EFFECT OF JET MILL OPERATING PARAMETERS DURING THE PRODUCTION OF ULTRAFINE LIMESTONE

by

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Thesis submitted in fulfillment of the
requirements for the degree
of Master of Science

JANUARY 2011

ACKNOWLEDGEMENTS

First of all, I would like to say Alhamdulillah to Allah S.W.T, for giving me the strength and health to do this project work until successful completion. I would like to thank School of Materials and Mineral Resources Engineering for giving me the opportunity to conduct and complete this study.

I wish to express my sincere gratitude towards Prof Khairun Azizi Mohd Azizli for her support and encouragement in completing this research. The greatest debt of gratitude is also owed to Dr. Samayamutthirian Palaniandy for his supervision, comments and a never ending of encouragement for me throughout my journey being a research student. I have gain a lot of experience from his guidance and motivation.

I'm thankful to all the technicians especially Mr. Mokhtar, Mr. Mohamad Zaini, Mr. Abdul Rashid, Mr. Mohd. Azam, Mr. Mior Muhammad Noh and Mr. Kemuridan for their valuable contribution and assistance during this project. I'm thankful to all my friends who had helped me trough out this project.

I would like to thank my parents, Mr. Jamil Hassan and Mrs Che Asiah Yahya, sister Noorsuziyana, brother, Syakirien and my family in law for their support and encouragement to complete this study.

Finally, I would like to express my thousand of appreciation and a special thanks to my lovely husband, Wan Mohd Arif and daughter, Wan Rifaa Rafhanah for supporting and giving me the strength from the beginning till the end.

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LIST OF ABBREVIATIONS

XRD	X-ray Diffraction
FTIR	Fourier Tranform Infrared
SEM	Scanning Electron Mocroscopy
Rj	rupture of joints
CI	cleavage
Ch	chipping
Gr	ultimate grinding
ICDD	International Center for Diffraction Data
FR	Feed rate
GP	Grinding pressure
CRS	Classifier rotational speed

LIST OF SYMBOLS

E_k	gas kinetic energy (J),
M_g	mass solid (kg)
V	velocity (ms^{-1})
E_{sp}	specific energy consumption, (Jkg^{-1}s)
Q_{solid}	solids flow rate, (kgs^{-1})
P	gas pressure (Pa)
S_{0p}	specific surface of product (m^{-1})
E_{sp}^{x}	power function of the specific surface energy
X_c	cut size
η	dynamic viscosity
ν_r	radial velocity
r	rotor radius
ρ_s	density of solids
ν_φ	circumfrential velocity
d(4,3)	Volume moment diameter
ψ	Span value
Dν	Crystallite size
ε	Lattice strain

LIST OF PUBLICATIONS

Noorina Hidayu Jamil, Samayamutthirian Palaniandy and Khairun Azizi Mohd Azizli. Mechanochemical Effect of Limestone during Fine Grinding in Jet Mill (2009). *17th Electron Microscopy Society Malaysia (EMSM) Scientific Conference, Kuala Lumpur,* MALAYSIA.

Noorina Hidayu Jamil, Samayamutthirian Palaniandy and Khairun Azizi Mohd Azizli. Microstrucute Study of Ground Limestone in Jet Mill, (2009). *4th International Conference on Recent Advances in Materials, Minerals and Environment and 2nd Asian Symposium on Materials and Processing (RAMM & ASMMP). Penang,* MALAYSIA

Noorina Hidayu Jamil, Samayamutthirian Palaniandy and Khairun Azizi Mohd Azizli. Effect of Operational Parameters on the Breakage Mechanism in Jet Mill (2009). *The 1st Regional Conference on Material (RCM). Penang,* MALAYSIA

Kesan Parameter Operasi Pengisar Jet Semasa Penghasilan Batu Kapur Halus

ABSTRAK

Pengisaran halus batu kapur di dalam pengisar jet telah dilakukan dengan mengubah kadar suapan, halaju putaran pengkelas dan tekanan pengisar pada lima peringkat. Selain itu, keadaan dalam kebuk pengisar seperti jisim lapisan terbendalir dan tekanan dandang pengisar juga direkodkan. Partikel terkisar dicirikan berdasarkan taburan saiz partikel dan taburannya, kesan mekanokimia dan penambahbaikan bentuk partikel. Produk terkisar menunjukkan taburan secara poli-model di mana diameter momen isipadu berada di dalam julat antara 2.11µm hingga 7.12µm, manakala nilai taburan adalah di antara 1.1 hingga 2.9. Partikel halus diperolehi pada keadaan tekanan atasan dan jisim lapisan terbendalir sebanyak 1500g. Kesan mekanokimia dicirikan melalui Belauan Sinar-X dan FTIR. Pola belauan Sinar-X menunjukkan penurunan pada puncak keamatan, kelebaran tapak puncak dan perubahan posisi puncak. Darjah pengkristalan pada partikel terkisar adalah di antara 27.56% hingga 97.12%. Saiz kristal pula di dalam julat 144.1nm ke 228.2nm manakala terikan kekisi antara 0.153 hingga 0.201. Pengembangan kekisi kristal ditunjukkan pada sampel terkisar. Penurunan pada ikatan O-H melalui spektra IR menunjukkan terdapatnya kesan mekanokimia. Bentuk partikel dicirikan melalui nilai kebulatan di mana terdapat 30 % penurunan pada produk partikel. Mekanisma pemecahan lelasan membantu pemecahan pada bucu partikel di mana menghasilkan partikel sub-mikron manakala mekanisma pemecahan hentaman menghasilkan partikel dengan saiz micron. Partikel batu kapur kurang daripada 10µm dengan taburan sempit dengan penambahbaikan bentuk partikel serta separa amorfus merupakan ciri-ciri yang sesuai untuk aplikasi pengisi di dalam pelbagai produk pembuatan.

Effect of Jet Mill Operating Parameters during the Production of Ultrafine Limestone

ABSTRACT

Fine grinding of limestone in jet mill was carried out by varying the operational parameters such as feed rate, classifier rotational speed and grinding pressure at five levels. Besides that the inside mill condition such as holdup mass and grinding camber pressure was noted as well. The ground particle was characterized for particle size and its distribution, mechanochemical effect and improvement in particle shape. The ground product exhibits poly-modal distribution where the volume moment diameter ranged from 2.11µm to 7.12µm whilst the span values are in between 1.1 to 2.9. Finer particles were obtained at overpressure grinding chamber condition and the mass of holdup of 1500g. The mechanochemical effect was characterized through X-ray diffractogram and FTIR. The X-ray diffraction pattern exhibits reduction in peak intensity, peak base broadening and shift in peak position. The degree of crystallinity of the ground particles ranged from from 27.56% to 97.12%. The crystallite size ranged from 144.1nm to 228.2nm whilst lattice strain ranged from 0.153 to 0.201. The expansion of crystal lattice was observed in the ground samples. The IR spectra exhibits reduction of O-H band which indicate the mechanochemical effect has taken place. The particle shape was characterized through circularity values where a reduction of 30% in this value was observed in the ground particles. Abrasion breakage mechanism facilitates breakage of particles edges which produces sub-micron particles whilst impact breakage mechanism produces micron size particles. Limestone particles below 10µm with narrow distribution and improved particle shape with partially amorphous characteristics is suitable for filler application in various manufacturing products.

CHAPTER 1

INTRODUCTION

1.0 Introduction

The demand for ultra fine mineral particles had continuously increased and it’s gaining much importance for application in various industries such as paper, paint, plastic, pharmaceuticals, ceramics, cosmetics, foods and fine chemicals (Boldyrev et al., 1996; Palaniandy et al., 2008b). Fine grinding can be defined when the particle size of ground product in the range of 10-100µm whilst particles predominantly below 10µm can be classified as ultrafine grinding (Balaz, 2008)

It is commonly known that high energy milling required high energy consumption. For example, in jet mills, less than 5% of the provided energy is used for effective fracture that is for creation of new surfaces (Lecoq et al., 2003). The energy consumption of jet mill is high compared to mills with loose grinding media which is an essential element for optimization (Tkacova, 1989). The estimation of energy and power consumption can be determined based on inlet of air flow rate to the grinding chamber, grinding chamber pressure and classifier current using kinetic energy. The energy used in grinding such as jet milling is depends on the total pressure and gas being used for grinding (Qian, 2000).Therefore, controlling the operating parameters and inside mill conditions is very important to optimize the size reduction process and also mechanochemical effect of the ground product. Although the main disadvantage of high-energy mills is the high amount of energy required for the grinding operation, it is increasingly used in industry because very fine grinding product with a narrow size distribution is attained without contamination as the milling occurs by inter particle collisions (Gommeren et al., 2000).

1.1 Effect induced during fine grinding in jet mill

The two major issues affected from fine grinding are the product fineness and mechanochemical effect of the ground product. The size reduction in grinding can be considered to be the result of fragmentation of particles such as impact, abrasion, compression and chipping (Lin, 1998). Furthermore, ground material is mechanically activated by increased of specific surface energy and elastic strain energy and this could be a problem when the smaller particles start to combine to form a larger particle. There are three stages of interaction between the particles which were adherence, aggregation and agglomeration. At adherence stage, the particles would coat on the lining and the grinding bodies. At aggregation stage, the particles were associated weakly by van Der Walls-type adhesion and it was reversible reaction. Agglomeration was defined as a very compact, irreversible interaction of particles with occurance of chemical bonding between the particles (Palaniandy et al., 2008b).

Mechanochemical effect is very pronounced in the high intensity grinding mills such as planetary mill, oscillating mill, vibration mill and jet mill (Palaniandy et al., 2007a). Zhang et al. (2007) and Lin (1998) summarize the mechanochemical phenomena into three parts as given below:

- Formation of dislocations and point defects in the crystalline structure
- Mechanical activation of solids materials
- Polymorphic transformation, amorphization and crystallization.

Mechanochemical stressing will lead to a structural changing because of the energy being supplied from the grinding mill will not be stored in the material as thermal energy but it will be used to bend or break the crystal (Palaniandy et al., 2008b). The changes of the material structure is related to the occurrence of structural defects such as changes of the surface, lattice distortion and conversion of long range order to short range order (Pourghahramani et al., 2006a).

They are several advantages of mechanochemial effect to the ground product such as reducing the annealing and sintering temperature and accelerate densification of ceramics powder, increase disintegration time and dissolution rate of pharmaceutical products, production of porous minerals, increase the reactivity of cementitious waste materials, reduction in phase transformation temperature, enhance leaching process, decrease thermal decomposition temperature and increase in particle reactivity (Palaniandy et al., 2008b; Zhang et al., 1996).

Besides mechanochemical effect, the particle shape is one of the important properties of fine particles as it will influence the end-use properties such as flowability, abrasivity, ability to be granulated and compacted, covering or light reflection properties and reactivity (Palaniandy et al., 2009a). Particle shape plays important properties in filler industry beside hardness, particle size, colour refractive index and chemical properties (Christidis et al., 2004). The formation of the particle shape is dependently to the particle size reduction as it was also controlled by fragmentation mechanisms such as the type of grinding machine and its operational parameter (Palaniandy et al., 2009a)

1.2 Application and advantages of jet mill

The rapid growth of fine grinding, and the advances applications of fine powders, several types of ultra fine grinding technology which been classified as high energy mills had been approached such as attrition mill, jet mill, planetary mill, oscillating mill, and vibration mill. According to Peukert (2004), the type of mill that has been chosen and its mode of operation will determine the stress intensity distribution and the number of stressing events. Among these types of mills, jet mill has marked its importance in producing particles below 10µm due to its several advantages compared to the other mills. As the jet mill is a static machine which does not have any grinding media, therefore, contamination can be avoided in the final product (Godet-Morand et al., 2002; Palaniandy et al., 2008b; Lecoq et al., 2003). The advantages of jet mills include a capability of this milling machine to obtain a narrow particle size distribution for the ground product with product fineness smaller than 10µm (Tuunila and Nystrom, 1998; Palaniandy et al., 2008; Chamayou and Dodds, 2007). Other advantages are high purity**,** low wear, small footprint, high degree of fragmentation and low noise (Palaniandy et al., 2008b; Berthiaux, and Dodds, 1999a). The main purpose in application of the jet mill is grinding including hard materials besides deagglomeration purposes, (Benz et al., 1996). Jet mills are commonly used to grind materials such as toners, high purity ceramics, foodstuffs, ultrafine metal oxides, pharmaceutical powders, pigments, polymer powders and ultrafine particles for powder coating. Jet milling can also be used to grind carbon nanotubes (McMillan et al., 2007).

Air jet milling or also known as fluid energy milling uses high velocity jets of gas to impart energy to particles for size reduction. The common features of air jet mills are no moving parts in the grinding chamber and energy for the size reduction is brought by the carrier gas. The milling component of the jet mill consists of a chamber with a nozzle or nozzles. The particles to be pulverized are accelerated by pressurized gas or stream jets and the grinding effect is produced by interparticle collision or by impact against solid surfaces (Chamayou and Dodds, 2007). Other features are that the adiabatic pressure release at the nozzles and high ratio of transport gas to solids loading makes for good cooling capacity allowing for processing of heat sensitive materials (Chamayou and Dodds, 2007).

Ultrafine grinding has found increased used in many fields due to some advanced properties of ultrafine powders affected from this process such as surface chemistry, packing characteristics, strength, optical properties and reaction kinetics (He et al., 2006). Raw materials naturally occur quite coarse grained, so they have to be ground to a required fineness, determined, for example by the needs of application (Tuunila and Nystrom, 1998). Mineral powders such as ground limestone and wollastonite are widely used as filler in plastic, rubber, paper, paint and other fields (Gai et al., 2005; He et al., 2006). Filler uses for limestone generally require white color and a high degree of mineralogical purity, control of particle size and shape, surface area and liquid absorptivity (Gullo, 1996; Christidis et al., 2004). The properties of ground limestone will contribute to the performance of final application. For example in recently research (Gullo, 1996) showed that limestone is used as paper filler and coating in alkaline papermaking, because both uses require high brightness, high purity, small particle size and lack of abrasion. Either ground natural or precipitated, limestone can provide opacity, high brightness, and improved printability due to its good ink receptivity to the applied materials. Whilst in plastic industry, ground limestone is the most commonly used as filler due to its low cost, low abrasion, low oil absorption, low moisture, high brightness, and easy dispersion with conventional mixing equipment and furthermore improve heat resistance, hardness, colour fastness and stability of materials (He et al., 2006)

1.3 Problem Statement

Nowadays, grinding of fine particles not only focusing on the size reduction but also the particle shape and the surface texture has become an important matter that needs to be optimized. Conventional fine grinding methods that are widely use in industry is commonly suffer to particle agglomeration that will lead to (wider) particle size distribution. Besides that, it is hard to control the particle shape and no mechanochemical effect occurs. Those, this study will use jet mill machine that is believed can improve the particle properties and solve the current problems. This can be achieved by controlling the parameters in jet mill which are feed rate, classifier rotational speed and grinding pressure. Although the main disadvantage of jet milling is the high amount of energy required for the grinding operation, but it is increasingly used in the industry because very fine grinding product with a narrow size distribution is attained without contamination as the milling occurs by inter particle collisions (Gommeren et al., 2000).

1.4 Objectives

The main objective of this study is to produce ultra fine particles which are below than 10µm in jet mill and the measurable objectives are:

1. To study the influence of jet mill operational parameter such as classifier rotational speed, grinding pressure and feed rate on the stability of the grinding-classification process, product fineness, grinding rate, particle shape and agglomeration issues.
2. To study on mechanochemical effect of calcium carbonate at various operating conditions which includes determination of degree of crystallinity, crystallite size and lattice stain of the ground product.
3. To study the effect of breakage mechanisms of calcium carbonate in jet mill.

1.5 Scope of work

Fine grinding of limestone was carried out in a jet mill by varying the operational parameters such as feed rate, classifier rotational speed and grinding pressure.The experiment using 5^3 full factorial designs. The total numbers of grinding test work in the jet mill is 125. Feed rate chosen were 4kg/h, 8kg/h, 12kg/h 16kg/h and 20kg/h. The grinding pressure chosen were 2 bar, 3 bar, 4 bar, 5 bar and 6 bar whilst the classifier rotational speed was 7000 rpm, 10000 rpm, 13000 rpm, 16000 rpm and 19000 rpm. The inside mill condition such as amount of hold up and the height of the fluidized bed will be measured. Other condition affected from operating parameter such as grinding chamber pressure, air flow rate and filter differential pressure will be measured. Then the weight of ground product will be measured. The ground product will be characterized via various analyses which include particle size analysis, X-ray diffraction, morphology study, FTIR and specific surface area. The breakage mechanism of the particles at different operating parameters will be studied as well.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

High demand for fine particles product from various manufacturing industries driving the technology advancement in grinding. The grinding technology influences the properties of the fine particles such as product fineness, particle density and morphology as each grinding mill has its own signature of particle breakage mechanism. In order to sustain a stringent demand from the manufacturing industry, the millers are focusing deeply on the quality of the product which is very much related to the particle's properties which is being controlled by the mill design and its operational parameter. Ultra fine grinding is defined as grinding particles below 10µm (Balaz 2008).

Comminution is an important step in many technological operations such as filler application, pharmaceuticals, agro-chemicals and cement. The process is defined as the mechanical breakdown of solids into smaller particles without changing their state of aggregation (Balaz 2008). The application of grinding is mainly used to create particle of certain size and shape, increase surface area and induce defects in solids which is needed for subsequent operations such as chemical reactions and sorption (Balaz 2008). The increment of surface area by grinding is more likely to increase the proportion of regions of high activity in the surface (Balaz 2008). The particles are reduced in size by a combination of impact and abrasion breakage mechanism either dry or suspension in water. The theory of grinding has mainly been developed in the mineral industry as a response to maximize the production capacity and minimizing energy use for value added products (Nakach et al., 2004). Besides the grinding machine, the properties of the material such as strength and toughness play an important role during grinding.

The feed materials to be ground are so diverse with various properties from the inorganic materials such as minerals and ceramics to the organic materials like resin, food, pharmaceuticals and the metallic materials. Properties of feed materials such as strength, toughness, hardness, cohesiveness, flowability and wetability will affect the grinding performance. Compression, attrition and impact breakage mechanisms are more preferred to grinding hard and brittle materials such as minerals and in this case, fluidized bed is more preferred compared to target impact type or attrition type because more impaction and attrition between the particles rather than the collision against the mill body or the target can be expected (Yokoyama and Inoue, 2007). Whilst for elastic resin and fibrous materials is conducted usually by mills with a shearing mechanism whilst for heat sensitive materials, special care is needed since grinding can cause the generation of considerable amount of heat.

2.2 Fine grinding

Fine grinding is the final stage of comminution process in order to obtain required particle fineness according to the needs by the manufacturing industries. Ultra fine grinding is unit operation process where particles were ground to a fineness where 80% of the particles are smaller than 10µm (Tuunila and Nystrom 1998). Ultrafine grinding in the submicron range has recently created an importance due to the development of new functional materials such as new ceramics and electronic materials for various industrial applications (Choi et al., 2004).

Various applications of ultra fine grinding is not only limited to minerals field, but for a broad material base including plastics, food, advanced ceramics, electronics, alloys and superconductors (Zhao and Schurr, 2002). In pharmaceutical industry, issue of insoluble drugs often influence the bioavailability, as the drugs absorption after oral administration is poor and very often below the therapeutic level. The decrease of drugs particle size can improve the rate of dissolution and prolong grinding may enhance the bioavailability of the drugs due to the change of solid state such as micronization and degree of crytstallinity (Choi et al., 2004). Generally, drugs in solid dosage forms are used in their crystalline form. However, the amorphous state had become of interest as it can improve the dissolution behavior of the drug (Choi et al., 2004).

The fine grinding mills are classified often into five major groups, impact mills, ball media mills, air jet mills, roller mills and shearing attrition mills. The types of mills that often used for ultra fine grinding are the attrition mill and the jet mill (Tuunila and Nystrom, 1998). Table 2.1 shows typical types of fine grinding mills in each group. The major grinding mechanisms are expressed in terms of impact, shearing, compression and attrition which are different combinations of the mechanical forces having different strength, direction and speed. Impact is caused by predominantly the normal force at high speed to pulverize the feed materials whilst shearing is exerted by the tangential force to cut the materials and the compression is performed principally by the normal force between two plates or rolls at rather lower speed to crush lumps or particles. Meanwhile attrition is carried out by the shearing force under compression to reduce the particle size. In most mills, these grinding mechanisms usually take place simultaneously (Yokoyama and Inoue, 2007).

Table 2.1 : Classification of grinding mills (Yokoyama and Inoue, 2007).

Group		Type / Model
Impact mill		High speed rotation disc type Hammer type Axial flow type Annular type
Roller mill		Roller tumbling type Roll type
Ball media mill	Vessel drive	Tumbling type Vibration type Planetary type Centrifugal fluidized bed type
	Agitator drive	Tower type Agitation vessel type Tubular type Annular type
Air jet mill		Target collision type Fluidized bed type Attrition type
Other type mills		Mortar and pestle Stone mill Powder bed attrition type mill Wet high speed shearing mill

2.2.1 Effect of ultra fine grinding

Ultra fine grinding is energy intensive process which provides materials in required fine size ranges to fulfill the properties of the final product however it also exhibits agglomeration and mechanochemical effect (Wang and Forssberg, 2007). High energy consumption and ineffienciency in communition technology for such materials as mineral, cement, pigment, chemicals and food have long been regarded as a major area for development, especially for producing particles below micron size (Wang and Forssberg, 2007).

Ultra fine grinding of minerals may change physical and chemical properties of the mineral which may affect the functionality of these fine particles. Fine grinding is also known to affect the structure and properties of various minerals used as industrial fillers. Grinding will causes delamination at the initial stages followed by destruction of the structure and subsequent amorphization, associated with reaggregation of the mineral grains (Christidis et al., 2004). Belaroui et al. (2002) mentioned that process design and operating conditions will affect the size and morphology of the product. In case of dry grinding, both the reduction in size and the increase in surface activity of the particles being ground are very important factors influencing the mutual interactions between the members of the particulate assembly and the grinding media in the course grinding (Tkacova, 1989).

2.2.1.1 Product fineness

Nowadays, the demand for fine product particle size is emerging as the advantages of fine particles with their large specific area and high activity of the particle surface and so forth (Balaz et al., 2004). The initial population of particles, characterized by a narrow size distributions, is progressively broken, which leads to an increase of the spreading of the distribution and a decrease of the median diameter. According to Frances et al. (2001), the performance of jet mill and stirred bead mill is much more efficient compared to ball mill and vibrated mill in producing ultra fine particles which regards to the fragmentation kinetics and the size fragments that can be produced.

Fluidized bed opposed jet mills are used for the industrial production of mineral powders. Previous researches reported on talc ground in jet mill in terms of particle size as a function of feed rate and amount of hold up. The main conclusions from these works are there are optimum value of feed rate and amount of hold up that exhibits minimal particle size and running the mills at flooding limit may not be optimal. Besides that, the operational parameters and characteristics of the integral classifier controls the product quality (Godet-Morand et al., 2002: Chamayou and Dodds, 2007). The typical results from these works are shown in Figures 2.1 and 2.2. Figure 2.1 shows the product talc size distribution as a function of classifier rotational speed which indicates that finer particles were obtained as classifier rotational speed increased.

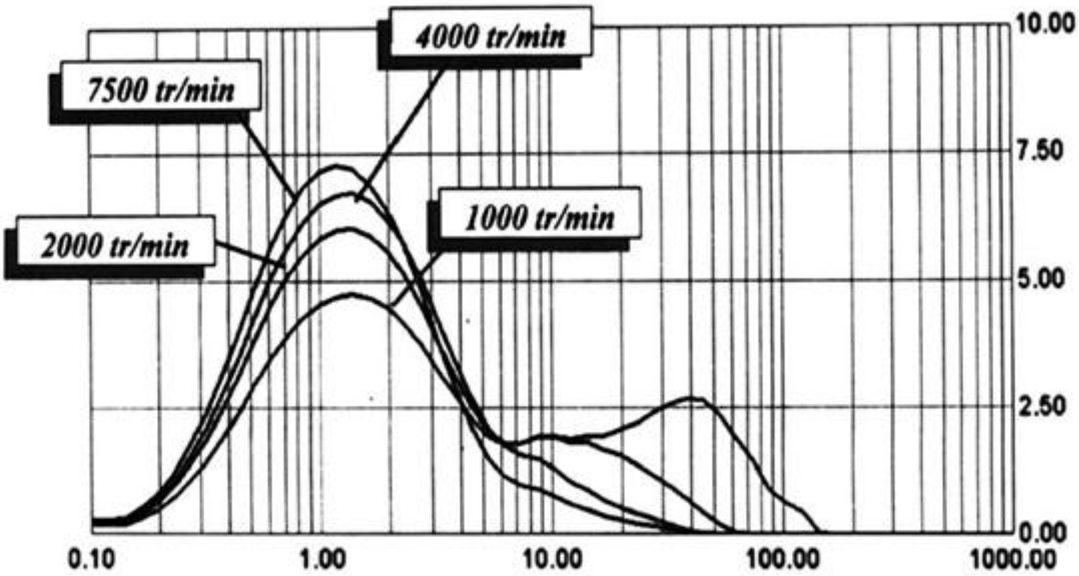
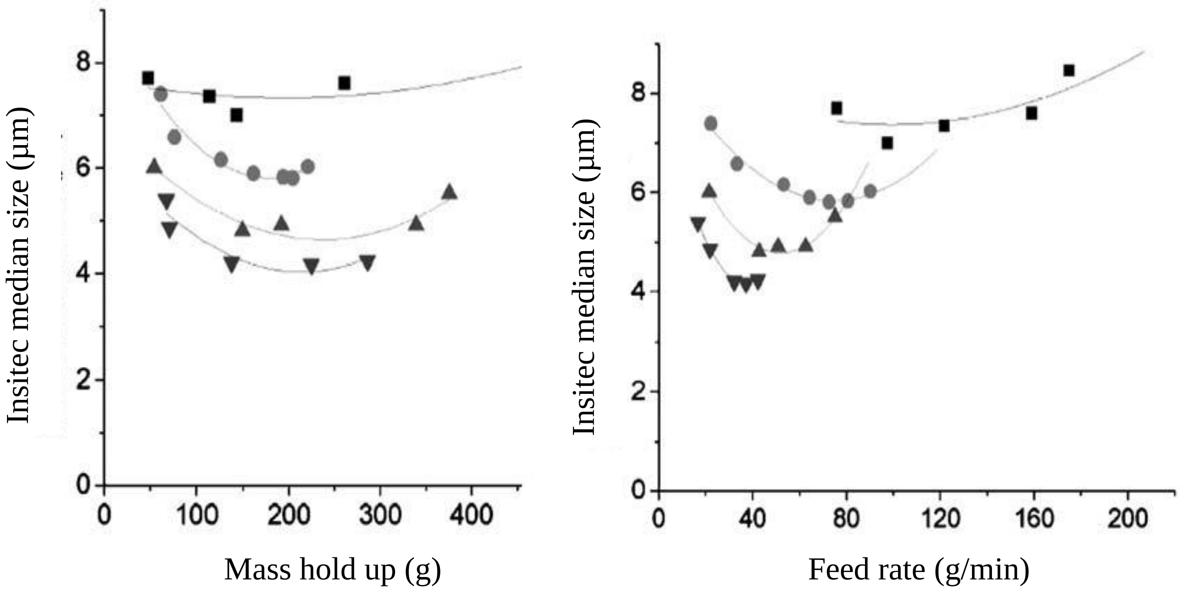


Figure 2.1: Product talc size distribution as a function of classifier speed (Chamayou and Dodds, 2007)



(a) (b)

Figure 2.2: Product median particle size as a function of (a) hold up in mill, (b) feed rate : 7000 rpm (■) 9000 rpm (●), 11000 rpm (▲) and 13000 rpm (▼) (Godet-Morand et al., 2002)

Figure 2.2 shows there is optimal amount of hold that correspond for a given classifier rotational speeds and feed rate in the mill chamber which results minimal particle size. The optimum mass hold up for every classification speed seems to be similar in each case. Low feed rates lead to low hold up, resulting low collision probability and thus in a poor breakage probability. Therefore, more coarse particles were produced. At high feed rates, but below the classifier flooding value, there exists an optimum value of mass of hold up in the mill chamber giving the highest breakage probalility and the finenest ground product will be produced (Godet-Morand et al., 2002). The particle size of medicinal materials is an important physical property that affects the pharmaceutical behaviors such as dissolution, chemical stability and bioavailibility of solid dosage forms. The size reduction of raw medicine powder is essential to formulate insoluble drugs or slightly soluble medicines and to improve the pharmaceutical properties such as the solubility, the pharmaceutical mixing and the dispersion (Choi et al., 2004).

2.2.1.2 Mechanochemical effect

Mechanical activation by means of fine and ultrafine milling is an effective procedure where an improvement in technological processes can be attained via a combination of several effects which influence the properties of applied solids (Balaz and Dutkova 2009). Mechanochemical effect will affect the mineral processing in producing finely ground particles, increased surface area and improved chemical reactivity of milled materials (Pourghahramani and Forssberg, 2006b). The process involved prolonged grinding and is reported to cause a variety of processes to take place such as generation of a new surface, formation of dislocations and point defects in the crystalline structure, phase transformations in polymorphic materials, chemical reactions, decomposition, ionic exchange and oxidation and reduction reactions (Pourghahramani and Forssberg, 2006b).

Decrease the particle size during mechanical activation beyond its initial size leads to changes in relaxation from brittle fracture to ductile fracture. These changes are accompanied with rises in strain. As a result the dislocations flows take place in the particles. Consequently, it leads to the growth of structure distortion. Those structural changes will determine the reactivity. The characterization of structural changes is important in the course of mechanical activation (Pourghahramani and Forssberg, 2006b). Recently the structural changes of various inorganic substances induced by the usual grinding technique have received much attention, from the viewpoint not only for better understanding of the mechanochemical effects but also of the relatively new method for producing several interesting materials.

Characterization of structural changes during fine grinding is essential to estimate and quantify the degree of structural changes in the ground particles. The structural changes in the crystal structure induced by fine grinding can be determined by various methods. The most common method to determine the structural changes is X-ray diffraction and infrared spectroscopy (Pourghahramani et al., 2008). X-ray diffraction line broadening is used to investigate the dislocations distributions due to the stress fields induced by the dislocations atoms are displaced from their ideal lattice positions, which causes diffraction line broadening.

Phase identification using X-ray diffraction relies mainly on the positions of the peaks in a diffraction profile and to some extent on the relative intensities of these peaks. Reduction of crystallite size can cause peak base broadening as well. The well known Schrrer equation explains peak broadening in terms of incident beam divergence which makes it possible to satisfy the Bragg condition for non-adjacent diffraction planes (Palaniandy et al., 2007a**)**. Once instrument effects have been excluded, the crystallite size is easily calculated as a function of peak width (specified as the full width at half maximum peak intensity (FWHM) and peak position (Palaniandy et al., 2007a; Pourghahramani and Forssberg, 2006b).

Distortion of crystal lattice is disorders which does not involve fundamental qualitative alteration of the crystal structure. This concept covers the formation of lattice defects which causes increase in strain, reduction in crystallite size, increase in the density, rearrangement of atoms within the lattice and alteration of planes distances due to appearance of dislocation and amorphism (Tkacova, 1989). Figures 2.3 and 2.4 shows the X-ray diffraction patterns of hematite as function of energy input in the stirred mill and tumbling mill respectively (Pourghahramani et al., 2008).

The diffraction peak shows an increment of peak base broadening, reduction of peak intensity and the shifting of reflections as the energy input increase by intensive grinding. The increase of the XRD line breadths is due to the plastic deformation and disintegration of hematite. The ground hematite in stirred mill indicate higher XRD line broadening and lattice strain, smaller crystallite size and particle size compared to the one ground in the tumbling mill. The X-ray phase content remains unaffected by different grinding environments. Generally, stirred mill with higher energy input results more mechanochemical effect compared to tumbling mill.

Fourier transforms infrared, FTIR spectroscopy is a useful tool in the molecular characterization of inorganic species. This vibrational technique which is common in many analytical laboratories has certain advantages such as requirement of small sample quantity, quick and easy sample preparation and also short analysis time. It is also allows the simultaneous study of organic and inorganic species, crystalline or amorphous compounds and in some cases, it even provides mineralogical information.

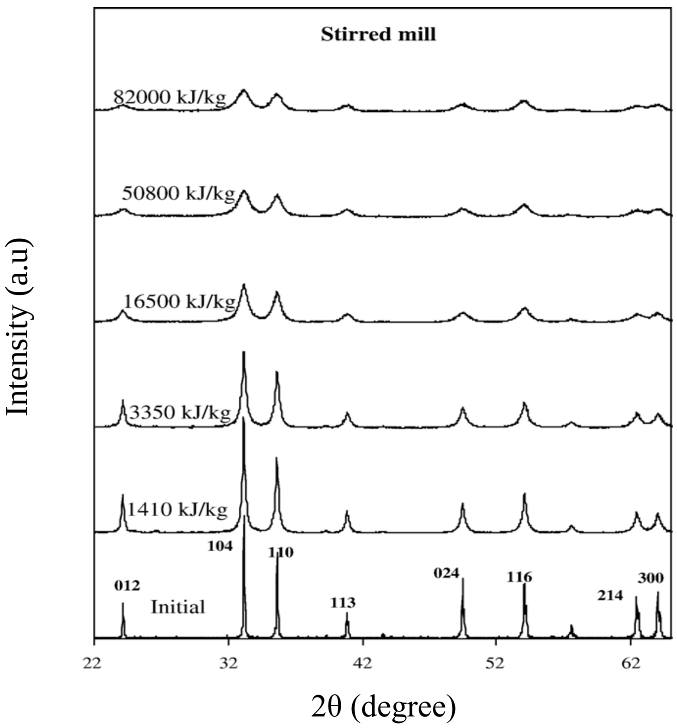


Figure 2.3: XRD patterns of the initial and ground samples as a function of energy input in a stirred media mill (Pourghahramani et al., 2008)

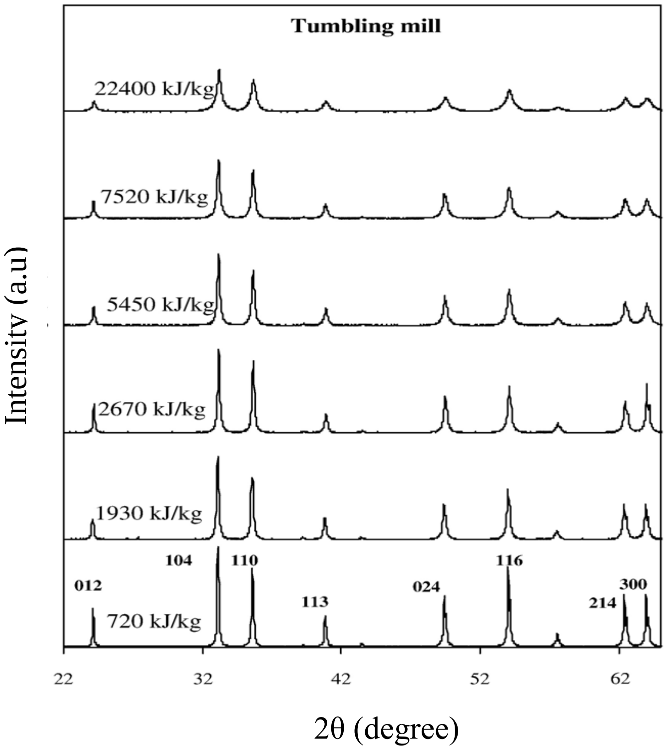


Figure 2.4: XRD patterns of the ground samples as a function of energy input in the tumbling mill (Pourghahramani et al., 2008).

The infrared spectra of inorganic compounds normally have wide absorption bands and irregular profile which make the assignation and identification of the cation-anion pair more complex. In the spectra of inorganic compounds, bands of water often appear (Reig et al., 2002). The crystalline structure is very important in the appearance of the spectra of the species in this group. Limestone has three crystalline structures named as the minerals, calcite, aragonite and vaterite and they all have the same chemical composition. Each crystalline form has a different infrared spectrum. In calcite, the ion CO_3^{2-} shows D_{3h} symmetry and in aragonite C_s. The symmetry for vaterite is unknown (Reig et al., 2002).

In FTIR analysis, a special emphasis is taken for observing new peaks in the spectra, which can be the characterization of mechanochemical effect of particle due high energy grinding besides the changes in the relative intensities, broadening and shifting of peak position as explained by XRD analysis (Pourghahramani et al., 2008). According to Figure 2.5, it is clearly observable that in the case of tumbling mill experiments, no significant changes occur leading to conclusion that no mechanochemical effect takes place in this mill type. Whilst in stirred mill, the new peaks were observed at around 3600cm^{-1}, indicates the O-H vibration mode. The relative peak increase with the milling time indicates the increment of specific surface area.

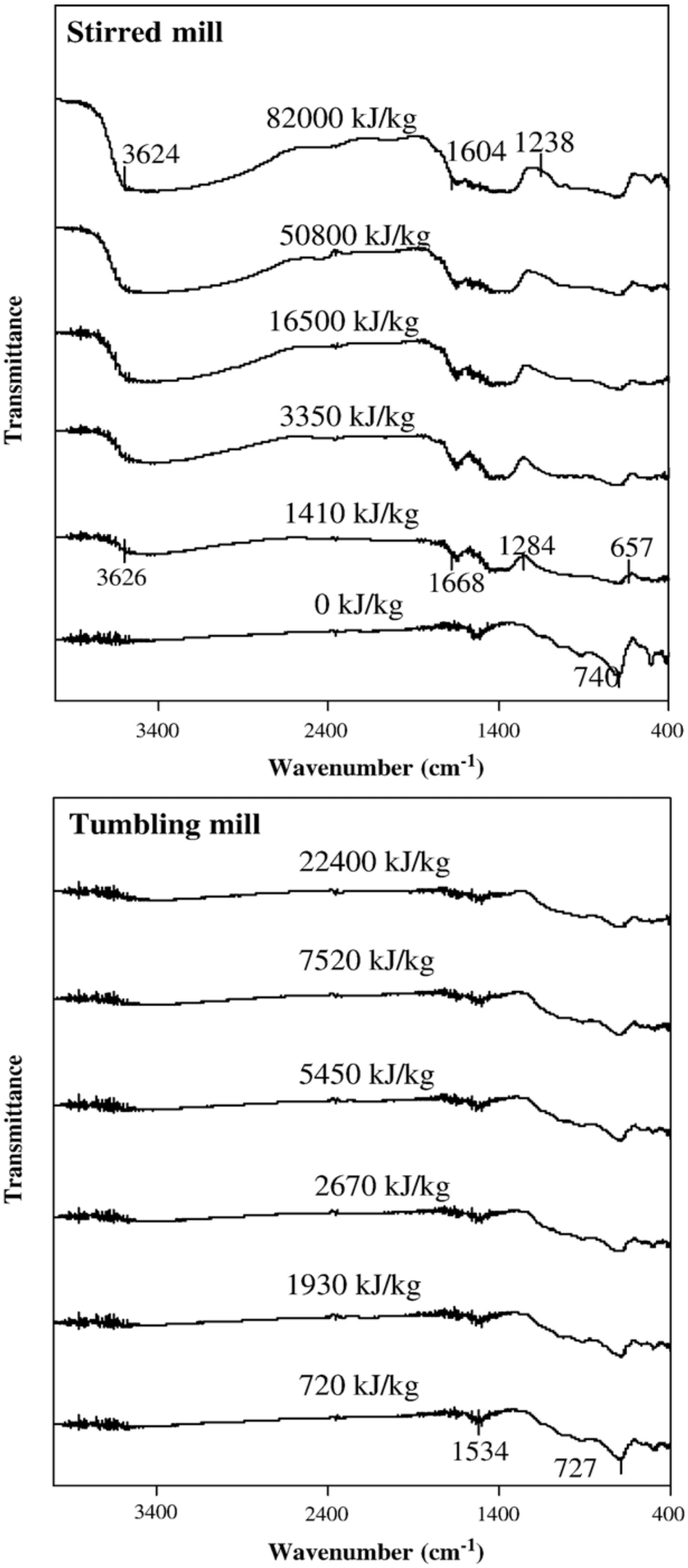


Figure 2.5: DRIFTS measurements of ground hematite in stirred media and tumbling mills as a function of energy input (Pourghahramani et al., 2008).

2.2.1.3 Agglomeration

As the grinding proceeds into ultrafine region, conditions which are of little significance during normal operations gradually become the controlling factor. These involve increasing resistance to fracture and increasing tendency to aggregate (Lin, 1998). The interaction between particles could be divided into three stages: adherence, aggregation, and agglomeration. The definition of each stage had been discussed in previous chapter. Agglomeration is defined as a very compact, irreversible interaction of particles in which chemical bonding may also play a role. Agglomeration became the disadvantageous to the grinding process and the quality of the product (Juhacz and Opoczky, 1990).

Prolonged dry milling in tumbling mill leads to agglomeration of finely milled particles of hematite (Pourghahramani et al., 2008). Previous researcher also reported on the agglomerations for sulfide minerals and oxide minerals, respectively (Pourghahramani and Forssberg, 2007a). This behavior is common during dry grinding and is usually explained by agglomeration of the structurally modified particles following the initial reduction of particle size. This phenomenon occurs due to the tendency of the activated material to reduce its surface free energy (Pourghahramani and Forssberg, 2007a).

Figures 2.6 and 2.7 show the evolution of the size distribution of $CaCO_3$ and SEM images of $CaCO_3$ fragments at different times, respectively. Initially, the distribution presents a main peak with a mode around 32 µm, which corresponds to the aggregates, and a small peak at 0.35 µm, which corresponds to a few elementary