant) gives higher mean growth rate than at high level of flow rate (40 mL/min). At low temperature at 25°C, the growth is controlled by surface integration

mechanism (Smyth, 1967) and higher flow may affect the surface integration by removing some of the absorbed layer, or affecting the cluster size that can reach the crystal surface.

Tables 4.2 and 4.3 are the statistical values for nuclei growth in impure solution. For fructose and glucose as an impurity, the statistical analysis results shown in Table 4.2 imply that the mean growth rate as fructose was added is higher than when glucose was added. At the same supersaturation, low levels of the I/W ratio (I/W = 0.25) give higher mean growth rate than high levels of the I/W ratio (I/W = 0.50). With sodium chloride and potassium chloride as impurities, at low levels of the I/W ratio, the system with NaCl as an impurity has higher mean growth rate than adding KCl. At high level of the I/W ratio, NaCl as an impurity results in a lower mean growth rate than KCl, as shown in Table 4.3. For KCl and NaCl as impurities, the mean growth rate increases as the supersaturation (ΔT) is increased: the one exception to this (NaCl as an impurity at a level of 0.2) has a very small decrease as supersaturation is increased, and the decrease is well within the 95% confidence intervals on the means. If NaCl is used as a impurity, as the impurity content increases the growth rate decreases significantly: this is to be expected, because adsorption of the impurity will increase as the impurity content increases, and the growth kinetics should be reduced. If KCl is an impurity, as the level of impurity increases the growth rate also increases. This is unusual, and may indicate that the solubility data of Kelly (1954) is not extremely accurate.

Table 4.1 Descriptive statistics of the growth rate distribution for nucleation in 40mL/min and stagnant pure solution.

Flow (mL/min)	40				0			
Temperature (°C)	25		40		25		40	
ΔT (°C)	5	10	5	10	5	10	5	10
Mean $\times 10^6$ (mm/s)	0.113	0.557	2.656	5.120	0.385	0.829	0.500	3.420
Median $\times 10^6$ (mm/s)	0.090	0.550	2.000	5.000	0.400	0.800	0.450	3.000
Mode $\times 10^6$ (mm/s)	0.200	0.200	4.000	4.000	0.200	1.000	0.800	3.000
Standard Deviation $\times 10^6$ (mm/s)	0.062	0.403	2.519	3.058	0.223	0.561	0.497	2.172
Variance $\times 10^{12}$ (mm/s)	0.004	0.162	6.345	9.353	0.050	0.314	0.247	4.717
Kurtosis	-1.145	2.682	1.512	-1.125	1.126	3.319	1.525	0.819
Skewness	0.544	1.177	1.197	0.183	0.916	1.661	1.017	1.031
Minimum $\times 10^6$ (mm/s)	0.030	0.080	0.090	0.600	0.050	0.100	0.007	0.200
Maximum $\times 10^6$ (mm/s)	0.200	2.000	10.000	10.000	1.000	3.000	2.000	10.000
Count	17	38	25	54	25	115	26	138
90% Confidence level on mean growth rate$\times 10^6$ (mm/s)	0.026	0.110	0.862	0.697	0.076	0.087	0.167	0.306
CV	0.546	0.723	0.949	0.597	0.580	0.676	0.995	0.635

Table 4.2 Descriptive statistics of the growth rate distribution for nucleation in impure solution – Fructose and Glucose as impurity.

Impurity	Fructose				Glucose			
Impurity/Water ratio (I/W)	0.5		0.25		0.5		0.25	
ΔT (°C)	10	5	10	5	10	5	10	5
Mean $\times 10^6$ (mm/s)	0.590	0.473	0.753	0.648	0.234	0.184	0.605	0.177
Median $\times 10^6$ (mm/s)	0.600	0.450	0.700	0.600	0.200	0.200	0.600	0.200
Mode $\times 10^6$ (mm/s)	0.600	0.400	1.000	0.500	0.200	0.200	0.600	0.200
Standard Deviation $\times 10^6$ (mm/s)	0.203	0.176	0.428	0.277	0.126	0.092	0.200	0.105
Variance $\times 10^{12}$ (mm/s)	0.041	0.031	0.183	0.077	0.016	0.009	0.040	0.011
Kurtosis	-0.204	-0.203	2.772	8.483	0.962	-0.510	-0.375	0.874
Skewness	0.329	0.093	1.391	1.796	0.838	0.509	0.296	1.003
Minimum $\times 10^6$ (mm/s)	0.200	0.100	0.100	0.100	0.030	0.060	0.300	0.050
Maximum $\times 10^6$ (mm/s)	1.000	0.900	2.000	2.000	0.600	0.400	1.000	0.500
Count	60	60	60	60	35	25	37	45
90% Confidence level on mean growth rate $\times 10^6$ (mm/s)	0.044	0.038	0.092	0.060	0.036	0.032	0.055	0.026
CV	0.344	0.371	0.568	0.427	0.537	0.501	0.330	0.594

Table 4.3 Descriptive statistics of the growth rate distribution for nucleation in impure solution – KCl and NaCl as impurity.

Impurity	KCl				NaCl			
Impurity/Water ratio (I/W)	0.4		0.2		0.4		0.2	
ΔT (°C)	10	5	10	5	10	5	10	5
Mean $\times 10^6$ (mm/s)	0.645	0.370	0.272	0.131	0.438	0.216	0.848	1.190
Median $\times 10^6$ (mm/s)	0.600	0.400	0.200	0.100	0.400	0.200	0.900	1.000
Mode $\times 10^6$ (mm/s)	0.600	0.400	0.200	0.200	0.400	0.200	1.000	1.000
Standard Deviation $\times 10^6$ (mm/s)	0.197	0.258	0.188	0.083	0.179	0.114	0.347	0.550
Variance $\times 10^{12}$ (mm/s)	0.039	0.067	0.035	0.007	0.032	0.013	0.120	0.303
Kurtosis	-0.753	-0.174	-0.492	-0.582	1.035	-0.228	4.454	0.741
Skewness	0.015	0.663	0.676	0.472	0.964	0.367	1.471	1.080
Minimum $\times 10^6$ (mm/s)	0.300	0.030	0.020	0.000	0.200	0.000	0.200	0.200
Maximum $\times 10^6$ (mm/s)	1.000	1.000	0.700	0.300	1.000	0.500	2.000	3.000
Count	60	54	49	25	60	60	60	60
90% Confidence level on mean growth rate $\times 10^6$ (mm/s)	0.042	0.059	0.045	0.028	0.039	0.025	0.075	0.119
CV	0.305	0.697	0.691	0.633	0.407	0.527	0.409	0.462

Table 4.4 Descriptive statistics of the growth rate distribution for crushed and uncrushed pure seed crystals grown in pure solution.

Type of seeds	Uncrushed pure seeds				Crushed pure seeds			
Temperature (°C)	25		40		25		40	
ΔT (°C)	5	10	5	10	5	10	5	10
Mean $\times 10^6$ (mm/s)	1.141	3.391	3.247	10.544	0.872	2.044	2.240	8.210
Median $\times 10^6$ (mm/s)	1.000	3.000	3.000	10.000	0.950	2.000	2.000	8.000
Mode $\times 10^6$ (mm/s)	1.000	3.000	3.000	10.000	1.000	3.000	2.000	10.000
Standard Deviation $\times 10^6$ (mm/s)	0.488	0.679	0.738	2.490	0.586	1.745	0.758	2.696
Variance $\times 10^{12}$ (mm/s)	0.238	0.460	0.545	6.200	0.343	3.046	0.574	7.268
Kurtosis	-0.350	0.199	2.077	11.295	-0.149	0.570	-0.201	7.751
Skewness	0.900	0.585	-0.617	3.571	0.637	0.632	0.083	1.690
Minimum $\times 10^6$ (mm/s)	0.200	2.000	0.200	9.000	0.030	0.020	0.800	2.000
Maximum $\times 10^6$ (mm/s)	2.000	5.000	5.000	20.000	2.000	8.000	4.000	20.000
Count	104	110	98	79	72	60	77	81
90% Confidence level on mean growth rate $\times 10^6$ (mm/s)	0.079	0.107	0.124	0.466	0.115	0.377	0.172	0.498
CV	0.427	0.200	0.227	0.236	0.672	0.854	0.338	0.328

Table 4.5 Descriptive statistics of the growth rate distribution for crushed impure seed crystals grown in pure solution.

Type of seeds	Crushed impure seeds			
Temperature (°C)	25		40	
ΔT (°C)	5	10	5	10
Mean $\times 10^6$ (mm/s)	1.045	2.389	2.163	7.218
Median $\times 10^6$ (mm/s)	0.900	2.000	2.000	7.000
Mode $\times 10^6$ (mm/s)	2.000	2.000	2.000	9.000
Standard Deviation $\times 10^6$ (mm/s)	0.912	1.195	0.970	2.198
Variance $\times 10^{12}$ (mm/s)	0.831	1.427	0.940	4.832
Kurtosis	0.785	4.404	-0.019	-0.201
Skewness	1.088	1.311	0.274	-0.617
Minimum $\times 10^6$ (mm/s)	0.030	0.100	0.100	1.000
Maximum $\times 10^6$ (mm/s)	4.000	8.000	5.000	10.000
Count	59	92	96	101
90% Confidence level on mean growth rate $\times 10^6$ (mm/s)	0.198	0.207	0.164	0.363
CV	0.873	0.500	0.448	0.305

The comparison of the mean growth rate between the two types of impurity – invert sugar (glucose and fructose) and salt (potassium chloride and sodium chloride), show that the maximum value is 1.19×10^{-6} mm/s at a NaCl/water ratio of 0.2 and ΔT = 5°C, and the minimum value is 0.131×10^{-6} mm/s, which is at the same condition but when KCl was added as an impurity.

The third part of experiment involves seed crystals grown in pure stagnant sucrose solution; the statistical values of this part are shown in Tables 4.4 and 4.5. The mean growth rate implies that uncrushed pure seed crystals can grow the fastest; 10.54×10^{-6} mm/s, in the system where the crystals were grown in pure stagnant sucrose solution at a temperature of 40°C and supersaturation of 10°C. However, crushed pure and impure seed crystals grow slower and are only slightly different in their mean growth rate. The highest mean growth rate for each type of seed is the conditions at a temperature of 40°C and ΔT = 10°C, which gives rates of 10.54×10^{-6} mm/s, 8.21×10^{-6} mm/s and 7.22×10^{-6} mm/s, for the uncrushed pure seed, crushed pure seed and uncrushed impure seed experiments, respectively. The slowest mean growth rate is 0.872×10^{-6} mm/s, which belongs to the crushed pure seed crystals grown at a temperature of 25°C and ΔT = 5°C. It is reasonable that the smooth crystals can grow more rapidly than the rough crystals, that is, the rough surface need to be fixed before the step of normal crystal growth can occur. The crushed crystals are also likely to have greater mechanical stress in the crystal, making integration more difficult. In addition, seed crystals can grow more quickly at high temperature (T = 40°C) and high supersaturation (ΔT = 10°C), where high reaction rates and high driving forces occur.

A comparison of the average mean growth rate between two types of impurity – invert sugars (glucose and fructose) and salts (potassium chloride (KCl) and sodium chloride(NaCl)) is shown in Figure 4.6. The figure implies that the average mean growth rate when adding glucose and KCl are less than when adding fructose and NaCl as an impurity, respectively, by about half.

A comparison of the average mean growth rate between pure and impure stagnant solutions at $\Delta T = 5°C$ and $T = 25°C$ is shown in Figure 4.7. The figure indicates that fructose and NaCl tend to increase the average mean growth rate but glucose and KCl tend to decrease the mean growth rate; that is, the mean growth rate of the solution without any impurity lies between the average mean growth rate of fructose and NaCl, and glucose and KCl.

The coefficient of variation (C.V.) is used as a measure of the degree of growth rate dispersion. The C.V. value of nuclei grown in pure solution with different solution flow rate, temperature and the supersaturation (ΔT) is between 0.5–1.0. In the second part of the experiment – nuclei grown in impure stagnant solution, C.V. values are between 0.3–0.7, and the third part – seed crystals grow in pure stagnant solution, C.V. values are between 0.2–0.9.

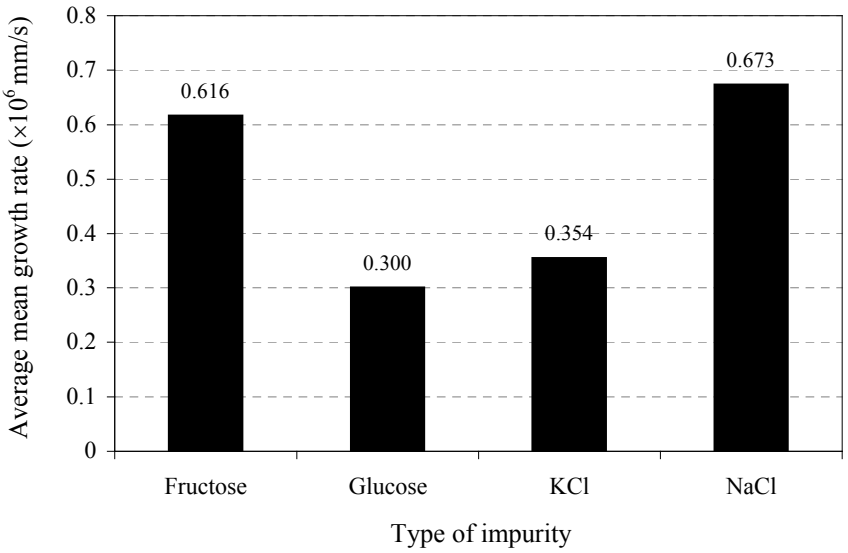


Figure 4.6 Comparison of the average mean growth rate for nuclei grown in impure stagnant solution.

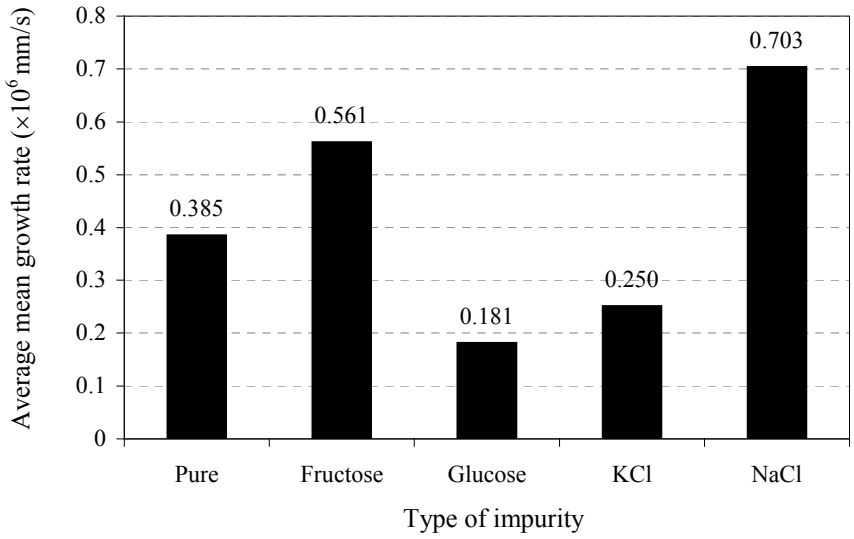


Figure 4.7 Comparison of the average mean growth rate between nuclei grown in pure and impure stagnant solution at $\Delta T = 5°C$ and $T = 25°C$.

Figure 4.8 shows the average C.V. for nuclei grown in impure solution in which KCl as an impurity gives the highest value – 0.582. This system has very high growth rate. The other systems show C.V. values that are smaller, so that narrower product size distributions are obtained. Figure 4.9 is a comparison between the average C.V. of pure solution and impure solution. The system where KCl is added has a higher average C.V. value than the pure solution, but adding other impurities result in a lower average C.V. being obtained. Thus, these systems have lower dispersion than the pure solution.

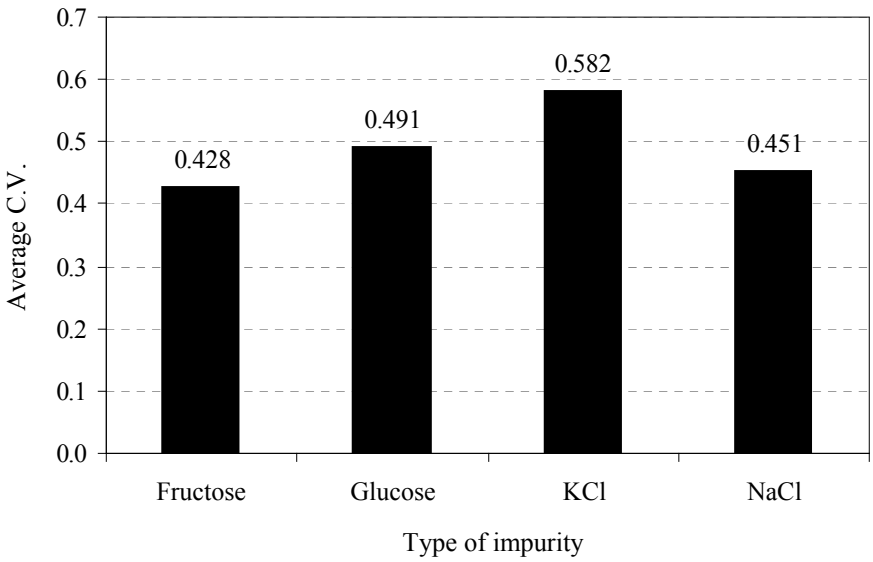


Figure 4.8 Comparison of the average C.V. of the system where nuclei grown in impure solution.

Figures 4.6–4.9 show that a low average C.V. often occurs in systems that have a high average mean growth rate, such as fructose and NaCl as impurities. High

average mean growth rates may result in lower average C.V. values, because the mean growth rate is the denominator of the C.V. definition.

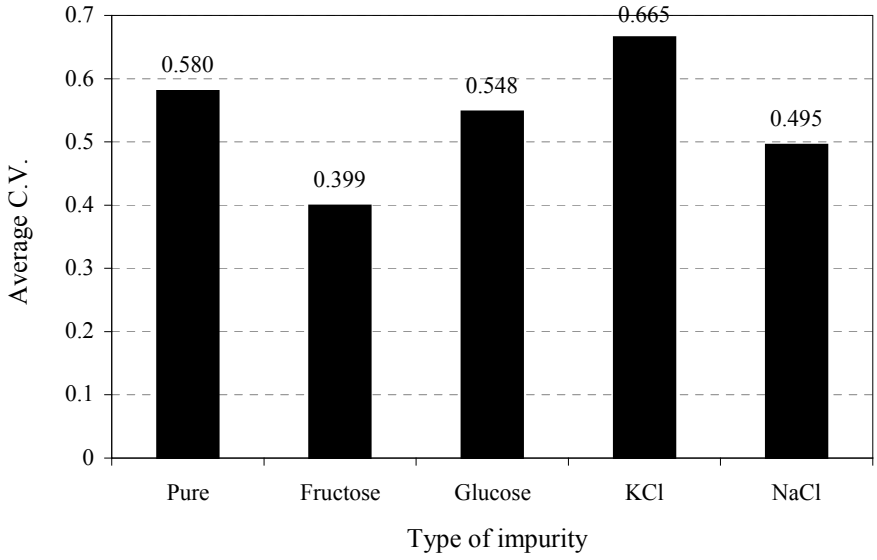


Figure 4.9 Comparison of the average C.V. of the system where nuclei grown in pure and impure solution at $\Delta T = 5°C$ and $T = 25°C$.

Figures 4.10 and 4.11 show a comparison of the average mean growth rate and average C.V., respectively, for three different kinds of seeds – uncrushed pure seed, crushed pure seeds and crushed impure seeds. The Figure implies that uncrushed pure seed crystals grow fastest with the average mean growth rate 4.58×10^{-6} mm/s, higher than the other two types at about 1.30×10^{-6} mm/s. The others two types have nearly the same average mean growth rate – 3.34×10^{-6} mm/s and 3.21×10^{-6} mm/s for crushed pure seeds and crushed impure seeds, respectively.

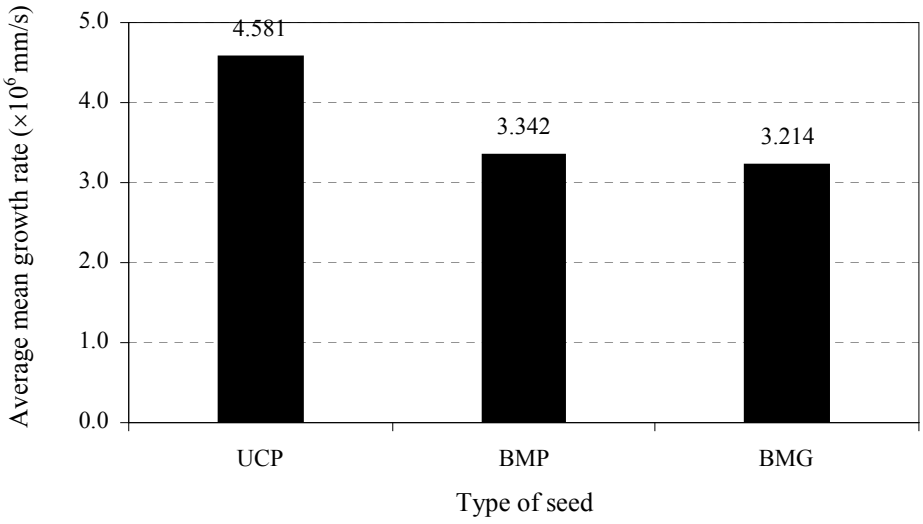


Figure 4.10 Comparison of the average mean growth rate of three different types of seeds obtained from the seed crystals grown in pure stagnant solution experiments: UCP = uncrushed pure seed; BMP = crushed pure seed; BMG = crushed impure seed.

Figure 4.11 shows the comparison of the average C.V. of the seed crystals experiment, where small C.V. values are evident in the system where seeds are pure and not ball–milled, but ball–milled seeds have an average C.V. value which is about 50 percent higher. This means that small variations in growth rate, or a narrow size distribution will be obtained if the seed crystals are pure and uncrushed.

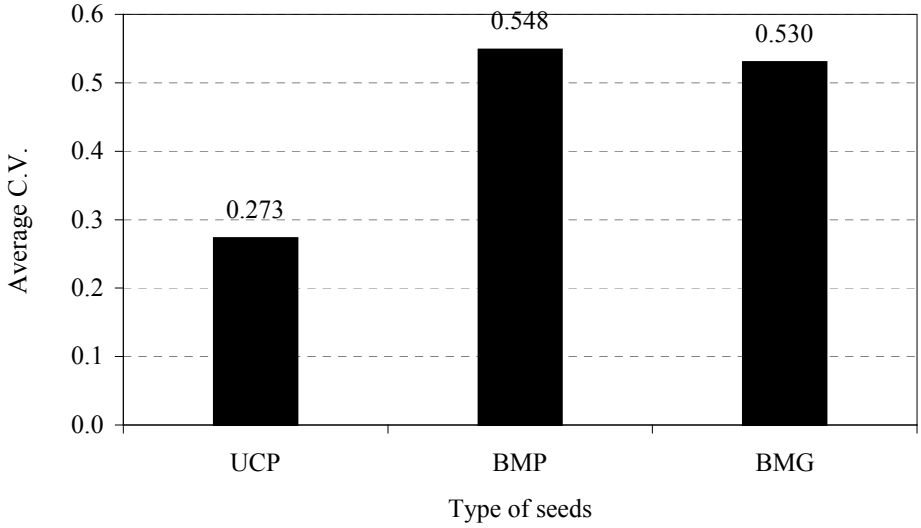


Figure 4.11 Comparison of the average C.V. of three different types of seeds obtained from the seed crystals grown in pure stagnant solution experiment: UCP= uncrushed pure seed; BMP = crushed pure seed; BMG = crushed impure seed.

Figures 4.12 and 4.13 show the comparison of the mean growth rate and C.V. of three different kinds of experiment – nuclei grown in pure and impure solution and seeds grow in pure solution, at the same condition – $\Delta T = 5°C$, $T = 25°C$ and stagnant solution. From Figure 4.12 the mean growth rate of the seed experiments is higher than the mean growth rate of nucleation experiments; this may be because seeds have got many selective growth sites on the surface, more than nuclei, or that the seeds are more perfect crystals, possibly due to having lower levels of mechanical stress.

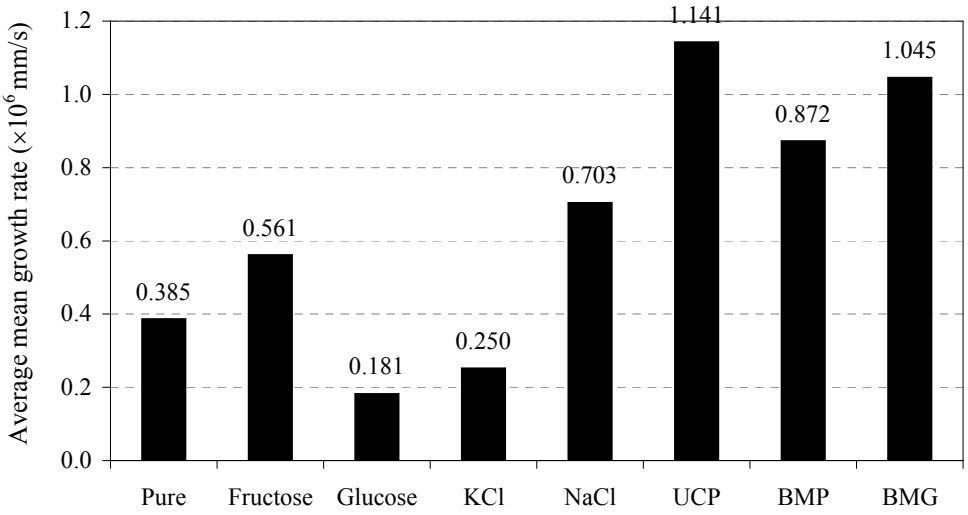


Figure 4.12 Comparison of the average mean growth rate of nuclei and seeds experiments with the supersaturation ΔT = 5°C, T = 25°C and stagnant solution.

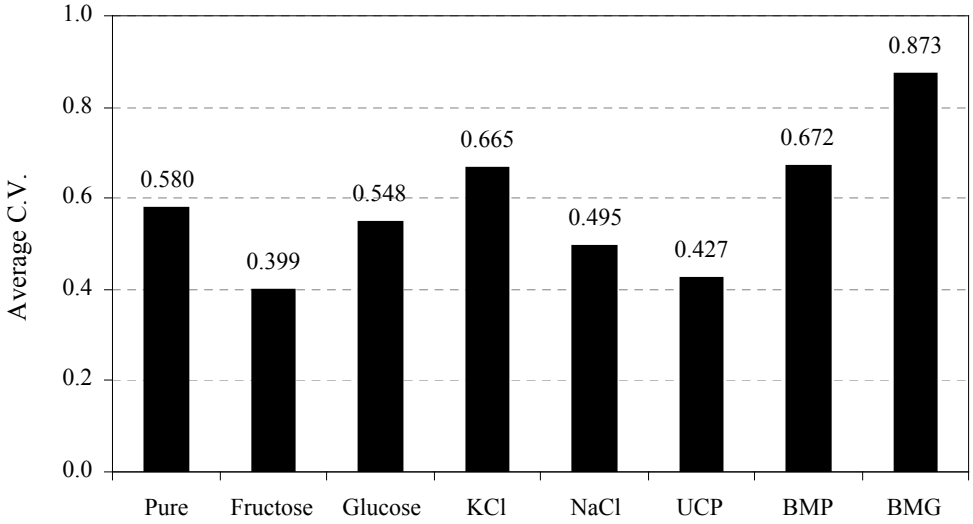


Figure 4.13 Comparison of the average C.V. of nuclei and seeds experiments with the supersaturation ΔT = 5°C, T = 25°C and stagnant solution.

For the skewness, all distributions show a positive value; that is, the behaviour of the distribution is skewed to the right of the mean growth rate. This is very likely because there is a limitation on the left side of the distribution, that is no crystals should display a negative growth rates (suggesting dissolution) if there is a positive value of the supersaturation: thus the growth rate distribution is limited to positive values of the growth rate. The common way to represent the distribution is graphically. Figure 4.14 shows an example of the distribution fitted by the log–normal distribution that displays the difference in distributions at different conditions more clearly. The sharp peak represents the narrow product size distribution, which is preferred in the crystallization process. This figure also shows that at higher mean growth rates, a wide size spread would be obtained, as in the descriptive statistic tables shown, the standard deviation is high if the mean growth rate is high. This change is reduced if the C.V. is used as a measure of the spread instead of the standard deviation.

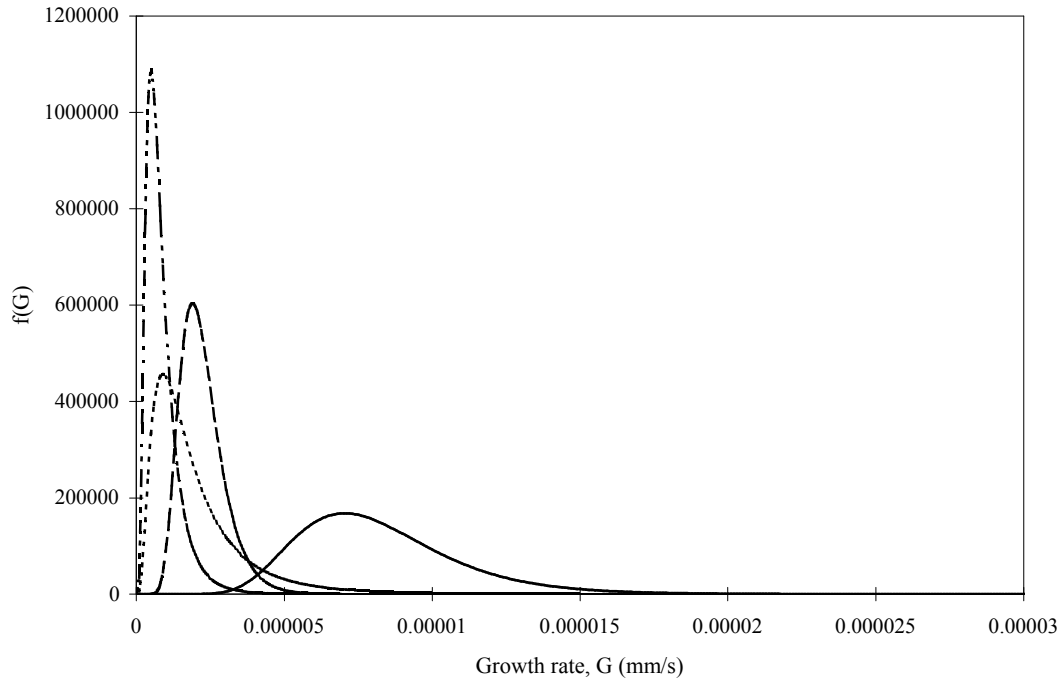


Figure 4.14 An example of the crystal growth rate distribution that is fitted by the log–normal distribution: crushed pure seeds grow in pure solution:

−··− T = 25°C; ΔT = 5°C; ····· T = 25°C; ΔT = 10°C;

---- T = 40°C; ΔT = 5°C; and —— T = 40°C; ΔT = 10°C.

4.3 Analysis of Variance (ANOVA)

Because most experiments determine the effect of one or more independent variables on one or more dependent variables, the statistical analysis technique should be flexible and not complex. The analysis of variance (ANOVA) is one of the techniques appropriate to use for judging significance of effects or independent variables on a dependent variable. In addition, its objective is to locate which independent variables are significant.

Tables 4.6–4.15 show the results obtained from the analysis of variance (ANOVA) technique applied both on the mean growth rate and the coefficient of variation (C.V.) of the crystal growth rate distribution. The comparison between F_0 and $F_{\alpha=0.1}$ can imply significant effects of the independent variable, or interactions between independent variables, on the dependent variables. F_0 is from the F–distribution based on the mean square for the independent variable, and F_α is the critical value of the F–distribution based on the level of confidence (1-α) required. The first part of experiment – nucleation in pure solution, results in the ANOVA for the mean growth rate and C.V. as shown in Tables 4.6 and 4.7, respectively. For the mean growth rate, the F_0 value of each independent variable, the supersaturation (ΔT), temperature and flow rate, are greater than the critical value at $F_{\alpha=0.1}$. It can be concluded that there is a significant effect on the mean crystal growth rate from each factor. The C.V. is not significantly different when ANOVA was tested on it; that is, all F_0 values are less than $F_{\alpha=0.1}$. There is no significant difference in C.V. at the significance level α=0.1 for changes in any of the dependent variables.

With nucleation in impure solution, a summary of ANOVA on the mean growth rate and C.V. are shown in Tables 4.8 and 4.9, respectively. All factors, the supersaturation, impurity/water ratio and type of impurity, and all interactions between each factor have a significant effect on the mean growth rate of nuclei grown in impure solution, because all F_0 values are greater than the critical value at the significance level α=0.1 or $F_{\alpha=0.1}$. This means that all independent variables are important for the mean growth rate. The ANOVA on the C.V. showed that the magnitude of the C.V. is dependent on the supersaturation, type of impurity, the interaction between the supersaturation and impurity/water (I/W) ratio, and the

interaction between the supersaturation and type of impurity. The others factor and other interactions give F_0 values less than the critical value at significance level α=0.1 or $F_{\alpha=0.1}$, that is, there is no significant effect on the C.V.

Table 4.6 Analysis of variance (ANOVA) on mean growth rate for nucleation in 40mL/min and stagnant pure solution.

Source of variation	SS	DF	MS	F_0	$F_{\alpha=0.1}$
A	9.76E-12	1	9.76E-12	*12.59*	3.46
B	2.96E-12	1	2.96E-12	*3.82*	3.46
C	2.38E-11	1	2.38E-11	*30.74*	3.46
AB	1.43E-13	1	1.43E-13	0.184	3.46
AC	4.81E-12	1	4.81E-12	*6.19*	3.46
BC	4.76E-12	1	4.76E-12	*6.13*	3.46
ABC	1.06E-13	1	1.06E-13	0.137	3.46
Error	6.21E-12	8	7.76E-13		
Total	5.26E-11	15			

Remark: A = ΔT; B = flow; C = temperature

Table 4.7 Analysis of variance (ANOVA) on coefficient of variation (C.V.) for nucleation in 40mL/min and stagnant pure solution.

Source of variation	SS	DF	MS	F_0	$F_{\alpha=0.1}$
A	0.001	1	0.001	0.033	3.46
B	0.072	1	0.072	2.318	3.46
C	0.024	1	0.024	0.773	3.46
AB	0.028	1	0.028	0.891	3.46
AC	0.010	1	0.010	0.311	3.46
BC	0.025	1	0.025	0.806	3.46
ABC	0.101	1	0.101	3.259	3.46
Error	0.248	8	0.031		
Total	0.508	15			

Remark: A = ΔT; B = flow; C = temperature

Table 4.8 Analysis of variance (ANOVA) on mean growth rate for nucleation in impure solution – all impurities: A = ΔT; B = I/W ratio; C = all impurities.

Source of variation	SS	DF	MS	F_0	$F_{\alpha=0.1}$
A	2.25E-12	1	2.25E-12	*19.20*	3.05
B	5.78E-12	1	5.78E-12	*49.29*	3.05
C	2.15E-11	3	7.16E-12	*61.10*	2.46
AB	5.24E-13	1	5.24E-13	*4.47*	3.05
AC	2.26E-12	3	7.53E-13	*6.42*	2.46
BC	2.46E-11	3	8.20E-12	*69.97*	2.46
ABC	4.92E-12	3	1.64E-12	*13.99*	2.46
Error	1.88E-12	16	1.17E-13		
Total	6.37E-11	31			

Remark: A = ΔT; B = I/W ratio; C = all impurities

Table 4.9 Analysis of variance (ANOVA) on coefficient of variation (C.V.) for nucleation in impure solution – all impurities.

Source of variation	SS	DF	MS	F_0	$F_{\alpha=0.1}$
A	1.163	1	1.163	*4.683*	3.05
B	0.610	1	0.610	2.456	3.05
C	6.673	3	2.224	*8.956*	2.46
AB	0.539	1	0.539	2.171	3.05
AC	1.187	3	0.396	1.593	2.46
BC	1.650	3	0.550	2.215	2.46
ABC	2.610	3	0.870	*3.503*	2.46
Error	3.973	16	0.248		
Total	18.405	31			

Remark: A = ΔT; B = I/W ratio; C = all impurities

Tables 4.10 and 4.11, and Tables 4.12 and 4.13 compare the results of an ANOVA test on the mean growth rate and the C.V. for nucleation in the system where two impurities are considered – fructose and glucose as impurity, and KCl and NaCl as impurity, respectively.

The ANOVA tables 4.10 and 4.11 show the results as two types of impurity are considered – fructose and glucose. The results show that there is a significantly difference in the mean growth rate for all factors – ΔT, I/W ratio and type of impurity. In addition, these independent variables influence the mean growth rate, and the main effect is the type of impurity, which has the highest F_0 value. The ANOVA on the C.V. showed that each individual factor and their interaction do not have a significant effect, with the exception of the interaction between ΔT and type of impurity. Thus the coefficient of variation is essentially constant for all conditions.

Table 4.10 Analysis of variance (ANOVA) on mean growth rate for nucleation in impure solution – fructose and glucose as impurity:

Source of variation	SS	DF	MS	F_0	$F_{\alpha=0.1}$
A	1.13E-13	1	1.13E-13	*34.58*	3.46
B	1.27E-13	1	1.27E-13	*38.95*	3.46
C	4.21E-13	1	4.21E-13	*129.22*	3.46
AB	3.53E-14	1	3.53E-14	*10.83*	3.46
AC	1.30E-14	1	1.30E-14	*3.98*	3.46
BC	3.19E-16	1	3.19E-16	0.098	3.46
ABC	3.98E-14	1	3.98E-14	*12.21*	3.46
Error	2.61E-14	8	3.26E-15		
Total	7.75E-13	15			

Remark: A = ΔT; B = I/W ratio; C = impurity (fructose & glucose)

Table 4.11 Analysis of variance (ANOVA) on coefficient of variation (C.V.) for nucleation in impure solution – fructose and glucose as impurity.

Source of variation	SS	DF	MS	F_0	$F_{\alpha=0.1}$
A	0.005	1	0.005	0.448	3.46
B	0.012	1	0.012	1.080	3.46
C	0.007	1	0.007	0.695	3.46
AB	0.002	1	0.002	0.187	3.46
AC	0.039	1	0.039	*3.604*	3.46
BC	0.032	1	0.032	2.949	3.46
ABC	0.043	1	0.043	*4.054*	3.46
Error	0.086	8	0.011		
Total	0.225	15			

Remark: A = ΔT; B = I/W ratio; C = impurity (fructose & glucose)

For KCl and NaCl as impurities, the ANOVA on the mean growth rate and CV results are shown in Tables 4.12 and 4.13, respectively. F_0 values, when tested on the mean growth rate, show all factors and all interactions are higher than the critical value $F_{\alpha=0.1}$, except the supersaturation (ΔT). The most important factor affect is the type of impurity.

Table 4.12 Analysis of variance (ANOVA) on mean growth rate for nucleation in impure solution – KCl and NaCl as impurity.

Source of variation	SS	DF	MS	F_0	$F_{\alpha=0.1}$
A	2.43E-14	1	2.43E-14	3.33	3.46
B	1.56E-13	1	1.56E-13	*21.39*	3.46
C	4.12E-13	1	4.12E-13	*56.42*	3.46
AB	1.26E-13	1	1.26E-13	*17.27*	3.46
AC	7.57E-14	1	7.57E-14	*10.37*	3.46
BC	9.78E-13	1	9.78E-13	*134.08*	3.46
ABC	4.38E-14	1	4.38E-14	*6.00*	3.46
Error	5.84E-14	8	7.30E-15		
Total	1.87E-12	15			

Remark: A = ΔT B = I/W ratio C = impurity (KCl & NaCl)

Table 4.13 Analysis of variance (ANOVA) on coefficient of variation (C.V.) for nucleation in impure solution – KCl and NaCl as impurity.

Source of variation	SS	DF	MS	F_0	$F_{\alpha=0.1}$
A	0.041	1	0.041	2.895	3.46
B	0.008	1	0.008	0.539	3.46
C	0.008	1	0.008	0.602	3.46
AB	0.085	1	0.085	*6.026*	3.46
AC	0.010	1	0.010	0.698	3.46
BC	0.002	1	0.002	0.173	3.46
ABC	0.126	1	0.126	*8.986*	3.46
Error	0.113	8	0.014		
Total	0.393	15			

Remark: A = ΔT B = I/W ratio C = impurity (KCl & NaCl)

For the last section of the experiment – growth of seed crystals in pure stagnant solution, three different types of seed were studied. The ANOVA results on the mean growth rate and the coefficient of variation are shown in Table 4.14 and 4.15, respectively. As Table 4.14 shows, all independent variables – temperature, the supersaturation (ΔT) and type of seeds, and an interaction between temperature and the supersaturation (ΔT) have an influence on the mean growth rate. Temperature and the supersaturation (ΔT) are very strong influence on the mean growth rate in which F_0 values are very high in comparison to the critical value at a significance level α=0.1 or $F_{\alpha=0.1}$, but type of seed crystals has got a quite low value of F_0, so that it has a quite weak effect on the mean growth rate as compared to temperature and the supersaturation. The ANOVA results as tested on C.V. are shown in Table 4.15.

Only the supersaturation and type of seeds have an F_0 value greater than $F_{\alpha=0.1}$, that is, there is small but significant effect on the C.V. The other factors give F_0 value smaller than the critical F at a significance level of 0.1; thus there is not a significant effect on the C.V.

Table 4.14 Analysis of variance (ANOVA) on mean growth rate for seed crystal growth in stagnant pure solution.

Source of variation	SS	DF	MS	F_0	$F_{\alpha=0.1}$
A	8.99E-11	1	8.99E-11	*167.60*	3.18
B	9.36E-11	1	9.36E-11	*174.52*	3.18
C	1.06E-11	2	5.29E-12	*9.86*	2.81
AB	3.19E-11	1	3.19E-11	*59.44*	3.18
AC	2.63E-12	2	1.32E-12	2.45	2.81
BC	2.43E-12	2	1.22E-12	2.27	2.81
ABC	8.17E-13	2	4.09E-13	0.76	2.81
Error	6.44E-12	12	5.36E-13		
Total	2.38E-10	23			

Remark: A = temperature; B = ΔT; C = type of seeds

Table 4.15 Analysis of variance (ANOVA) on coefficient of variation (C.V.) for seed crystal growth in stagnant pure solution.

Source of variation	SS	DF	MS	F_0	$F_{\alpha=0.1}$
A	0.078	1	0.078	1.312	4.49
B	0.471	1	0.471	*7.873*	4.49
C	0.402	2	0.201	*3.360*	3.24
AB	0.017	1	0.017	0.289	4.49
AC	0.019	2	0.010	0.162	3.24
BC	0.224	2	0.112	1.875	3.24
ABC	0.012	2	0.006	0.102	3.24
Error	0.718	12	0.060		
Total	1.942	23	0.084		

Remark: A = temperature; B = ΔT; C = type of seeds

Figures 4.15–4.26 are plots between an independent variable (such as temperature, supersaturation, or flow) and a dependent variable (such as the mean growth rate or the C.V.) that are generated to display the effect between the variables based on the ANOVA results. If the lines are not parallel or cross, there is some interaction between two independent variables that is responsible for an effect on the dependent variable; that is, the dependent variable can be changed depending on the relative levels of the independent variables. If the lines are parallel, a different result would be obtained, where there is no interaction between the variables. In this case, if two independent variables are altered, the net change in the dependent variable is due only to the sum of the changes due to the base independent variables; the interaction between the variables does not alter the response of the dependent variable.

Figures 4.15 and 4.16 are the effect of the supersaturation and temperature, respectively, on the mean growth rate, for the condition that nuclei grow in different flow rates of solution. These Figure show that each pair of lines is not parallel, that is, the mean growth rate can be changed by the supersaturation and temperature interaction, and also the flow – supersaturation interaction. Figures 4.17 and 4.18 are the effect of the supersaturation and impurity/water ratio, respectively, on the mean growth rate for the experiments where impurities were added. Both figures show nearly horizontal lines in the system where fructose was added as an impurity, so that the amount of fructose added does not have a strong effect on the mean growth rate of sucrose nuclei. However, the other lines are either not parallel or cross, and the interaction between these impurities and their amount, and the experiment temperature have an affect on the mean growth rate. Figures 4.19 and 4.20 are the effect of the supersaturation and temperature, respectively, on the mean growth rate for seed crystals grown in stagnant pure sucrose solution. The Figures show that each pair of lines is not parallel as in the previous sections. This means that the interaction between supersaturation and temperature has a strong effect on the mean growth rate.

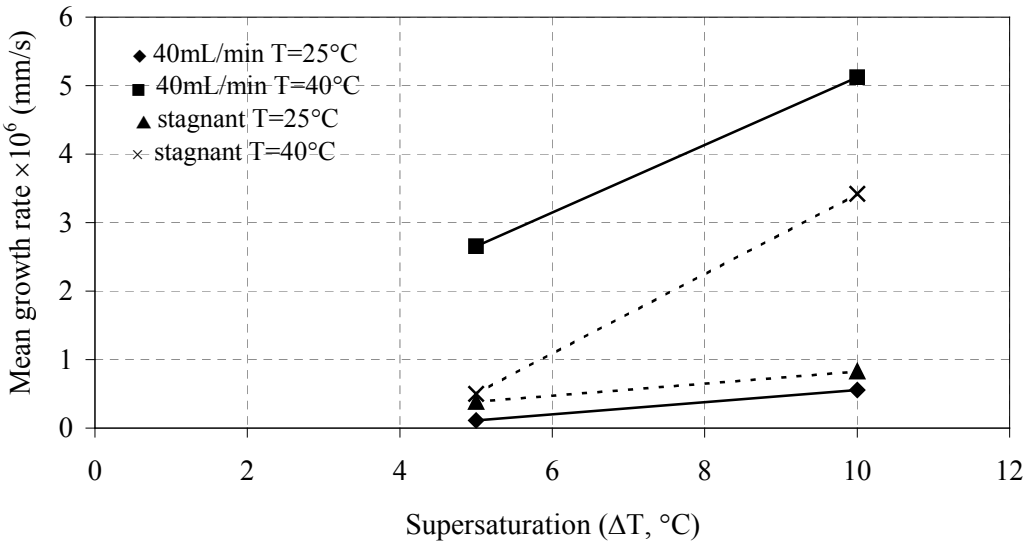


Figure 4.15 ANOVA interaction graph for the effect of the supersaturation level on the mean growth rate for nuclei grown in pure sucrose solution at a flow of 40mL/min and stagnant.

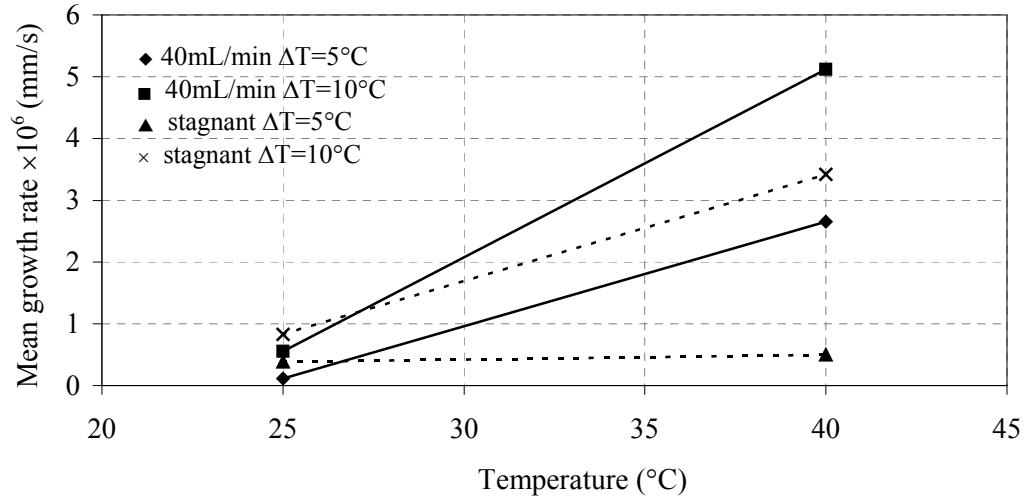


Figure 4.16 ANOVA interaction graph for the effect of temperature (T) on the mean growth rate for nuclei grown in pure sucrose solution at a flow 40mL/min and stagnant.

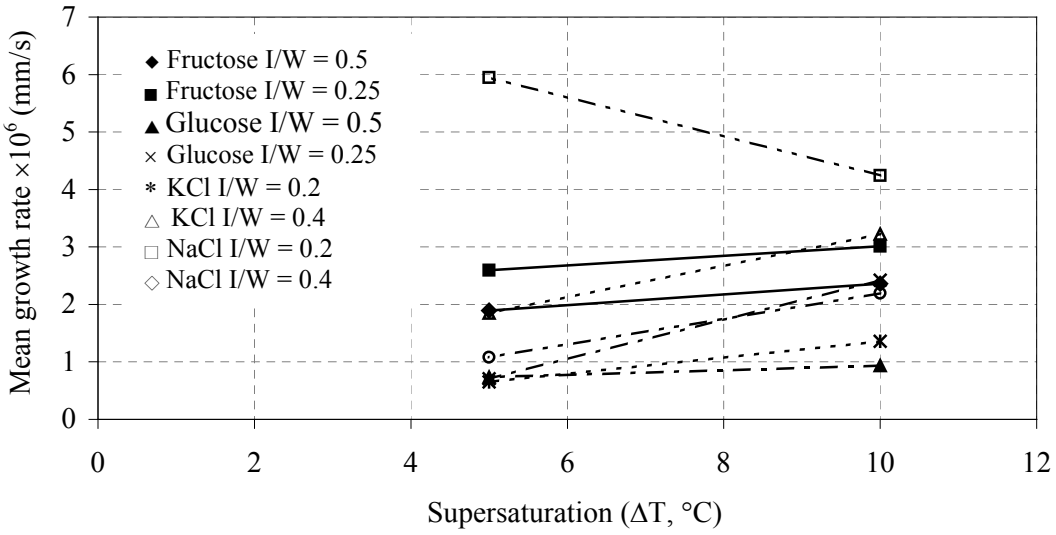


Figure 4.17 ANOVA interaction graph for the effect of the supersaturation (ΔT) on the mean growth rate of nuclei grown in impure solution.

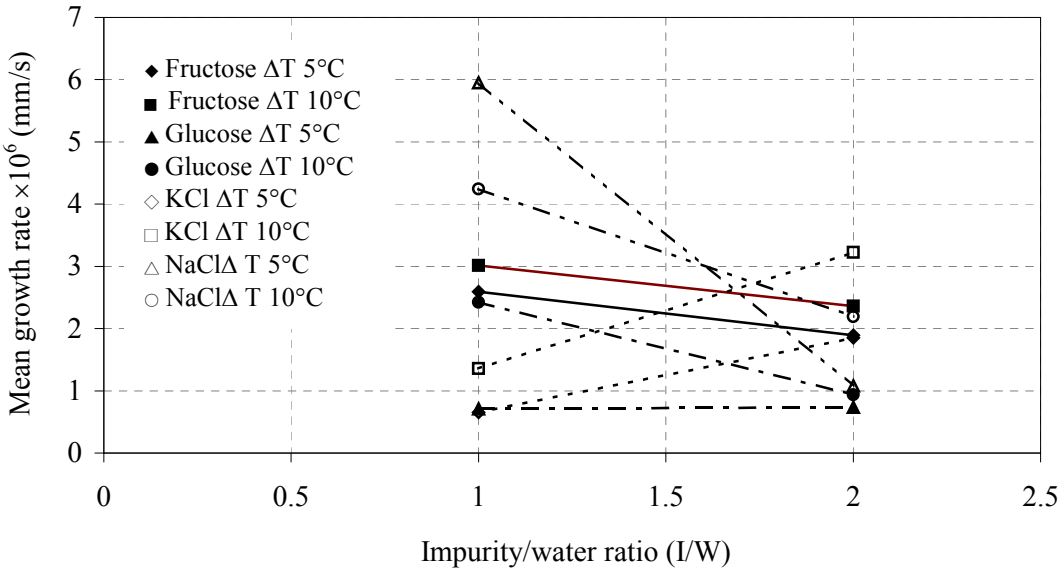


Figure 4.18 ANOVA interaction graph for the effect of impurity/water ratio on the mean growth rate of nuclei grown in impure solution.

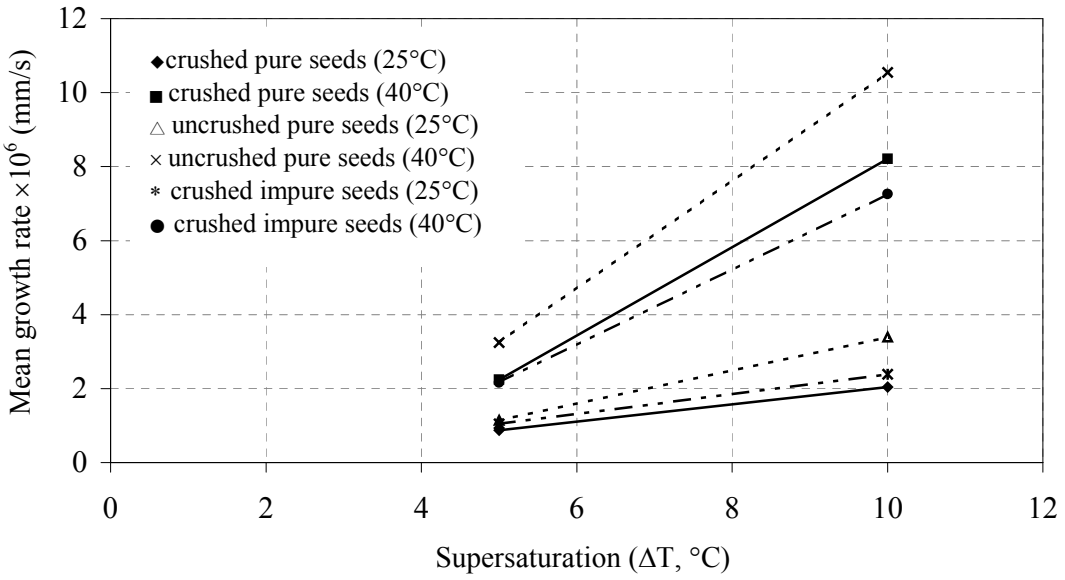


Figure 4.19 ANOVA interaction graph for the effect of the supersaturation (ΔT) on the mean growth rate of seed crystals grown in pure sucrose solution.

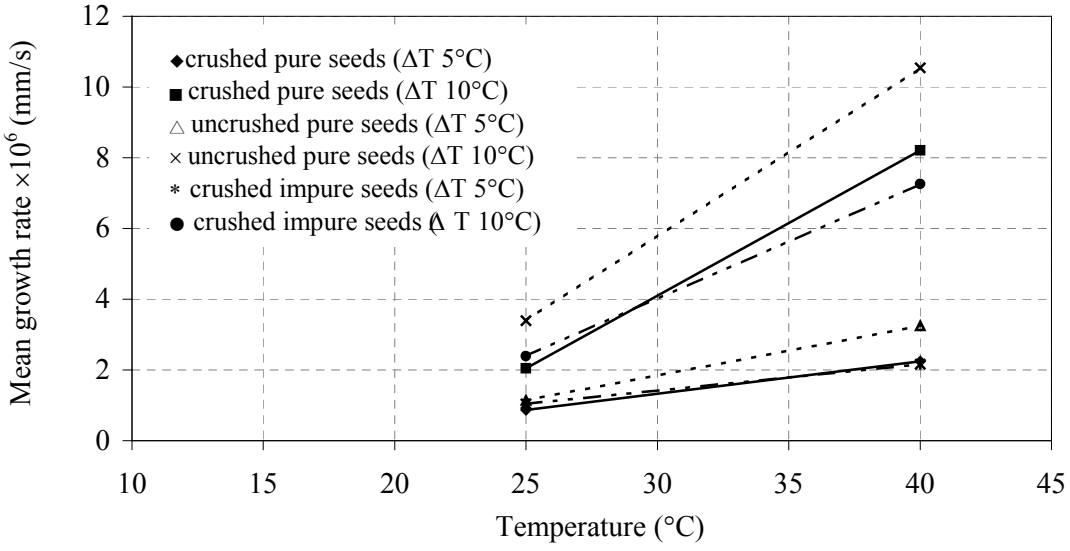


Figure 4.20 ANOVA interaction graph for the effect of temperature on the mean growth rate of seed crystals grown in pure sucrose solution.

Figure 4.21–4.26 show the effect of the supersaturation and temperature on the coefficient of variation (CV). Figure 4.21 and 4.22 represent the nuclei grown in pure sucrose solution with different flow rates. Each pair of lines cross, showing there is an effect of the supersaturation and temperature interaction on the coefficient of variation, or the variation in mean growth rate is affected by these two factors. Figure 4.23 and 4.24 show the effect of the supersaturation and impurity/water ratio, respectively, on C.V. for the system that impurity was added. There are not pairs of parallel lines, that is, temperature driving force and amount of impurity interactions affect the variation of the growth rate. Figures 4.25 and 4.26 show the effect of the supersaturation and temperature, respectively, on the coefficient of variation for the seed crystals grow in pure sucrose solution. They re unparallel and intersect, so that these two variables have an effect on the variation in the mean growth rate.

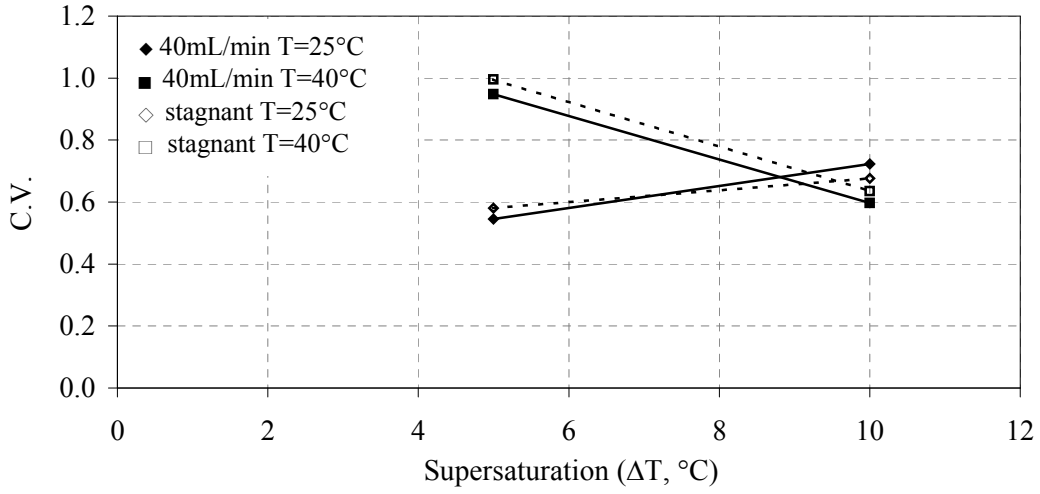


Figure 4.21 ANOVA interaction graph for the effect of the supersaturation (ΔT) on the coefficient of variation (C.V.) for nuclei grown in pure sucrose solution at a flow of 40mL/min and stagnant.

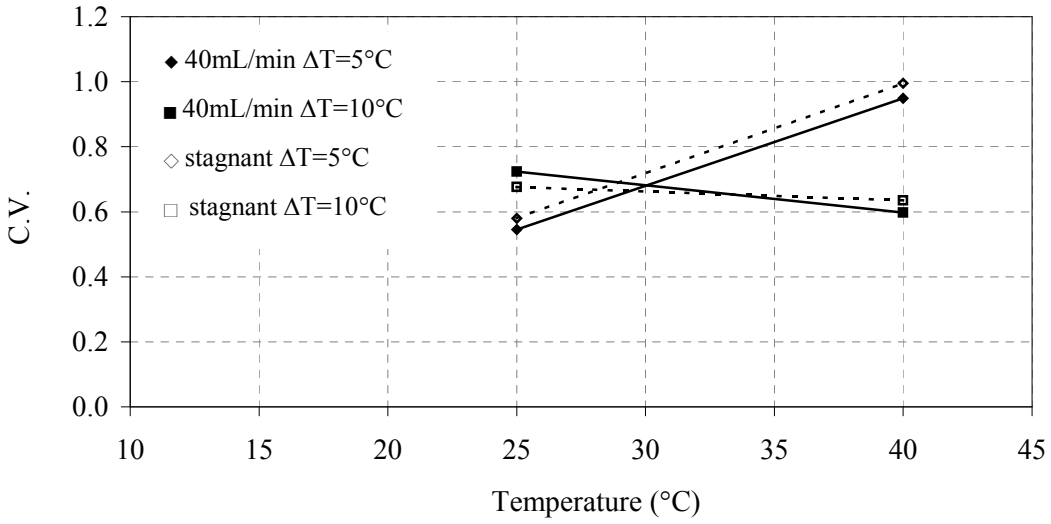


Figure 4.22 ANOVA interaction graph for the effect of temperature (T) on the coefficient of variation (C.V.) for nuclei grown in pure sucrose solution at flow 40mL/min and stagnant.

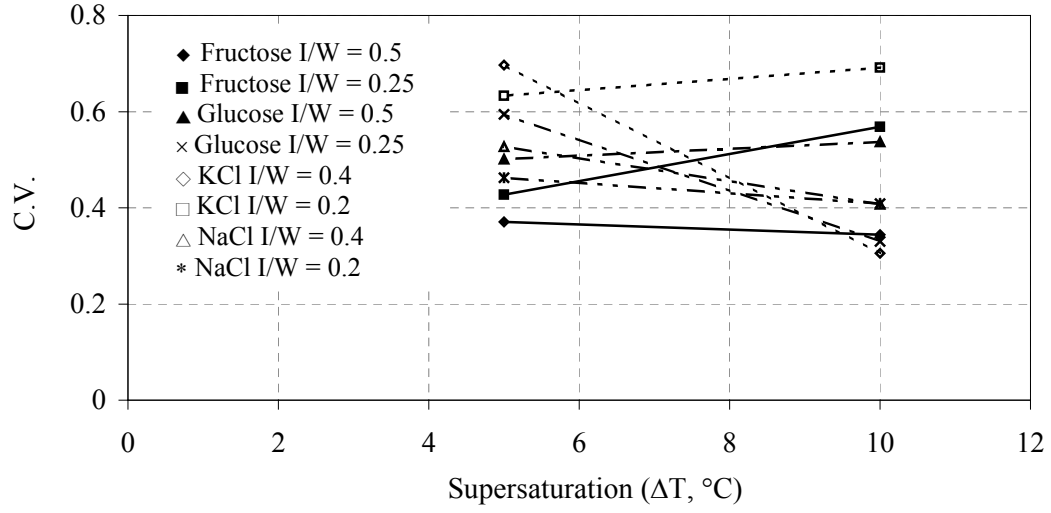


Figure 4.23 ANOVA interaction graph for the effect of the supersaturation (ΔT) on the coefficient of variation (C.V.) for nuclei grown in impure solution.

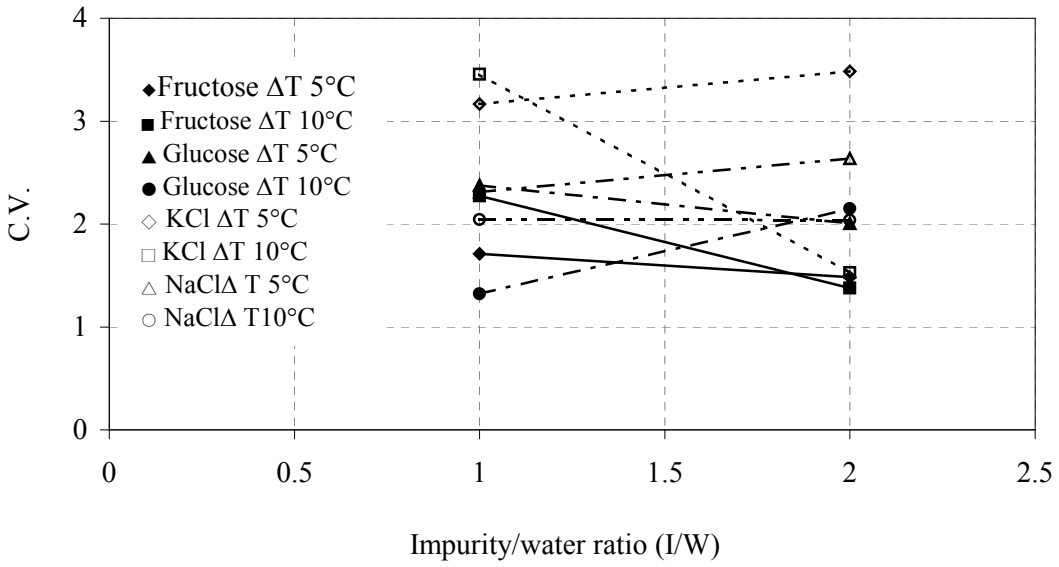


Figure 4.24 ANOVA interaction graph for the effect of impurity water ratio on the coefficient of variation (C.V.) for nuclei grown in impure solution.

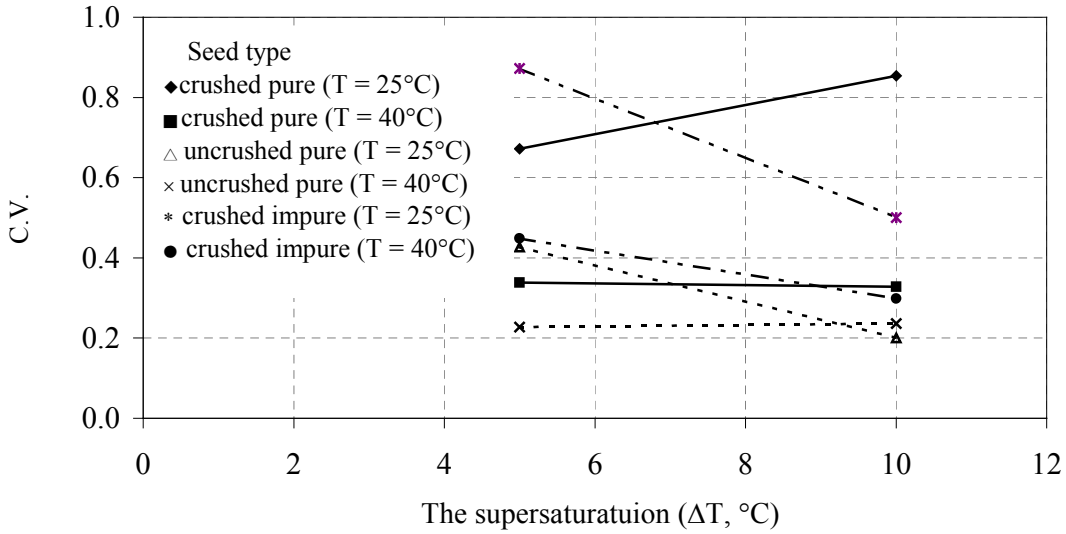


Figure 4.25 ANOVA interaction graph for the effect of the supersaturation (ΔT) on the coefficient of variation (C.V.) for seed crystals grown in pure sucrose solution.

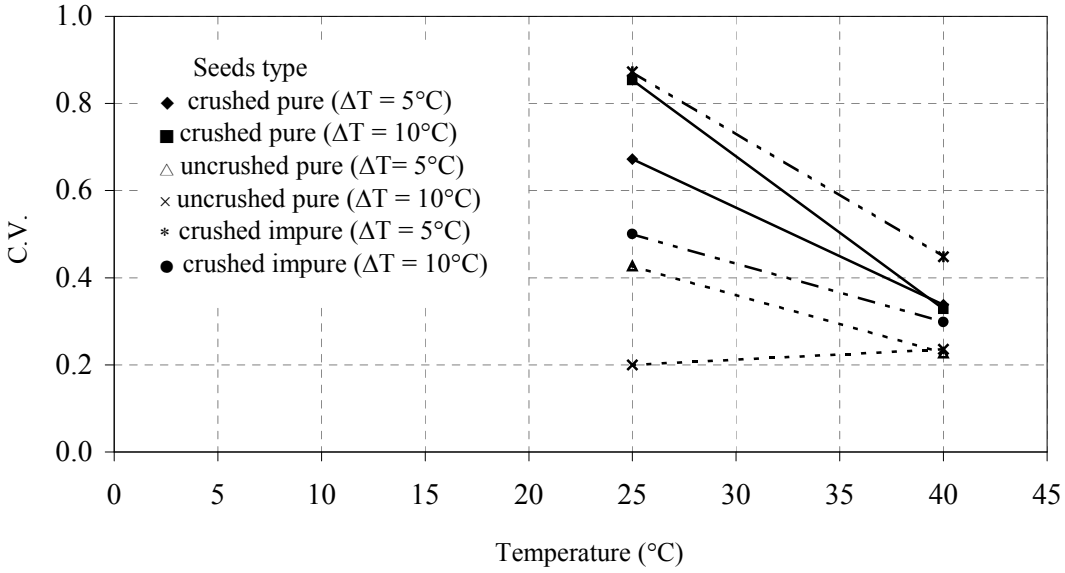


Figure 4.26 ANOVA interaction graph for the effect of the supersaturation (ΔT) on the coefficient of variation (C.V.) for seed crystals grown in pure sucrose solution.

Chapter 5

Conclusions

5.1 Conclusions

5.1.1 Secondary nuclei can be generated by the contact nucleation method where a parent crystal is slid lightly over any surface that immersed in the supersaturated solution. Visible contact nuclei will be generated within approximately a minute of the contact.

5.1.2 Each crystal has its own growth rate, or they grow with different rates although they are in the same condition or environment. This phenomenon is called growth rate dispersion (GRD).

5.1.3 Growth rate dispersion can be observed in all systems, which can be shown by the coefficient of variation (C.V.) values, and log–normal distribution plots of the growth rate distribution. The comparison from the plot of the distribution between nuclei and seeds grown in pure stagnant solution indicates that they have the same trend, that is, the narrowest distribution is obtained at the condition of ΔT 5°C and operating temperature 25°C. However, the widest distribution is obtained when the system is operated at high levels of supersaturation (ΔT = 10°C) and operating temperature (40°C). With the intermediate conditions of ΔT = 10°C; operating temperature 25°C, and ΔT = 5°C; operating temperature 40°C, both distributions are slightly different and lie between the previous ones.

5.1.4 The statistical values of the crystal growth rate distributions have been shown in chapter 4; Table 4.1–4.5. These values are calculated from growth rates obtained from the slope of size vs. time plot of each experiment. The most important values considered are the mean growth rate, and coefficient of variation (C.V.) of the growth rate distribution, that are used to describe the behaviour of the population of crystal growth rates. The mean growth rate is an average of how fast the nuclei grow. The C.V. value shows how much the growth rate is spread about the mean value. These two values can be concluded as follows.

5.1.4.1 For experiment section one; the study of the growth of contact nuclei in pure solution with different flow rates, involves three factors, flow rate, temperature and supersaturation. By the statistical values shown in Table 4.1, the mean growth rate varies between 0.113–5.12×10^{-6} mm/s. The condition with solution flow rate at 40mL/min, operating temperature at 40°C, and the supersaturation at ΔT = 10°C, gives the fastest growth rate, 5.12×10^{-6} mm/s. At the same solution flow rate – 40mL/min, but with an operating temperature at 25°C and the supersaturation at ΔT = 5°C, the slowest mean growth rate, 0.113×10^{-6} mm/s, is obtained.

In order to present the growth rate dispersion of nuclei, the coefficient of variation is considered. High coefficient of variation (C.V.) represents high dispersion resulting in a wide product size distribution, which is not desirable in industrial crystallization. The range of coefficient of variation (C.V.) for this section is between 0.546 and 0.995. The maximum dispersion in this section is the condition at operating temperature 40°C, the supersaturation ΔT 5°C and stagnant solution flow rate, where the coefficient of variation (C.V.) is equal to 0.995.

5.1.4.2 Experiment section two; in this section contact nuclei were grown in impure stagnant solution with four different impurities – glucose, fructose, potassium chloride and sodium chloride. Table 4.2 shows the statistical values of this section: the mean growth rate is $0.131–1.190\times10^{-6}$ mm/s; the range lies within the mean growth rates obtained from the first section. In addition, nuclei in impure solution grow faster than the slowest growth of nuclei in pure solution and grow slower than the fastest growth of nuclei in pure solution. Nuclei where NaCl was added as impurity grow the fastest, but adding glucose results in the lowest growth rate. Fructose and NaCl tend to increase the mean growth rate, but glucose and KCl tend to decrease the mean growth rate as compared to the mean growth rate of nuclei grow in pure solution.

The coefficient of variation (C.V.) for this part is between 0.305 and 0.679. Adding glucose and KCl as impurities widens the growth rate spread obtained, but adding fructose and NaCl achieves a narrower growth rate spread. When comparing the coefficient of variation (C.V.) value of this section to the first section, it shows that nuclei grown in impure solution with KCl added as impurity results in higher growth rate dispersion, but adding fructose and NaCl result in lower growth rate dispersion. For glucose as an impurity, the coefficient of variation (C.V.) is only slightly different from where a pure solution is used.

5.1.4.3 Experiment section three; three types of seed crystals – uncrushed pure seeds, crushed pure seeds, and impure seeds, were grown in pure stagnant solutions. The mean growth rate obtained was between 0.872 and 10.54×10^{-6} mm/s when the initial size was in the range 0.106–0.150 mm. The seeds were sieved in order to obtain a narrow size range. Uncrushed pure seed resulted in

the highest mean growth rates. Crushed pure and impure seeds grown in pure stagnant solutions resulted in slightly lower mean growth rates.

The coefficient of variation (C.V.) for the seed crystal experiment is between 0.200 and 0.873, with the minimum value obtained from the uncrushed pure seeds experiments. In addition, narrow growth rate dispersion occurs in the system that used uncrushed pure seed crystals. For the others type of seeds, the coefficient of variation (C.V.) is quite similar to the distribution for the high quality seeds.

5.1.5 In order to determine with confidence which independent variables or process conditions have an influence (and are significance to) the growth rate distribution of sucrose crystal growth from aqueous solutions, the analysis of variance or ANOVA method was used to test the mean growth rate and the coefficient of variation (C.V.) results. The results were shown in table 4.6–4.15. The first part of research – nucleation in pure solution, displayed results that show that each processing condition (the supersaturation (ΔT), temperature and flow rate), influences the mean growth rate; that is, change in any of these factors can change the mean growth rate of the system. The most importance factors are the temperature and the supersaturation (ΔT), respectively, that can change the mean growth rate very significantly. However, flow rate also has a smaller, but significant effect on the mean growth rate. With nucleation in impure solution, the ANOVA results show that all factors (the supersaturation (ΔT), impurity/water ratio (I/W) and type of impurity), are strong influences on the mean growth rate, where changes in processing conditions changes the mean growth rate very significantly. The last part of the study, seed crystal growth in pure sucrose solution, studied three different types of seeds –

uncrushed pure seeds, crushed pure seeds and crushed impure seeds. The ANOVA results show that there is a weak effect on the mean growth rate when type of seeds is considered. However, the temperature and the supersaturation (ΔT) are very strong effects on the mean growth rate, so that changes in these two factors changes the mean growth rate significantly.

5.1.6 In the system where pure sucrose solution is used to grow nuclei and seed crystals, as studied in the first and the third section, the supersaturation (ΔT) and operating temperature have a strong influence on the mean growth, rate but the other factors, flow rate and type of seeds, are weak effects. If impurities were added into the solution, the main effects that can change the mean growth rate will be the amount and type of impurity. However, the supersaturation gives a quite small effect on the mean growth rate as compared to the amount and type of impurity. The main factor in growth rate dispersion is the coefficient of variation (C.V.) of the growth rate distribution, and fewer variables have an effect on the coefficient of variation (C.V.) than on the mean growth rate. The only variables to have a strong effect on the coefficient of variation (C.V.) are the supersaturation, impurity and type of seeds.

5.2 Recommendations

5.2.1 It is also possible that the pH value may be involved in the determination of the mean growth rate and the value of the C.V. It is believed that this effect may not be a strong as the other effects that were studied. The C.V. can vary in raw sugar manufacture depending on the impurities in the cane, particularly the biological impurities.

5.2.2 The current study involves only a single solute grown from aqueous solutions. It would be interesting to confirm if the same variables are most significant in variations in the growth rate distributions of other solute types (in particular salts, large organic molecules, and biological molecules such as proteins).

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Biography

Miss Srisuda Puagsa was born on June 10, 1976 in Pakchong District, Nakhon Ratchasima Province. In 1994, she began studying for the Bachelor degree at the School of Chemical Engineering, Institute of Engineering at Suranaree University of Technology, Nakhon Ratchasima Province. After graduating, she worked as a research assistant in a project involving crystallization of sugars particularly glucose and fructose. The work resulted in publication of the paper: A. E. Flood and S. Puagsa "Refractive Index, Viscosity, and Solubility at 30°C, and Density at 25°C for the system Fructose + Glucose + Ethanol + Water" Journal of Chemical Engineering Data, Vol. 45(5); 902–907 (2000). In 2001, she continued study for a Masters degree at the School of Chemical Engineering, Institute of Engineering, Suranaree University of Technology.