CRYOGENIC SIZE REDUCTION AND ENGINEERING PROPERTIES OF BLACK PEPPER

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For the award of degree of

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in

FOOD ENGINEERING

by

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CERTIFICATE

This is to certify that the thesis entitled **Cryogenic Size Reduction and Engineering Properties of Black Pepper** submitted to the **University of Mysore,** for award of the degree of **Doctor of Philosophy in Food Engineering,** by Mr. C.T.Murthy, is the result of the research work carried out by him in the Department of Food Engineering, Central Food Technological Research Institute, Mysore, India, under my guidance during 1996-2000.

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Mysore

DECLARATION

1 hereby declare that the thesis entitled **Cryogenic Size Reduction and Engineering Properties of Black Pepper** submitted to the **University of Mysore, for** award of the degree of **Doctor of Philosophy in Food Engineering,** is the result of the research work carried out by me in the Department of Food Engineering, Central Food Technological Research Institute, Mysore, India, under the guidance of Dr. Suvendu Bhattacharya, during 1996-2000. I further declare that the results have not been submitted for award of any other degree or fellowship.

C.T.Murthy

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C.T.Murthy

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a	Major axis of the seed (mm)
a_r	Sphere radius in diffusion equation (m)
A	Empirical constant in Eq. (2.13) (dimensionless)
A_c	Area of the smallest circumscribing circle (mm^2)
A_p	Largest projected area of the object in natural rest position (mm^2)
b	Medium axis of the seed (mm)
c	Minor axis of the seed (mm)
C	Celsius (degree)
C_o	Constant concentration at the surface in Eq. (3.7) (dimensionless)
$\mathrm{Cos}\phi$	Power factor (dimensionless)
d_g	Geometric average of two successive sieve openings (mm)
d_{ga}	Geometric mean particle diameter of powder (mm)
d_{go}	Optimal geometric mean particle diameter of powder (mm)
dj	Average particle diameter of black pepper berries (mm)
d_m	Arithmetic mean of two successive sieve openings (mm)
d_{sa}	Surface mean diameter of powder (mm)
D	Characteristic size of particles in Eq. (2.8) (mm)
D_I	Initial size of particles before size reduction (mm)
D_2	Final size of particles after size reduction (mm)
D_e	Effective diffusion coefficient of oil from powder to water (m^2s-l)
E_d	Deformation modulus (N mm-^{l})
E_r	Energy for failure (1)
E_G	Energy spent for grinding (kJ kg^{-1})
E_o	Work index in Bond's energy equation (kJ kg^{-1})
E_s	Theoretical energy required for size reduction (kJ kg^{-1})
F	Farenhiet (degree)
F_a	Applied force (N)
F_r	Force at failure (N)
F_o	Fourier Number (D t/r_s^2) (dimensionless)
I	Measured current during grinding (A)
l_0	No load current (A)

K	Slope in Eq. (3.10) (S^{-1})
kg	Empirical constant in Eq. (2.8) (kJ kg-^{1} when m=l)
kk	Kick's empirical constant as in Eq. 2.10 (kJ kg^{-1})
k_r	Rittinger's empirical constant as in Eq. 2.9 (kJ mm kg^{-1})
	Elongation at breaking point (m)
m	Empirical constant in Eq. (2.8) (dimensionless)
M'	As defined in Eq. (3.10) (mL/100g)
M	Moisture content of conditioned seeds (%, dry basis)
M_r	Initial essential oil content of powder (mL/100g)
Mo	Initial moisture content (%, dry basis)
M,	Final moisture content of the dried and sprayed sample (%, dry basis)
M_l	Essential oil released from the powder at time t (mL/100g)
n,	Empirical constant as in Eq. (2.13) (dimensionless)
p	Probability level (dimensionless)
P	Electric power for grinding (W)
q	Empirical constant in Eq. (2.12) (dimensionless)
r	Correlation coefficient (dimensionless)
rl	Space coordinate in Eq. (3.8) (dimensionless)
rs	Surface mean radius of powder (m)
Rt	Roundness of seed (dimensionless)
S	Sphericity of seed (dimensionless)
	Distillation time (s)
t_g	Grinding time (min)
T	Temperature of ground product (C)
T_i	Initial temperature of the feed (C)
u	Variable to simplify the diffusion equation in spherical coordinates
V	Line voltage (Y)
Yo	V olatile oil content (dry basis, mL/100g)
V_w	Volume of water (mL)
W,	Initial weight of the seeds at an initial moisture content of Mo (g)
W_{IOOO}	Weight of 1000 seeds (g)
W_2	Final weight of the seeds at a moisture content M, (g)
Wi	Weight fraction of powder retained on i^{th} sieve.(dimensionless)

K	Slope in Eq. (3.10) (S^{-1})
kg	Empirical constantin Eq. (2.8) (kJ kg^{-1} when m=l)
kk	Kick's empirical constant as in Eq. 2.10 (kJ kg^{-1})
kr	Rittinger's empirical constant as in Eq. 2.9 (kJ mm kg^{-1})
I	Elongation at breaking point (m)
m	Empirical constant in Eq. (2.8) (dimensionless)
M^1	As defined in Eq. (3.10) (mL/100g)
M	Moisture content of conditioned seeds (%, dry basis)
Mr	Initial essential oil content of powder (mL/100g)
Mo	Initial moisture content (%, dry basis)
M_1	Final moisture content of the dried and sprayed sample (%, dry basis)
M_t	Essential oil released from the powder at time t (mL/100g)
n_1	Empirical constant as in Eq. (2.13) (dimensionless)
p	Probability level (dimensionless)
P	Electric power for grinding (W)
q	Empirical constant in Eq. (2.12) (dimensionless)
r	Correlation coefficient (dimensionless)
r_1	Space coordinate in Eq. (3.8) (dimensionless)
r_s	Surface mean radius of powder (m)
R_d	Roundness of seed (dimensionless)
S	Sphericity of seed (dimensionless)
t	Distillation time (s)
t_g	Grinding time (min)
T	Temperature of ground product (C)
Ti	Initial temperature of the feed (C)
u	Variable to simplify the diffusion equation in spherical coordinates
V	Line voltage (V)
V_o	Volatile oil content (dry basis, mL/100g)
V_w	Volume of water (mL)
W_1	Initial weight of the seeds at an initial moisture content of M_o (g)
W_{1000}	Weight of 1000 seeds (g)
W_2	Final weight of the seeds at a moisture content MI (g)
W_1	Weight fraction of powder retained on ith sieve.(dimensionless)

W_s	Weight of sample (g)
x	Variable expressed in coded level (dimensionless)
X	Variable expressed in actual level (characteristic unit)
XI	Feed rate of black pepper in Section4.3.4.2 (kg hr^{-1})
X_2	Product temperature of black pepper in Section 4.3.4.2 (C)
Y	Response function in coded level (dimensionless)
Y	Response function in actual level (characteristic. unit)
Y_1	Volatile oil content of spice powder (mL/100g)
Y_2	Particle diameter of spice powder (mm)
Y_3	Energy expenditure for grinding (kJ kg^{-1})
Y_4	Monoterpenes content (%)
Y_s	Sesquiterpenes content (%)

0	Dynamic angle of repose (degree)
11	Motor efficiency (dimensionless)
ex.	Relaxation time that characterises material response (s)
s	Strain during compression (%)
't	Stress at time t in stress relaxation (N m-^{2})
Pb	Bulk density of seeds (kg m-^{3})
Sf	Failure strain (%)
	Linear limit of strain in the force-deformation curve (%)
	Initial stress during stress relaxation (N m-^{2})

ANOVA	Analysis of variance
DMRT	Duncan's multiple range test
CV	Coefficient of variation (equal to SDx100/Mean)
Db	Dry basis
LN2	Liquid nitrogen
RSM	Response Surface methodology
Rs	Rupees (Indian currency)
SD	Standard deviation

CHAPTER 1: INTRODUCTION

CHAPTER 1

INTRODUCTION

Spices are important agricultural commodities throughout the world due to their high unit price. This is particularly true for India which produces about 2.5 million tonnes (valued at 3 billion US$) of spices, processes, markets in domestic sector and exports them to various countries to earn a handsome foreign exchange. India's share in the world trade amounts to 46% of the total in quantity (about 30% in monitory terms) (Anon, 2001a). It is, therefore, necessary to give due attention to this commodity with particular reference to quality and value addition.

Spices occupied an important place in the world trade amounting to more than half million tonnes valued at US$ 2.0 billion during 1998-1999 and with a projected quantity of about 0.6 million tonnes valued at US$ 3.0 billion in 2001. Export of spices from India during 1998-1999 was around 0.2 million tonnes valued at about Rs. 1650 crores (US$ 400 million) (Peter, 1999) and was estimated to grow to about Rs. 1860 crores (US$ 430 million) during 1999-2000 (Anon, 2001a). The demand for value added products such as volatile oils and oleoresins has also increased in the international market from 1,330 tonnes in 1998-1999 to 1,575 tonnes (valued at Rs. 159 crores) in 1999-2000 (Anon, 2001 b).

Of all the spices produced in India, black pepper *(Piper nigrum* L.), also called the 'King of Spices', is one of the major spices being exported amounting to more than 35,000 tonnes during 1998-1999 valued at about Rs. 650 crores (Peter, 1999) and estimated to increase to about 42,000 tonnes valued at Rs. 865 crores during 1999-2000 (Anon, 2001a). Black pepper is a common spice produced in oriental countries (mostly in south east Asia including India, Indonesia and Malaysia) but is used worldwide for its characteristic pungent flavour and taste. *Piper nigrunz* L., from which pepper is derived, is a perennial climbing vine or shrub. Fruits, botanically called drupes but generally called berries, are dark green turning bright orange and red when ripe, and have a thin testa. On sun-drying, it turns greyish to dark brown colour, and hence popularly known as black pepper. This spice is used in foods as whole, cracked, coarse, medium or fine grinds, and also used in the form of oleoresins (total extracts), The piperine, volatile oil, starch and fibre content values show marked variations and are indicative of the quality of black pepper. The chemical composition data of black pepper are: moisture: 8.7-14.1 %, total nitrogen: 1.62.6%, nitrogen in non-volatile ether extract: *2.7-4.20/0,* volatile ether extract: 4.4- 12.0%, starch (by acid hydrolysis): 28.0-49.0%, crude fibre: 8.7-18.0%, crude piperine: 2.8-9.0%, piperine: 1.7-7.4%, total ash: 3.6-5.7%, and acid insoluble ash: 0.03-0.55% (Gopalan *et at.,* 1993; Pino *et al.,* 1990; Govindarajan, 1977; Pruthi, 1974).

The characteristic aromatic odour of pepper is 'due to the presence of volatile oils in the cells of the pericarp. On steam distillation, crushed black pepper yields 1.0-2.6% (up to a maximum of 4.8%) of the volatile oil. The volatile oils are classified into categories like monoterpenes and sesqueterpenes. The monoterpenes are the lower molecular weight compounds; while sesquiterpenes possess higher molecular weights.

Many spices including black pepper are ground to coarse or fine particles to provide convenience to the human consumption. Further, the unit operation of grinding adds to the cost and hence becomes a process of value addition. The immediate question that arises is the quality of the ground material; a processor always tries to maintain the same quality in the finished product compared to the original sample (whole seed). It is obvious that some portion of input mechanical energy is transformed into thermal energy during grinding. The extent of transformation of mechanical energy depends on several factors including raw material attributes, type and design of grinding system, and grinding characteristics of the material. Thus, there is a need to know how these factors affect the quality and characteristics of the finished product. The other question that arises at this point is that the extent of deterioration of quality. If so, to what extent and how they are related with those above mentioned factors because quality directly affects the price. In the present era of competitive world trade, it is very important that the 'quality of the product should be of international standards. The last question that arises here is how to maintain or improve the quality of the product. Not much work has been carried out to find the answers for these questions. There have been few research reports to show that loss in quality taken place during grinding. But detailed scientific data are still lacking to solve these problems.

The term 'grinding' has become generic in common usage (Perry, 1950). In the present study, the terms' grinding' and 'size reduction' are used as synonyms though the former has been used here because of its common usage. Grinding is a very important step in the post harvest processing of spices requiring special attention in order not to lose the aroma and flavour compounds present in them (Gopalkrishnan *et al.* 1991). Spices are ground at one stage or the other before consumption though whole spices are also used in culinary practices to a certain extent. Generally, spices are ground either for direct use or making value-added products, such as, ground spices, mixes, oleoresins, and spice oil extracts which have vast industrial applications. Spice volatile oils are used in food, cosmetics, perfumery and personal hygiene products like tooth paste, mouth paste and aerosols besides a variety of pharmaceutical formulations (Anon, 2001a). Volatile oils of black pepper are extensively used in colognes where it adds tenacity. Aroma, therapists describe it as useful in massage to alleviate muscular tension (Sharp, 1991). Its antibacterial and antifungal activities has also enhanced its applications in pharmaceuticals (McAlpine, 1991). Therefore, the demand for these value-added products has been increasing in the world trade (Peter, 1999; Pruthi, 1991).

The aim of spice grinding is to obtain smaller particle size with good product quality in terms of flavour and colour (Singh and Goswami, 1999a). Food processing industry is frequently using the grinding or size reduction equipment which are generally meant for chemical processing industries. These mills are not designed to grind the heat sensitive commodities like spices. In such grinding process, heat is generated when energy is used to fracture a particle into smaller sizes and this heat is detrimental to the product and results in significant losses of volatile oils of spices. During grinding, the temperature of the product rises 42-95 C (Pruthi and Misra, 1963), depending on the type of mill and spice, and on oil and moisture content of spices. Naturally, exposure to such a high temperature leads to considerable loss of aroma, and flavour, which should be reduced as spices with low flavour and aroma would fetch poor returns to the processors.

Therefore, it may be desirable to practice grinding at a low temperature. Chilling and freezing are the possible ways to achieve a product with higher content of volatile oil components. Low temperature could also be obtained by different methods, viz., circulation of chilled water or a refrigerant externally to cool the grinding equipment, mixing of dry ice (solid CO_2) with whole spice and then grinding. But these methods are not viable for industrial scale operations due to inefficient heat transfer rates (Singh and Goswami, 1999a).

However, cryogenic technology is known to be an efficient method of cooling of several food products. In this technique, the liquid nitrogen at -195.6 C provides the refrigeration needed to pre-cool the spices and maintain the desired low temperature by absorbing the heat generated during the grinding operation. In addition to maintaining the low temperature, vapourisation of liquid nitrogen to the gaseous state, in effect, creates an inert and dry environment for additional protection of spice quality. Pre-cooling of raw spice and the continuous low temperature maintained within the mill reduces the loss of volatile oils and moisture thereby retaining most of the flavour strength per unit mass of spice to yield a product of good quality.

A limited number of research findings on cryogenic grinding of spices have been reported. Some work has been carried out on conditioning of spices using liquid nitrogen before grinding to reduce the loss of volatile oils of spice (Anon, 1962). Wistreich and Schafer (1962) worked on the cryogenic grinding of spices viz., black and white pepper, ginger, coriander, caraway and celery using liquid nitrogen and achieved an increase of (about 30%) in the content of volatile oil. Strause (1967) while working on cryogenic grinding of nutmeg and white pepper, has obtained samples with reduced microbial load as well as increased content of volatile oil. Pesek *et al.* (1985) and Pesek and Wilson (1986) have worked on spices viz., white pepper, nutmeg, cinnamom, cumin and orenago. Their results supported the hypothesis that (1) the light and highly volatile components were more readily retained through cryogenic grinding than the ambient grinding process and (2) the high molecular weight components were retained equally well for the two grinding techniques employed. Gopalkrishnan *et al.* (1991) have observed that cryogenic grinding using liquid nitrogen and dry ice provided a superior quality product in terms of volatile oil contents in cardamom. Mckee *et al.* (1993) have worked on three different grinding methods viz., ambient, chilled and liquid nitrogen during grinding of nutmeg, and have observed non-significant differences between the methods in terms of volatile oil content. Recently, Singh and Goswami (1999b) have' worked on cryogenic grinding (-160 to -70 C) of cumin seeds and have observed that the content of volatile oil was significantly higheras compared to ambient (40 to 85 C) grinding. Similar results were also observed during cryogenic grinding of cloves (Singh and Goswami, 2000).

The reported results on cryogenic grinding gave the following advantages over ambient grinding: (1) cryogenic grinding reduced the loss of volatile and increased the flavour strength, (2) extremely fine grinding of spice was possible as it became brittle due to very low and (3) cryogenic grinding reduced the oxidation of spice volatile oils as evaporating LN_z tended to expel air from the grinding mill. However, the above results were obtained at laboratory scale grinding studies (200-500 g batch size) and their findings were more general to all the spices.

The objective of the present research is thus to examine the advantages of cryogenic grinding of black pepper in particular, and comprises of following main areas:

a) Determination of engineering properties of black pepper seeds

b) Studies on the ambient grinding characteristics of black pepper

c) Studies on the cryogenic size reduction (or grinding) of black pepper at both laboratory and pilot scales, and comparing it with ambient grinding technique with particular reference to quality of product and grinding characteristics.

CHAPTER 2: REVIEW OF LITERATURE

CHAPTER 2

REVIEW OF LITERATURE

This chapter on Review of Literature provides an exhaustive analysis of details on researches conducted on cryogenic grinding of spices. In doing so, introductory subchapters on spices, engineering properties of foods, grinding of spices, grinding and energy laws, cryogens, cryogenic freezing and use of cryogenics in food processing have been included in order to make this chapter more meaningful.

2.1 Spices

Spices constitute an important group of agricultural commodities which are virtually indispensable in the culinary art. The term 'spices' applies to such natural plant or vegetable products or mixtures thereof, in whole or ground form, as are used for imparting flavour, aroma and piquancy to and for seasoning of foods (Pruthi, 1974).

There are about 80 spices grown in different parts of the world. Many of these spices are grown in India. Spices may comprise different plant components or parts such as floral parts (clove, saffron, etc.) or fruits (cardamom, chillies, etc), or berries (allspice, black pepper, juniper), or seeds (aniseed, caraway, celery, coriander), or rhizomes (ginger, turmeric), or roots (angelica, horse raddish and lovage), or leaves (bay leaves, mints, marjoram and tejpat), or kernel (nutmeg), or aril (mace), or bark (cinnamom and cassia), or bulbs (garlic, onion, etc.), or other parts of spice plants.

Spices are well-known as appetisers and are considered volatile in the culinary art all over the world. They add a tang and flavour to otherwise insipid or bland foods. Some of them also possess antioxidant properties, while others are used as preservatives in some foods like pickles and *chutneys.* Some spices also possess strong anti-microbial activities. Many of them possess medicinal properties and have a profound effect on human health. For instance, spices intensify salivary now and the secretion of amylase, neuraminic acid and hexosamines. They flavour the cleansing of oral cavity from food adhesion and bacteria; they may help to check infection and caries, and to protect the mucous membrane against thermic, mechanical and chemical irritations. Spices increase the secretion of saliva rich in ptyalin which facilitates digestion of starch in the stomach, rendering the meals which are rich in carbohydrates, easily digestible.

In India, the major spices are black pepper, ginger, cardamom, turmeric and chillies. Pepper is the most important spice of India and, is termed as 'King of Spices', and is also known as 'Black Gold of India' followed by cardamom, which is called the 'Queen of Spices'.

The present thesis is on Indian spices particularly, black pepper. Hence, the subsequent section will deal with that spice.

2.1.1 Black Pepper

The botanical name for black pepper, green pepper and white pepper is *Piper nigrum Linn.* They belong to family of Piperaceae.

Black pepper constitutes an important component of culinary seasonings throughout the world and is an volatile ingredient of numerous commercial foodstuffs. It is an important constituent of whole pickling spice and many ground spice formulae of seasonings; examples include poultry dressings, sausages, soups, hamburger and frankfurter seasonings.

Black pepper is the dried mature but unripe berries (fruit) of *Piper nigrum,* a branching vine or climbing perennial shrub mostly found in hot and moist parts of Southern India, notably Kerala (contributing about 96% of India's, production), Karnataka, Tamil Nadu and Pondicherry. It is one of the most ancient crops cultivated in India and has probably originated from the hills of South-Western India where it is grown in the wild state in the rain forests from North Kanara (a district in Karnataka, India) to Kanyakumari. It is also cultivated in Indonesia, Malaysia, Sri Lanka, Brazil, Thailand and other tropical countries (Pruthi, 1974).

There are many varieties of black pepper known in the world trade. They take their names from the localities where they are grown or from the ports through which they are exported e.g., Tellicherry, Malabar, Alleppey, Lampong, Saigon, Penang and Singapore. These varieties of black peppers differ marginally in their physical and chemical characteristics, colour, size, shape, flavour and bite. Peppers from Tellicherry and Alleppey are large, attractive, dark-reddish-brown to black and highly aromatic. The Malabar variety of pepper alone accounts for nearly 90% of the total export from India. Lampong and Singapore pepper are smaller, more shrivelled but almost equally pungent There are nearly 24 varieties of black pepper grown in India and their identification is rather difficult, since some of them go by different names in different regions.

The spikes/fruits are ready for harvest when they are fully mature and start yellowing or become yellowish. At this stage, the whole spikes are removed from the vines with the aid of ladders. The spikes are kept for a day or so, thereafter the berries are removed by rubbing or scrubbing, and dried in the sun, or the spikes are directly dried in the sun for a few days on mats or on clean concrete floors. They are turned over and later, berries are removed by rubbing, threshing or trampling. When completely dry, the outer skin of the berries becomes dark brown to black and get shrivelled. Generally, 100 kg of fresh berries yield about 26-39 kg of black pepper of commerce. Of course, the yield of pepper varies widely in different producing areas depending on several factors such as elevation, temperature, distribution of rainfall, soil fertility, cultural practices, types or variety of pepper and age of the pepper vine, etc. In India, the yield varies from 110 kg to 335 kg per hectare (Pruthi, 1974).

1.

In addition to black pepper, the pepper is also available in the following processed forms such as white pepper and processed green pepper which is described in the subsequent sections.

2.1.2 White Pepper

White pepper and black pepper are prepared from the berries (fruits) of the same plant or spices *(P. nigrum).* The only difference is that for preparing black pepper, spikes are harvested when berries are fully mature, but unripe, i.e., when green or greenish yellow, but for preparing white pepper, the harvesting of berries is delayed until they become ripe i.e., yellowish red or red in colour. White pepper is prepared by removing the outer pericap (skin) of the harvested berries, either before or after drying.

2.1.3 Processed Tender Green Pepper

Tender green pepper spikes are harvested when they are semi-mature and these are sold in market for use in pickles. Besides, canned of tender green berries in 2% brine in different sizes of cans are also made available. The optimum stage of maturity for harvesting, for canning and processing purposes have been determined to find ways to prevent the triple problems of cloudiness in brine, rupturing of berries and sedimentation (Pruthi, 1974).

2.1.4 Constituents of Black Pepper

Analysis of 23 types of black pepper from Kerala, South and North Kanara regions, Coorg and Assam gave the average ranges of'values as follows: moisture: 8.714.1 %; total nitrogen: 1.6-2.6%; ether extractives: 4.4-12.0%; starch (by acid hydrolysis): 28.0-49.0%; crude fibre: 8.7-18.0%; crude piperine: 2.8-9.0%; piperine: 1.7-7.4%; total ash: 3.6-5.7% and acid in soluble ash (sand): 0.03-0.55% (Pruthi, 1974). The wide variation in moisture content is due to maturity level, time of harvest and variety. The high content of fibre gives the spice the rigidity and structural integrity.

2.1.5 Volatile oil of Black Pepper

The characteristic aromatic odour of pepper is due to the presence of a volatile oil in the cells of the pericarp. On steam distillation, crushed black pepper yields 1.0-2.6% (up to a maximum of 4.8%) of volatile oil. The yield depends mainly on the age of the dried fruits. Oil of pepper is an almost colourless to slightly greenish liquid with a characteristic odour of pepper and also of phellandrene. The oil has a mild but not pungent taste, and has the following range of values viz., specific gravity at 15 C: 0.873 _ 0.916; optical rotation: _10° to +3°; refractive index: 1.480 - 1.499. Pino *et al. (1990)*

have identified and reported as many as 46 compounds present in volatile oil of black pepper (Table 2.1).

Table 2.1

Constituent compounds of black pepper volatile oil

(Pino *et al., 1990)*

Compound	% oil*	Compound	% oil*	Compounds present in trace quantities
limonene	19.0	(E)sabinene hydrate	0.4	β-elemene
sabinene	19.0	camphor	0.1	δ-elemene
car-3-ene	16.0	terpinen-4-ol	0.8	α-guaIene
β-pinene	12.0	α-terpineol	0.2	α-cubebene
β-caryophyllene	10.0	α-copaene	0.2	α-curcumene
α-pmene	8.2	1,8-cineol	0.1	δ-guaiene
nerolidol	2.5	(Z)-:sabinene hydrate	0.7	nerol
myrcene	1.2	linlool	0.8	eugenol
α-phellendrene	1.3	α-humulene	0.3	cadinene
α-thujene	0.8	α-selienene	0.6	β-selinene
caryophyllene Ox.ide	0.7	β-bisabolene	0.6	(E)(E)-β- farnesene
camphene	0.1	(E) -β-ocimene	0.1	(Z)(E)-farnesol
α-terpenene	0.1	γ-terpene	0.2	
p-cymene	0.3	terpinolene	0.2	
(Z)-β-ocimene	0.1	β-eudesmol	0.6	
clemol	0.9	humtilene oxide	0.1	
δ-cadanol	0.5	guailol	0.2	

* Values are out of total volatile oil basis

The volatile oils are categorised into monoterpenes and sesqueterpenes. The monoterpenes are the lower molecular weight compounds, while sesquiterpenes are higher molecular weight compounds. The characteristics (chemical formula, molecular weight and boiling point) of the ten major compounds are shown in Table 2.2.

Table 2.2

Characteristics of compounds of black pepper volatile oil (Burdock, 1995; Buckingham, 1995)

Compounds of V Volatile oil	Chemical formula	Molecular weight	Boiling Point (C)
(A) Monoterpenes			
1 α-thujene	$C_{10}H_{16}$	136.23	163-165
2 α-pinene	$C_{10}H_{16}C$	136.23	156
3 β-pinene	lOH 16	136.23	162-166
4 1,8-cineole	$C_{10}Hl_{80}C$	154.24	176-177
5 limonene	$C_{10}H_{16}$	136.23	176-178
6 myrcene	$C_{10}H_{16}$	136.23	65-66
(B) Sesqueterpenes			
1 α-copaene	$C_{15}H_{24}$	204.34	246- 251
2 β-caryophyllene	$C_{15}H_{24}$	204.34	254- 257
3 β-bisabolene	$C_{15}H_{24}$	204.34	-
4 caryophyllene oxide	$C_{15}H_{26}O$	222.00	-

- Data not available

2.2 Engineering Properties of Food

Engineering properties of foods are important for scale-up, product/process design and optimization, and for storage of foods. Though engineering properties can vary widely, they may be roughly categorised as physical properties related to size, shape etc., mechanical properties, thermal properties, rheological properties and aerodynamic properties. The subsequent sections will discuss these properties related to grinding of species

2.2.1 Physical Properties of Food

The physical properties of food may be defined as those properties that lend themselves to description and quantification by physical rather than chemical means. Their importance stretches from product handling to processing to consumer acceptance (Szczesniak, 1983). The parameters which are important in handling are shape, size; roundness, sphericity, volume, density, surface area, etc. Further, storage of grains and seeds in bins and silos, mechanical harvesting, and transport of fruits and vegetables over long distances require that the products withstand static and dynamic loading, the latter being impact type loading. Thus, the engineering parameters having a bearing on the behaviour of foods on handling must encompass the stress-strain-time relationship. Friction, as in silos, both against the surface of the grain and against the surface of the construction material is another physical system of importance.

2.2.1.1 Size **and** Shape

The size and shape of an agriculture commodity, or of a processed product, not only affect the degree of consumer acceptance but in many cases influence packaging, distribution of stresses when forces are applied, and processability. As pointed out by Medalia (1980) "to define the shape of a body fully, one must specify the location of all points on the external surface." This is not only a time consuming process but also poses mathematical difficulties for more irregular shaped commodities. Therefore, qualitative shape description is the most popular with food graders. The shapes of fruits and vegetables have been classified into 13 categories such as round, oblate, oblong, conic, elliptical, truncated, ribbed, etc. (Mohsenin, 1980). Figure 2.1 shows the charted standard for describing the shape of apple fruit.

The most prevailing method for quantitative shape description involves calculations of similarity to a sphere:

$$\text{Sphericity } (S) = (a\ b\ c)^{1/3} \times \text{I00}/a \qquad (2.1)$$

where 'a' is the major axis of the product, 'b' is the medium axis of the product and 'c' is the minor axis of the product. Published values for the sphericity of fruits are of the order 89-97. These values are expressed as the percentage; the higher the number, the greater the similarity to a sphere. Oblong-shaped products, such as rice, would exhibit a low value of sphericity (Mohsenin, 1986).

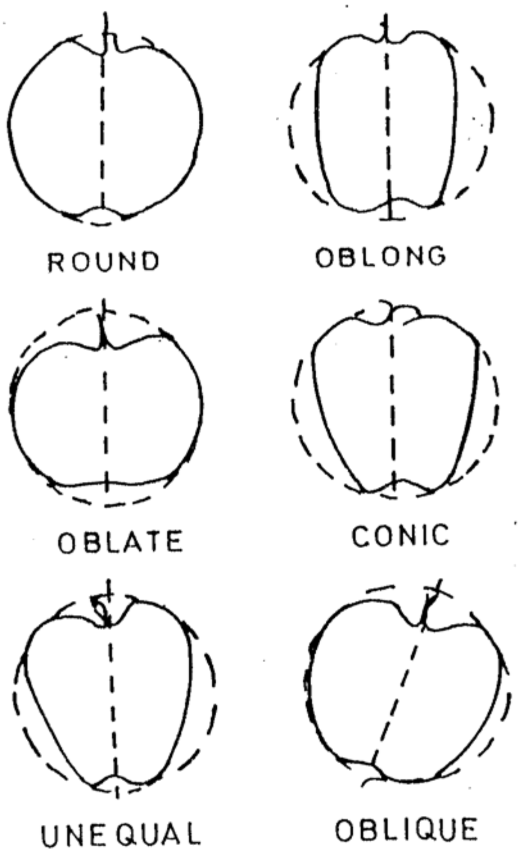


Fig. 2.1 Some standard shapes for describing the shape of an apple.

Other ways of describing the shape of an object involve estimations of roundness, i.e., sharpness of the corners, measurement of axial dimensions, resemblance to geometric bodies (Mohsenin 1986), an'd angle of curvature (as in pickles).

$$\text{Roundness } (R_d) = A_p / A_c \qquad (2.2)$$

where Ap is the largest projected area of the object in natural rest position and Ac is the smallest circumscribing circle. A value of roundness (R_d) equal to unity is a perfect sphere, and increase in the value indicates more sharpness in the product.

Size is usually characterized in practice by determining the opening, as in a sieve or screen, through which the product will or will not pass. This method is used with both whole and ground materials. Although simple and widely used for grading agricultural commodities (e.g., peas, cherries, potatoes), the method had considerable disadvantages, the main one being the fact that sieving separates the product according to the narrowest dimension. It is most appropriate for products that are approximately spherical in shape. For oblong materials, such as rice, slit screens are used (Szczesniak, 1983).

Other practical methods of determining the, sizes of fruits and vegetables are diameter or length measurements, and counts per weight or volume. With fruits, the larger size is most desirable for the trade market. The other way of expression is weight per 100 or 1000 seed.

Only recently that serious attention has begun to be paid for originating more appropriate methods for characterising the three-dimensional shapes and sizes of food powders. This has come with the realisation that these physical properties affect aerodynamic and hydrodynamic characteristics, mixing, segregation, and other types of behaviour that often lead to processing problems, as well as detract from quality in the hands of the consumer.

2.2.1.2 Volume and Density

Measurements of volume and density of liquid foods are relatively easier methods, other than proper control of moisture content and temperature at which the measurements are made. Standard volumetric methods for volume quantification and pycnometer or commercial density meters for density are simple and straight forward techniques. But, measurements are more complicated for solid foods, especially those of porous nature. Volume of agricultural products, especially those exhibiting an irregular shape, is usually determined by liquid (water or kerosene) displacement method. The product is weighed in air and in water (using any analytical balance, or a special gravity balance) and the volume is calculated:

$$\text{Volume} = (\text{Weight in air} - \text{Weight in water})/\text{Weight density of water} \qquad (2.3)$$

Density of solids can be calculated as the ratio of weight and volume, or can be determined by floatation in liquid of a different density. The density of liquid in which the product would neither sink nor float is equivalent to the density of the product. Separation by density in floatation is also used with many agricultural commodities to remove defective materials and extraneous matter.

Food powders pose problems in volume and density measurements because of their packing characteristics. Generally, two types measurements are useful: free flow density and tapped density, the difference being in the manner of filling the volumetric container. Tapped density gives a higher number than free flow density because of partial displacement of air from between the particles. Free flow and tapped density relate to the container fill and settling during shipment and handling.

2.2.1.3 Surface Area

Surface area has a bearing on heat transfer in heating and cooling, during storage and handling processes. A number of methods have been developed for calculating the surface area of products such as fruits and eggs based on shape factor measurement (e.g., area of transverse cross sections, transverse diameters, areas of actual or longitudinal cross sections). Many empirical equations have been developed relating weight or volume to surface area. These resulted in reasonable values of the correlation coefficient and can be used to estimate the surface area by knowing weight of the fruit or egg. Typical values for the surface of fruits are apples, 17.2-25.2 sq.in., plums, 5.4 -7.0 sq.in, pears, 22.2-23.0 sq in. (Mohsenin, 1980).

2.2.1.4 Colour

Colour is one of the most important quality attributes because it directly affects appearance and subsequently the consumer acceptance. It can signal a high quality product (such as the golden yellow of a table orange) or can alert the consumer to a potential physiological danger (such as green processed meat). Furthermore, it is well recognised that colour has important psychological implications that can influence the mood and emotional state of the human being. Techniques for measuring the colour of food are quite advanced. It is known that human vision responds to a tri-stimulus in the sensory perception of colour. The eye possesses three types of light-sensing devices each corresponding to different bands of wave lengths. It is generally accepted that these are red, green and blue. Spectrophotometric methods for colour description are also based on three dimensions: reflectance (lightness or value), dominant wavelength (hue), and purity (chroma or intensity). The popular instruments viz., Hunter, Gardner or Macbeth makes use the opponent colour scales (L a b type). The L dimension defines the lightness; the a dimension reference to red-green hues; and the b dimension refers to blue-yellow hues (as shown in Fig. 2.2) (Szczesniak, 1983). Advanced colour measuring system such as cm methods can express colour completely and are now used widely.

2.2.2 Mechanical Properties of Food

Mechanical properties of food have received the greatest attention lately. The reason for this activity is the fact that, in addition to affecting the mechanical behaviour of the product during transport, handling and processing, the mechanical properties form the basis for the sensory property or texture. During mastication and industrial size reduction processes (e.g., slicing, grinding, pureeing) it is desirable to have a 'weak' product - one that will disintegrate in the proper manner when forces are applied. On the other hand,

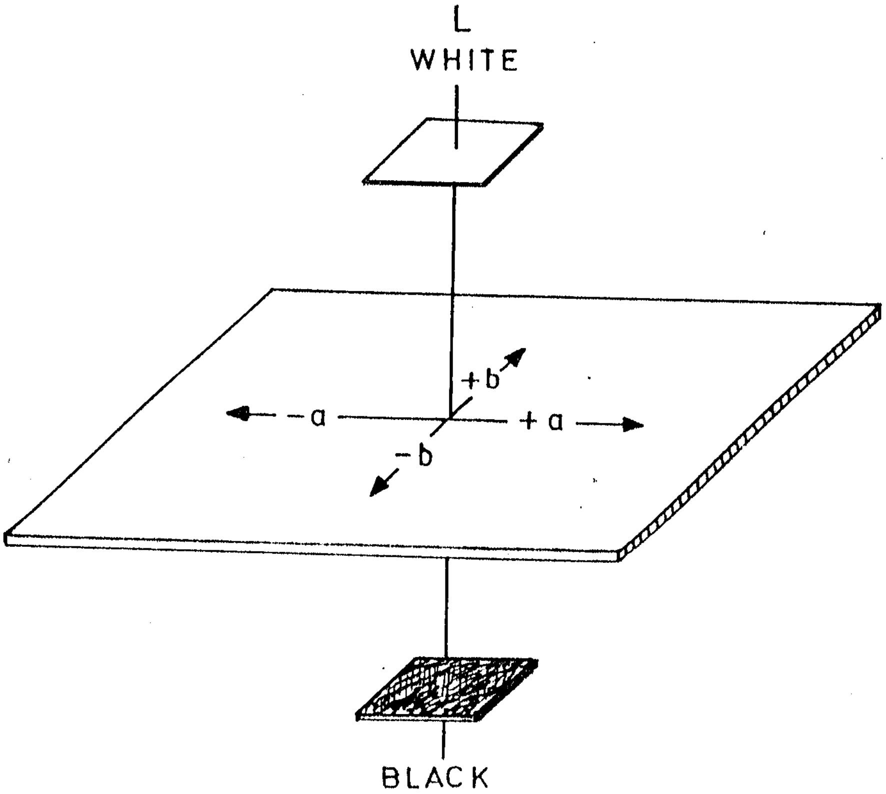


Fig. 2.2 **Hunter (L** a b) **colour description and quantification.**

during transport and industrial handling, it is desirable to have a 'strong' product _ one which will not suffer any substantial damage when impact or static compressive forces are applied (Szczesniak, 1983).

Mohsenin *(1980)* has defined the mechanical properties "as those having to do with the behaviour of the material under applied forces." Rheology has been defined as "a science devoted to the study of deformation and flow," and more recently as "the study of those properties of materials that govern the relationship between stress and strain" (Dealy, 1982). Stress is defined as the intensity of force components acting on a body and is expressed in units of force per unit area. Strain is the change in size or shape of a body in response to the applied force. Strain is a non-dimensional parameter (reported as a ratio or percentage) and is expressed as change in relation to the original size or shape.

The ratio of stress to strain is called the 'modulus' - compression modulus, tensile modulus$_1$ or shear modulus. When an elastic material is compressed, the stress-strain plot is a straight line starting at the origin and its slope is called "Young's modulus of elasticity." Many foods exhibit this behaviour under small compressions before the socalled 'limit of elasticity' is reached. The maximum stress that the material is capable of sustaining before rupture is called "strength" - compressive strength, tensile strength, or shear strength.

Szczesniak (1983) has defined mechanical characteristic (in relation to sensory attributes) of food:

(a) Hardness -the force necessary to attain a given deformation

(b) Cohesiveness - the strength of the internal bonds making up the body of the product (c) Viscosity - the rate of flow per unit force

(d) Springiness - the rate at which a deformed material goes back to its undeformed condition after the deforming force is removed

(e) Adhesiveness - the work necessary to overcome the attractive forces between the surface of the food and the surface of other materials with which the food comes in contact (e.g., tongue, teeth, finger, palate, etc.)

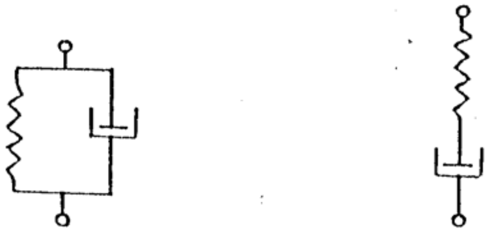
(f) Fracturability - the force with which the material fractures. It is related to the primary parameters of hardness and cohesiveness. In fracturable materials, cohesiveness is low and hardness can vary from low to high levels

(g) Chewiness - the energy required to masticate a solid food product to a state ready for swallowing. It may be related to the primary parameters of hardness, cohesiveness and springiness

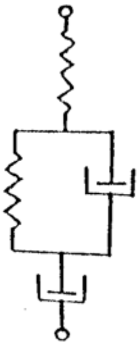
(h) Gumminess - the energy required to disintegrate a semi-solid food product to a state ready for swallowing. It is related to the primary parameters of hardness and cohesiveness. With semi-solid food products, hardness is low.

2.2.2.1 Rheological Properties

Rheologically, a material may deform in three ways: elastic, plastic, or VISCOUS. In an ideal elastic body, deformation (or strain) occurs instantly the moment stress is applied, is directly proportional to stress, and disappears instantly and completely when the stress is removed. In an ideal plastic body, deformation does not begin until a certain value of stress (called the yield stress) is reached. Deformation is permanent and no recovery occurs when the stress is removed. In an ideal viscous body, deformation occurs instantly, the moment stress is applied, but - in contrast with an elastic body - it is proportional to the rate of strain and is not recovered when the stress is removed. These three types of behaviour are denoted by a spring, a friction element, and a dash pot, respectively. They can be arranged in series or in parallel and in any number to depict the fact that a real material usually exhibits a combination of rheological behaviour types. Figure 2.3 shows some typical rheological models. Food products usually behave as a combination of elastic and viscous elements; such materials are called viscoelastic and their stress-strain relationship depends on the rate of strain that introduces the time dependency. When the stress-strain ratio is a function of time alone, the material is said to be linearly viscoelastic. When the stress-strain ratio is a function of stress, the material is said to be non-linearly viscoelastic (Szczesniak, 1983).



Kelvin-Voigt model Maxwell model



Burger model

Fig. 2.3 Commonly used rheological models based on springs and dashpots.

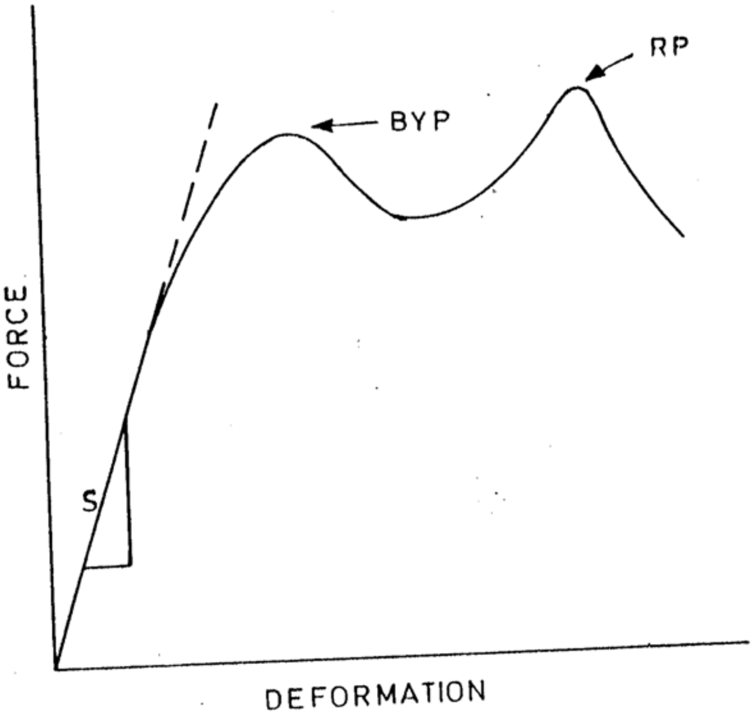
2.2.2.2 Behaviour of Solids

The behaviour of foods in compression is one of the easiest and most important mechanical tests to perform. Universal testing machine such as Instron, provides means of applying, detecting, and recording the forces of sample resistance. A typical compression force-deformation curve for a foodstuff is shown in "Fig. 2.4. As indicated, a number of mechanical parameters can be quantified from such a curve. The slope of the initial straight line portion is taken as the elastic modulus and is often considered to be a measure of firmness. The Fig. 2.4 also shows two yield points. The first point of inflection indicates a bio-yield-failure of some structural elements in the tested biological material. The final yield point is the rupture yield - massive failure of the specimen. It is equivalent to the compressive strength. Compression testing of foods is usually done at deformation rates of 20-500 mm min-^{1} whereas impact testing involves very high deformation rates of the order of 90 m min-^{1} and upward (Szczesniak, 1983).

Tensile measurements, in general, are difficult to perform on foods because of their geometry and gripping problems with materials whose geometry lends itself to this type of a test. Tensile parameters are important in mastication since the wedging action of teeth imposes tensile stresses (Voisey and deMan, 1976). However, the commonly used measurement technique for foods involves compression than tension.

2.2.2.3 Stress Relaxation

When a constant strain is applied to a body, the decrease in stress as a function of time is called stress relaxation. It is called by the inner flow of the material, which is governed by its viscosity. The ratio of viscosity to the shear modulus is called the relaxation time. A typical stress relaxation curve for an agricultural product is shown in Fig. 2.5. It illustrates that the rate of relaxation and residual stress at any given time depend on the initial force and deformation applied and the rate at which the test material is initially deformed. The greater the extent of initial deformation and of applied force, the higher the residual stress, and faster the relaxation rate. The slower the rate of initial deformation, the slower the material appears to relax.



S : modulus of elasticity; BYP : bioyield point; RP: rupture point

Fig. 2.4 Force-<leformation curve during compression of food.

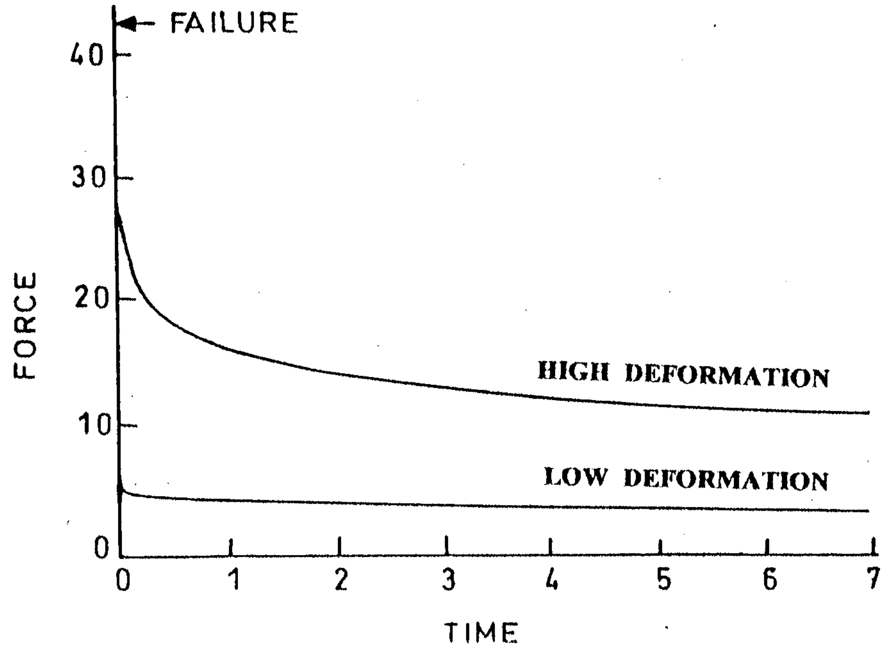


Fig. 2.5 **Stress relaxation curves at different extent of initial compression.**

A convenient way of expressing stress relaxation is to measure the time required for the force to relax to a given percentage (e.g., 60%) of its initial value. The equation for a viscoelastic body is given by

$$'t(t) = 't_o \,.\, \exp(-t/\acute{a}) \qquad (2.4)$$

where 't(t) is the stress at time t, 'to is initial stress and a is the relaxation time that characterises the material response. This quantity is determined by plotting log $t(t)/t_o$ versus time. t_o is the initial stress. The slope of the linear portion of the curve is $(-1/\alpha)$.

The stress relaxation test is a very useful supplement to the compression test (Peleg, 1977; Peleg and Calzada, 1976). The shape of the curve can be related to the elements in the rheological model. The test can also yield information about the structural changes that might have occurred on previous deformation and about the material's rheological memory and the past history.

2.2.2.4 Creep

When constant stress is applied to a body, the increase in strain as a function of time is called creep. The ratio of strain at any time t to the constant stress is called creep compliance. Creep testing instrument requires a special capability with the Instron to keep the stress constant and record the change in deformation (creep) as a function of time (Szczesniak, 1983). At present, sophisticated rheometers usually have the facility to conduct creep testing.

2.2.2.5 Bulk Properties

The bulk properties of fine powders are always interdependent, and are determined by both the physical and chemical properties of the material (e.g., composition, moisture content), the geometry, size· and surface characteristics of the individual particles, and history of the system as a whole (Peleg, 1983).,The shape of the container can affect flowability, and the powder density usually increases as a result of vibration for example. Numerical values assigned to such properties, therefore, ought to be regarded as useful only under the as said conditions or as indicators of an order of magnitude only.

2.2.2.5.1 Bulk Density and Porosity

Bulk (or apparent) density is the mass of particles that occupies a unit volume of the bed. It is usually determined by weighing a container of a known volume and dividing the net weight of the powder by the container's volume. Porosity is the fraction of volume not occupied by a particle or solid material and therefore, it can be expressed (Peleg, 1983) as either

$$\text{Total porosity} = 1 - (\text{Bulk density}/\text{Solid density}) \qquad (2.5)$$

or

$$\text{Inter particle porosity} = 1 - (\text{Bulk density}/\text{Particle density}) \qquad (2.6)$$

As powders are compressible, their bulk density is usually given with an additional specifier: loose bulk density (as poured), tapped bulk density (after vibration), or compact density (after compression).

2.2.2.5.2 Angle of Repose

The angle of repose (Fig.2.6) is an indispensable parameter in the design of processing, storage and conveying systems. Its magnitude, however, depends on the way in which the sample or powder heap is formed (e.g., the impact velocity), and therefore published values are not always comparable (Brown and Richards, 1970). In cohesive powders, the measurement of the angle itself is sometimes difficult because of the irregular shapes that the heaps can assume. The angle of repose is sometimes confused with the angle of internal friction. Although its magnitude is certainly influenced by frictional forces (especially in free-flowing powders) it is also affected by inter particles attractive forces - a factor that becomes dominant in wet and cohesive powders.

According to Carr (1976), angles of up to about 35 degree indicate free flowability, 35-45 degree some cohesiveness, 45-55 degree cohesiveness (loss of free

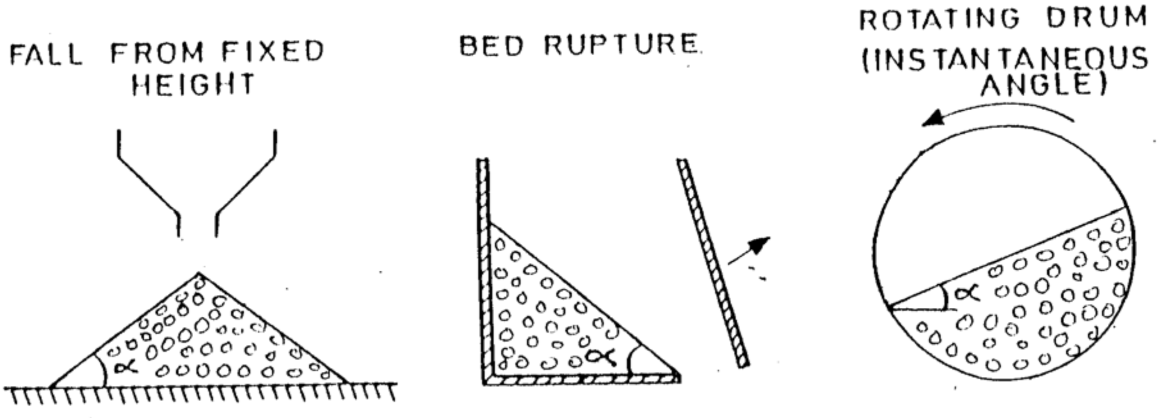


Fig.2.6 Measurement of angle of repose by different methods.

flowability), and 55 degree and above indicates very high cohesiveness with limited flowability.

2.3 Theory of Size Reduction

The present thesis deals with studies on the cryogenic grinding of spice, and hence, it is desirable to discuss different aspects of grinding. According to Cleef (1991), in the early 1980s, more than a billion tonnes of solid materials were mechanically reduced in sizes - crushed and ground - annually in the United States, as the demand for powders was growing both in quantity and sophistication.

The comminution or size reduction (Prasher, 1987) deals with solids in which complex cohesive bonds exist between atom and atom, and between molecule and molecule, which are arranged in ordered arrays, unlike in gases, for which the atoms and molecules are disordered. Not only are there cohesive bonds, but there are also repulsive forces or a solid would tend to shrink and so increase in density at constant temperature, which is not true. There exist both attractive and repulsive forces between the atoms or molecules which get neutralised, resulting in a state ,of equilibrium. This equilibrium is not static but dynamic, and the inter-atomic distance fluctuates because of the thermal motions of the atoms; but it has a mean value which increases with temperature. Rupture is possible because the net force of attraction between two atoms becomes very small at a distance as little as 10% greater than the mean atomic distance at room temperature.

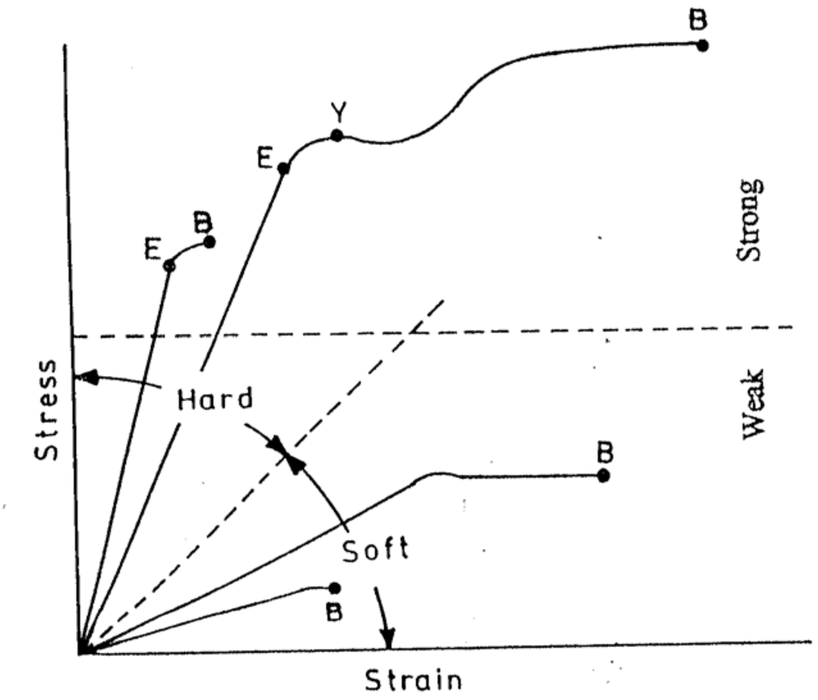
Rupture takes place usally by tensile stress. Compressive stress just pushes atomic nuclei closer together. When compressive forces applied to a particle produce rupture, they generate tensile stresses within the particle. When shear accompanies compression, there is a tendency for layers of atoms to slide over each other, and with sufficient shear, particle rupture can occur. Fracture can be produced by thermal means alone because increase in temperature implies an increase in mean atomic distance as well as increased amplitude of vibrations. These manifest themselves in thermal expansion, and differential thermal expansion leads to rupture. Similarly, rupture c~n be aided by chemical means because stressed bonds between atoms and molecules are more prone to chemical attack than are unstressed bond (Prasher, 1987).

The theory of cracking in brittle materials, developed by Griffith (1920) focuses on how a chunk of material spends its energy budget. He noted that real solids are weaker than they might seem, because they contain microscopic flaws. A crack (or any flaw) in a brittle material reduces its tensile strength and leads to instability. If the material is subjected to sufficient stress, the built-up strain energy is expended rapidly in the creation of multiple failures. Once the crack starts, if the strain in not rapidly relieved, the system becomes unstable and crack propagation accelerates to high velocities, reaching 40% of the speed of sound in the solid. During this rapid progress, the strain energy relaxed will exceed the energy associated with new surface produced, and the surplus energy can concentrate on other cracks in the material and propagate these also. Hence, once a crack begins to spread, multiple fracture can occur.

Figure 2.7, shows the stress-strain diagram for various types of solids (Loncin and Merson, 1979). When the applied stress remains below a limiting value, the deformation which the material experiences is elastic, i.e., the material returns to its original shape when the force is removed. If the stress exceeds the elastic limit, the material undergoes permanent (inelastic) deformation until it reaches the yield point and it begins to flow (region of ductility) under the action of the applied stress until it finally breaks. This process defines the elastic stress limit, yield stress, the breaking stress, and the region of ductility.

The breaking stress or ultimate stress is a property of the material. Breaking in a piece occurs along cracks or defects in the piece structure. For a large piece, which has many such defects, a small stress may cause breakage with very little deformation. As the size of the piece is reduced, fewer defects remain and the breaking strength increases. In the limit of very small particles, purely intermolecular forces must be overcome.

Elastic state of material is described often by Hooke's law. The most important characteristic is the modulus of elasticity, which is the stress causing a unit change in length in the same direction as the applied force. The Poisson coefficient or bulk modulus permits prediction of the transverse contraction or expansion, which occurs when a stress is applied longitudinally. The modulus of rigidity expresses the relationship between shear stress and shear strain.



E : elastic limit; Y : yield point; B : breaking point

Fig. 2.7 Stress-strain diagrams of various solids

Inelastic behaviour is defined for stresses greater than the elastic limit but smaller than the breaking limit. Hardness is an. important property of the material. The empirical scale of Mohs is often used; Diamond having highest hardness (l0 Mohs) and Talc having the least hardness (l Mohs) in this scale.

2.3.1 Mechanism of Size Reduction

Loncin and Merson (1979) have reported that size reduction could be achieved by different mechanisms and sometimes with combination of two or more such mechanisms. The method of application of force to a particle is found to affect the breakage pattern. The basic methods of force application (Loncin and Merson, 1979; Prasher, 1987) are, (1) impact - particle concussion by a single rigicl force, (2) compression - particle disintegration between two rigid forces, (3) shear - the wrenching apart of a particle by the action of rigid force or swirling of a fluid, (4) attrition or rubbing - the scraping of , one surface on another, be it particle against a rigid force or particle against particle. Figure 2.8, shows stress mechanisms which can result during particle size reduction.

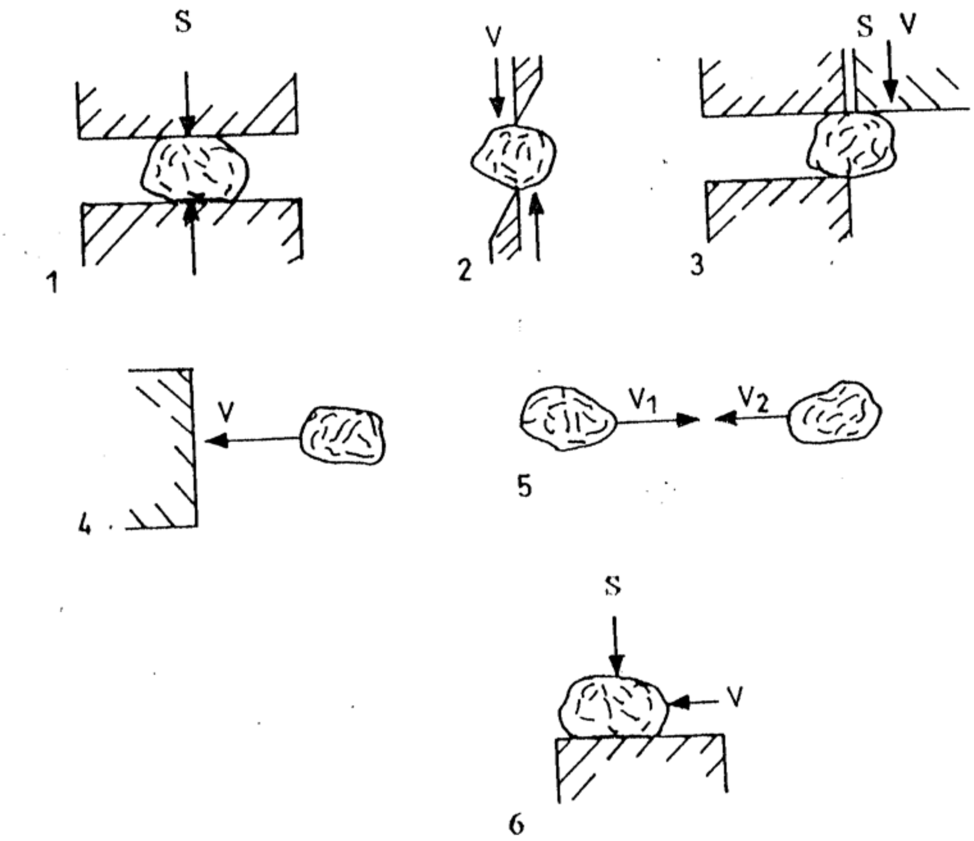
Various commercial size reduction or grinding machines have been listed Crable 2.3) which are used for food applications, and the schematic diagrams have been given (Fig. 2.9). Cracking behaviour of a material depends on whether the material is brittle or ductile, and on the type of stress applied (Cleef, 1991). Many mechanisms have been developed, such that some machines squeeze, or apply stress between two solid surfaces, resulting in compression as well as friction between the pieces being squeezed. Another group of machines uses impact, or stress against a single surface; the surface may be a plate or another particle. And yet another mechanism is cutting, which creates shear stresses, used primarily for tough, plastic materials. A brittle material, which deforms elastically before cracking, develops cracks that extend from the point to point of impact. A ductile material deforms plastically under compression, forming a contact surface from which meridional fractures develop (Rumpf, 1990; Austin, 1984).

Table 2.3

Types of grinders and their applications

(Lone in and Merson, 1979)

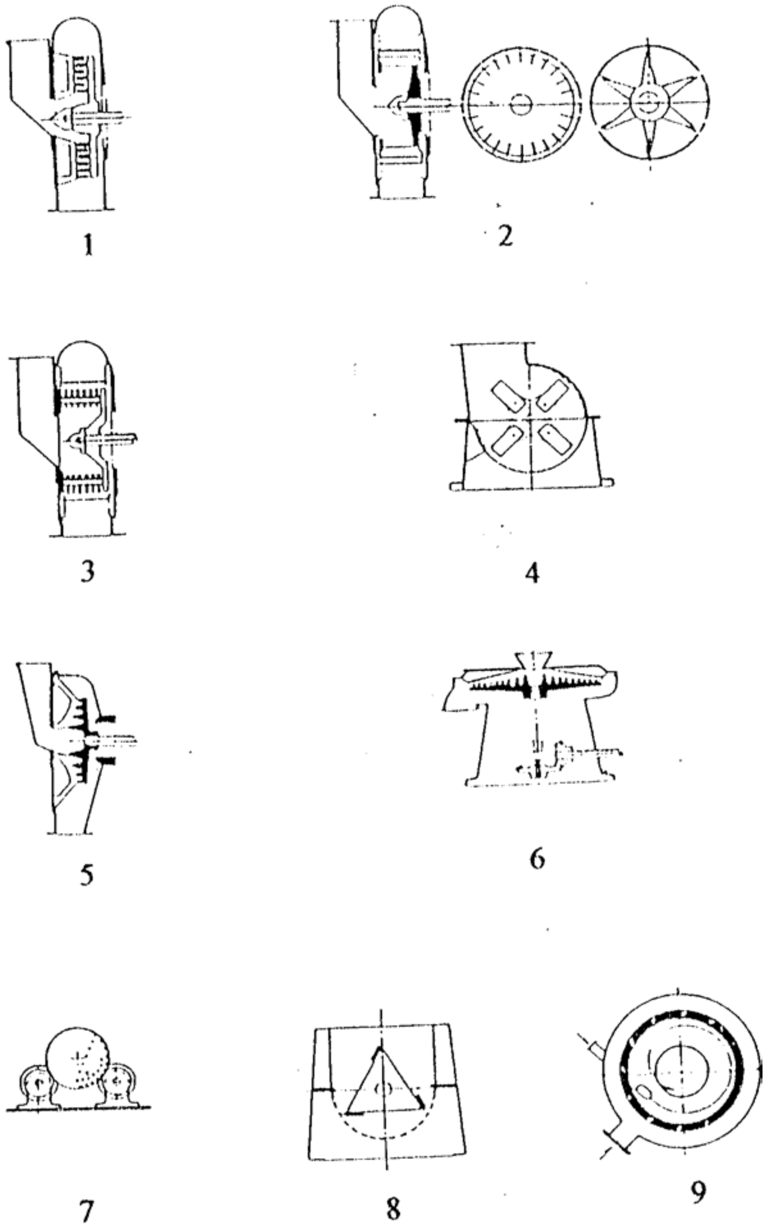
Method of size reduction	Name of the equipment	Peripheral speed (m s-1)	Materials ground
2. Impact forces	Pinned disk mill	80-160	Pepper, nutmeg, clove, mustard, roasted nuts, sugar, cocoa.
	Hammer mill	40-50	Sugar agglomerate, cocoa, press cake, tapioca, dry vegetables, extracted bones.
	Blast mill	40-110	Pepper, pectin, cocoa, dry protein, sugar.
	Hammer cage mill	70-90	Ginger, root & bark, drugs, tobacco leaves and stems
2.Impact and shear forces	Ring beater mill	50-70	Pepper, vegetables, oil press cake, pectin, algae, paprika
	Disk beater mill	70-90	Common cereal grains, dry whey, milk powder, lactose
3. Abrasion	Toothed disk mill	5-16	Wheat, pepper, linseed, fennel, bitter orange, corn, junifer berries
4. Section	Cutting granulator	5-18	Fish meal, dried fruit, dried vegetable, frozen coffee extract, cocoa, press cake



1,2. Stress and cutting between surfaces, 3. Shear stress, 4. Impact against a solid surface, 5. Impact with another particle, and 6. Rubbing friction.

S - represents stress and V -represents motion

Fig. 2.8 Common stress mechanism for particle size reduction.



1. **Pinned** disk milk; 2. Blast mill and wing beater mill; **Hammer-cage mill**

4. hammer mill; 5, 6. Toothed disc mill, vertical and horizontal; 7. Ball mill;

8. Cutting granulator; 9. Air jet mill

Fig.2.9 Commercial size reduction machines

2.3.2 Energy for Size Reduction

Grinding is an energy intensive operation wherein almost 99% (Loncin and Merson, 1979) of the energy dissipated as heat resulting in high temperatures of product and equipment. Only about 1 % of energy is useful in creating new surfaces. There is no general method for predicting the energy needed for size reduction. Elastic and plastic properties of a given food material often vary with moisture content and the distribution of water in the material. Further complications arise because these properties are often strongly unisotropic, the various layers or parts having extremely different mechanical resistances. Also the properties of materials can vary with the rate at which the stress is applied; some materials are plastic and ductile if the stress is applied slowly, but can be elastic or brittle if the stress is applied as by impact.

The minimum work of distortion can be measured by placing a sample in tension (or compression) in a machine (such as an Instron universal testing machine) which simultaneously measures both the applied force (Fa) and the elongation (l) upto the breaking point (Loncin and Merson, 1979). The energy (Er) for breaking the piece is obtained by mathematical integration of applied force over the limits of elongation (Eq. 2.7);

$$E_f = \int_0^l F_a \, dl \qquad (2.7)$$

However, if several particles of same material, size and geometry are stressed in turn under similar conditions of stress application, the amount of comminution energy is found not to be a unique quantity, but varies with the flaw pattern of the individual particle (Prasher, 1987). Hence, to obtain an unique measurement of comminution energy, a sufficient number (Beavan, 1980) of such particles must be similarly stressed to obtain a statistical average energy.

2.3.3 Energy Laws

The energy laws for causing breakage must be related to initial and final particle size conditions. For single-particle tests, the initial conditions may be the diameter of the sphere used or for irregularly shaped particles, two narrowly spaced sieve sizes. For particle bed tests, the initial condition may be an assemblage of spheres of stated diameters, or irregularly shaped particles between two sieve sizes, or a full distribution of sizes. In all cases, the final condition after breakage will be a complete size distribution.

The equations for estimating the energy needed for grinding solids have been developed based on the energy needed for causing deformation, creating new surface, or enlarging cracks. An empirical equation for grinding energy (Es) per unit mass of material is given by Walker *et al.* (1937):

(2.8)

$$dE_s = -k_g\,(dD/D^m)$$

where D is a characteristic size of the particles, and kg and m are empirical constants. The following laws have been derived based on the Eq. (2.8).

2.3.3.1 Rittinger's Law

Rittinger (1867) postulated that the particles which would not deform before breaking would be infinitely brittle. Therefore, the energy needed to break a particle depended only on the change in surface area. Hence, he used m =2 in the Eq. (2.8), and integrated between the initial size D, and final si/.e D_2 10 arrive at the following equation

(2.9)

$$E_s = k_r\,(1/D_1 - 1/D_2)$$

where k_r is the Rittinger's constant. The brittleness is most important for large-sized particles, and Rittinger's law appears to hold best for large brittle products.

2.3.3.2 Kick's Law

Kick (1885) postulated that deformation of the piece was primarily responsible for the energy required for size reduction, and assumed m=l in the Eq. (2.8), and integrated between the initial size Dl and final size D_2 to arrive at the following equation

(2.10)

$$E_s = k_k\,\ln(D_1 / D_2)$$

where kk is the Kick's constant. The deformation is most apt to be important for very small particles, and in fact, Kick's law best corresponds to small particles. A ductile material deforms plastically under compression, forming a contact surface from which meridional fractures develop (Rumpf, 1990; Austin, 1984).

2.3.3.3 Bond's Law

Bond (1952) used a value of m=1.5 in Eq.(2.8) to define a work index, Eo in dimensionless form, using 100 11m as the reference particle size, and suggested the following equation

$$E_s/E_o = [(100/D_2)^{1/2} - (100/D_1)^{1/2}] \qquad (2.11\ )$$

where, the term work index E_o. is the total energy required to break from infinite size to 80% passing through 100 microns. The Eq. (2.11) is an empirical one; Dl is defined as diameter (in 11m) of the sieve opening which will allow to pass 80% of the weight of material before grinding and D_2 is the opening which will pass 80% after grinding. The values of Eo for hard, brittle foods such as sugar and grain are in the range of 40 - 80 kJ kg^{-1} . If Rittinger's law is best applicable for large particle sizes and Kick's law for small particle sizes, the Bond's law is best suited for medium sized particles. The typical plots of energy utilization versus specific energy when the laws of Rittinger, Kick and Bond are applicable are shown in Fig. 2.10 (Prasher, 1987) .

2.3.3.4 Holmes' Law

Holmes (1957) introduced a variable exponent q in place of the power 0.5 as has been used by Bond (1952), because the three laws cited here have inadequacies to express surface-energy relationships. Therefore, the Eq. (2.11) becomes

$$E_s/E_o = [(100/D_2)^{q} - (100/D_1)^{q}] \qquad (2.12)$$

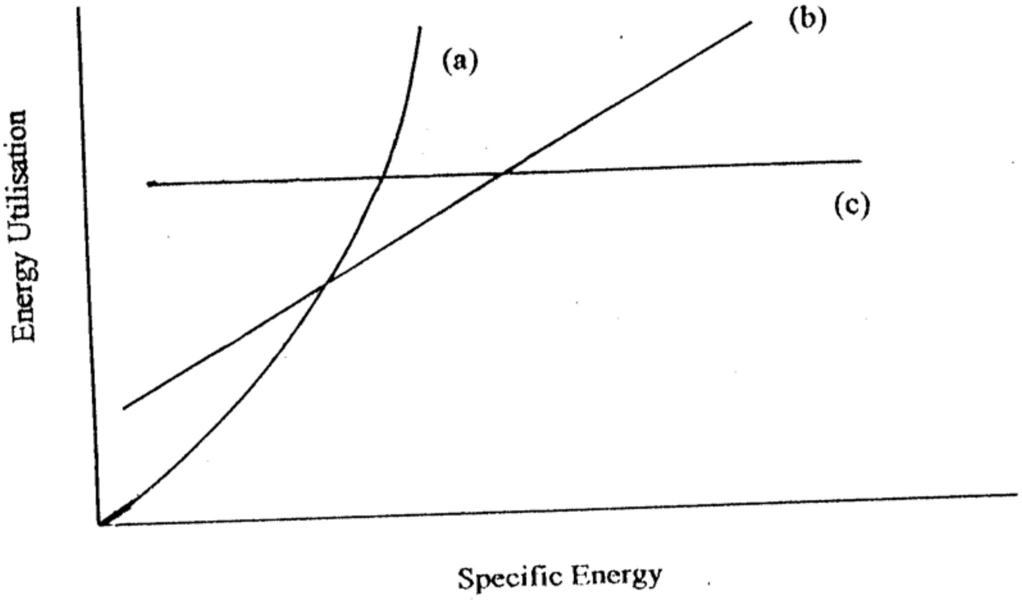


Fig 2. 10 Plots of energy utilisation versus specific energy using (a) Kick, (h) Bond and (c) Rittinger energy laws [37]

Charles' Law

(2.13)

Charles (1952) also incorporated a variable exponent into the energy equation and gave

where n_l is the slope of the straight-line portion of the plot.

$$E_s = A\ (D_l)^{-n_l}$$

2.4 Size Reduction or Grinding of Spices

Size reduction or grinding of spices is an important step in processing as it involves the loss of volatile oil and aroma present in' them. Generally, spices are ground either for direct use or for making value added products like oils or oleoresins. Grinding facilitates the release of aroma and flavour components and uniform mixing with food materials. At the same time, the grinding of spices results in considerable loss of aroma due to heat generated during ambient grinding of spices. The temperatures of ground material and the mill can reach during grinding can be as high as 95-100 C (Wistreich and Schafer, 1962). Since the spices are valued for their aroma and flavour, prevention of their losses assumes importance (Gopalkrishnan *et al.,* 1991). In large scale industrial grinders where continuous grinding is undertaken, gumming of grinder walls and sieves (Anon, 1962) results in frequent stopping of mill for cleaning works and hence reduces the grinding rate and production capacity. Spices which are fibrous in nature, consume enormous energy and time during grinding.

2.5 Cryogenics

"Cryogenics" is defined as 'making icy cold' and is often used as a synonym for extreme cold. The National Bureau of Standards (NBS), UK (Kim and Hung, 1994) has defined cryogenic temperatures as -150 C. Parker (1984) has defined cryogenics as a branch of engineering specialising in technical operations at low temperature, about -160 to -50 C in range.

Cryogenic Fluids and Their Properties

Cryogenic fluids (or cryogens) are those which boil at cryogenic temperature at atmospheric pressure. Many fluids, for example, hydrogen, helium, nitrogen, oxygen, inert gases, air, methane, carbon dioxide, etc., exhibit this property. Liquid nitrogen and carbon dioxide (liquid or solid) are the two major cryogens used for food applications. Table 2.4 shows the properties of major cryogens used in food systems. It indicates that LN_2 not only posesses the lowest boiling point but also highest thermal conductivity and highest total usable refrigerating effect, which is desirable for cryogenic food processing applications.

Table 2.4

Properties of cryogenic fluids used in food systems

(Fellows, 1988)

Properties of cryogens	LN_2	CO_2	Freon-12
Density (kg m^{-3})	784	464	1485
Boiling point (C)	-196	-78.5	-29.8
Thermal conductivity (W m^{-1} K^{-1})	0.29	0.19	0.10
Specific heat capacity (liquid, kJ kg^{-1} K^{-1})	1.04	2.26	0.98
Latent heat of evaporation (kJ kg^{-1})	358	352	297
Total usable refrigeration effect (kJ kg^{-1})	690	565	297

2.5.2 Theory of Cryogenic Size Reduction of Food

Cleef (1991) reported that conditions such as temperature also affect materials response to stress; tough, rubbery materials, for instance, sometimes crack easily at very low temperature. Mixtures that easily melt and crystallise, such as cocoa press cake (the form in which the cocoa beans are processed), also require cooling, since impact energy is dissipated as heat. At the same time, repeated stress can cause changes in the properties of a material, causing a ductile material to crystallize and become brittle. Size reduction, then, is a process that can have many stages; it may incorporate cooling and series of rapid, repetitive stresses that create a brittle solid packed with internal dislocations and strain energy when cryogens are employed.

Kim and Hung (1994) studied the freeze-cracking phenomenon in foods as affected by physical properties and reported that products with higher density and lower porosity are generally more susceptible to freeze-cracking. Exposing food materials to a cryogenic medium will cause internal stress build up due to fast freezing rate in such food materials during freezing. This internal stress may lead to cracking or shattering of frozen material. The cracking or shattering induced by cryogenic freezing has been explained mostly from volumetric changes associated with the water-ice phase transition. Fennema and Powrie (1964) described volume expansion and amount of empty space in microstructure as the primary factors affecting the degree of freeze cracking (mechanical damage) on cells during freezing. However, two conflicting presumptions were made, on the cause of freeze cracking at the microscopic level. Reeve and Brown (1968) stipulated that the cracking was probably the result of non-uniform contraction following solidification. The other presumption was that volume expansion of water-ice phase transition caused internal stress development. Sebok *et al.* (1991) indicated that both contraction and expansion might cause freeze-cracking.

2.5.3 Cryogenic Freezing of Food

Fruits and vegetables, marine products and spices have become important foreign exchange earners for the country. Indian marine product exports were worth a whopping Rs. 2,500 crores in 1993-94, exporting mainly to Japan, USA and UK. As the developed countries have a stringent quality specifications, using cryogenic technology makes exports more competitive. In view of the government's intention of bringing about one lakh hectares of land under shrimp farming by 2000 A.D. (Anon, 1995), to enhance the production, the application of this latest technique is gaining importance. Shrimp is considered as the pink gold of the sea and export can be made further lucrative by value addition in the form of individually quick frozen (lQF) packs.

During the freezing of sea-foods, fruits and vegetables and other food products, chemical and physical changes take place in the flesh of the product. Freezing causes the crystallisation of most of the water present in the product. The formation of ice increases the concentration of solutes or dissolved substances in the liquid phase surrounding the individual cells. This increased concentration causes an osmotic imbalance, resulting in the transfer of fluids from cell to intra-cellular spaces where it freezes to form ice. Higher the water leaving the cell, the larger the ice crystals are formed. Separation of the water from the cell continues until complete solidification of the product is attained. Therefore, the slower the product is frozen, the more complete the movement of water out of the cell and conversely, the quicker the solidification point is reached, the more water is retained within the cell and the smaller the intra-cellular spaces.

The degree of change that occurs during freezing is dependent upon the freezing time and the quality of the product before freezing. If the product is frozen slowly in an ordinary mechanical freezer, for example, it will be found that 'drip loss' is more (as high as 10-15% for sea food). Microscopic examination of frozen commodities shows a relatively small number of the smaller ice crystals, whereas rapid freezing demonstrates the formation of a large number of small crystals, and virtually no large injurious crystals. Rasmussen and Olson (1972) reported, for freezing of green beans, that a cross section of a bean frozen with liquid nitrogen closely resembled the structure of a fresh bean, having little cellular damage as compared to slowly frozen in an air blast.

Many types of freezers are available viz., cold store using still air as coolant, air blast freezer using forced air, plate freezer using contact to cold surface, and fluidised-bed freezer using fluidising air or liquid nitrogen as coolant.

Cryogenic freezing and preservation using LN_2 has several advantages, such as,

(a) Cryogenic freezing reduces bacteriological deterioration as food spends minimum time in bacteriological damage zone of +5 to +60 C which also retards the growth of disease producing organisms.

(b) Cryogenic freezing reduces oxidation, enzyme activity and metabolic deterioration resulting in preservation of nutritional properties.

(c) Cryogenic freezing improves retention of original colour and texture leading to uniform, glazing and attractive product which can fetch maximum market value.

(d) In cryogenic freezing, the freezing times are very low. For example, it is about 50% less compared to other types of freezing system, and hence, production capacity increases.

(e) Cryogenically frozen products have a longer shelf-life compared to those obtained in other similar systems

(f) Cryogenic freezing systems require low and easy maintenance as compared to mechanical systems and hence have a higher productivity.

(g) In cryogenic freezing systems, the heat transfer coefficient is very high (2000-5000 W $m^{-2} K^{-1}$) as compared to conventional freezing (100-200 W $m^{-2}K^{-1}$) systems.

However, the operating cost of freezing of foods is higher in case of liquid nitrogen freezing systems as compared to mechanical refrigeration systems (Gupta, 1992). Still, cryogenic freezing may be feasible for high cost foods, and from the point of improved product quality.

Different types of freezing systems using liquid nitrogen are on-line freezer, spiral freezer, immersion or dip freezer, batch cabinet, etc. Table 2.5 indicates both positive and negative features of these freezing systems (Wilhoft, 1987). The fluidised bed freezer using LN_2 as cryogen has been discussed by Reid and Stark (1974). This method has the advantage of uniform freezing and is ideal for foods of granular geometry, but not suitable for sticky and non-fluidisable materials.

One of the latest techniques of freezing is "crusta-freezing", or "cryo-mechanical system" wherein liquid nitrogen is used for initial rapid freezing of the crust, and the food is then frozen slowly in a mechanical system (George, 1993). This offers the advantages of both the systems - the flexibility and other benefits of cryo-freezing system together with the low unit-cost factors of mechanical systems. This technique has been claimed to be economical as existing mechanical systems need not be replaced.

Table 2.5

Types of liquid nitrogen freezing systems

(Wilhoft, 1987)

Type of freezing	Positive features	Negative features
Immersion	Very fast heat transfer resulting in high production capacity. Small floor area and low capital cost. More effective for producing instant quick freezing products.	Damages the product due to enormous thermal stresses. Only benefits from the latent heat of LN_2 Uses almost twice the amount of gas as with in-line freezing.
In-line	Rapid freezing in 3-8 minutes. High efficiencies of up to 90% achievable if LN_2 is re-circulated. Good product quality. Machines are generally available in different ranges of belt width to accommodate constraints on factory floor space.	Certain types of freezer designs makes them difficult to clean. Need to establish this temperature as well as whether fan motors are resistant to freezing up.
Spiral	Low floor space and high throughput. Can store product in freezer overnight. Dwell time is about 1 hour for freezing. Well suited for chilling of foods.	Major exercise is to clean and de-frost. Lengthy start-up time. Quality benefits of rapid freezing linked with small ice crystals are lost. Current spiral designs are not designed to operate counter-current heat transfer and hence some loss in efficiency occurs.
Batch cabinet	Ideal for catering operations too small to handle by any other method. Faster cycle time, is about one half that of a mechanical blast freezing. Shelf life extension over mechanical type when used for cook-chilling.	Effective between 50 and 70%. Labour intensive system.

2.5.4 Cryogenic Size Reduction or Cryogenic Grinding of Spices

The process of cryogenic grinding of spices is slowly being implemented throughout the world. The present section thus deals with the published literature on the same with an emphasis on finished product characteristics.

Miller (1951) has reported that the use of LN_2 during grinding assured fine powder in a single pass in spice grinding. It has been reported that conditioning of spices prior to grinding curbed the loss of flavour volatile oils both in storage and during milling (Anon, 1962). It was suggested to condition and to store spices at proper temperature and humidity, and to grind them with minimum handling and under optimum quality retaining conditions. A loss of volatile oils to the tune of 40% during grinding of unconditioned spices was reported, and the powder was turning mouldy and losing its colour if stored in rooms which were too warm. Conditioning the spices for milling also increased throughput up to 20% and curbed shrinkage during milling. Spice volatile oils were not only retained during storage, but also during milling regardless of type of mill employed for milling. In contrast, when spices stored at room temperature were ground, they were heated up and lost some of their volatile flavours. Moreover, they tend to smear and blind the screens of impact type mills, or 'cake' onto rolls. Mills then had to be shut down for maintenance at the expense of production. However, chilled spices conditioned at least 2 to 3 weeks were friable and grindable. They went through mills easily, without smearing, blinding or coating the mills. They could be ground faster, with less build up of flavour robing heat and size reduction was easier because the more brittle the spices were, more easily they shear.

Wistreich and Schafer (1962) worked on cryomilling process and observed that it could be applicable to a wide variety of foods such as cocoa and chocolate, vanilla-sugar, coconut, coffee, tea, dehydrated meat, etc. Freeze-grinding of spice was accomplished by controlled injection of liquid nitrogen directly into the mill's grinding zone. Instantaneous evaporation of the liquid refrigerant quickly chilled both the spice and the mill. It also absorbed the frictional heat of grinding. Thus, the temperature in the grinding zone generally were well below -100 F and theoretically could approach as low as -320 F. In contrast, conventional milling could raise spice temperatures to as high as 200 F. The process of cryomilling permitted extremely fine grinding because the spice oils solidified became brittle at these low milling temperatures. These fine and ultra fine spice powders dispersed flavour uniformly throughout the final' product and they eliminated specking problems. The low temperature of freeze-grinding also curbed the usual loss of lee aromatics (Table 2.6) and moisture. Therefore, the ground products retained much the original flavour strength and weight. On the average, 7 g of freeze-ground spices had the same flavouring power as 10 g of the conventionally milled counter parts. Use of LN_2 minimized oxidation of spice oils because, as liquid evaporates in the grinding zone, it tended to expel any air in the mill. Freeze-ground spices had proved to be considerably more stable than conventionally ground products. Possibly the spice adsorbed or in some (Way retained some of the nitrogen. Further, low temperature treatment had a pasteurizing effect on the spices. Grinding rates were increased because the mills low-temperature operation curbed 'gumming up' of grinding surfaces and screens.

Table 2.6

Steam-distillable volatile oil of different spices
(Wistreich and Schafer, 1962)

Spice	Grinding method	
	Ambient (% v/w)	Cryogenic (% v/w)
Black pepper	1.40	1.84
Ginger	1.44	1.80
White pepper	0.40	0.80
Coriander	0.26	0.40
Caraway	2.96	4.40
Celery	1.70	2.25

Strause (1967) had made studies on cryogrinding of nutmeg which was very difficult to mill due to its oily and sticky nature. Milling temperatures tested were in the range from room temperature (25 C) to 100 C, and speeds of the grinder were 3,000 and

5000 rpm. It was observed that the efficiency of milling of nutmeg depended mainly on the milling temperature because of the high oil content. Low temperature or cryomilling prevented the milled powder from sticking to the mill. Speed rate of 3000 rpm gave better results. There was less loss of volatile oil and moisture and also less iron content in cryomilled nutmeg than in the correspondjng control sample of stamp mill. The percentage of volatile oils in cryomill was 10.9 as against 9.6 obtained by stamp mill (control). In general, microbial load was less in liquid nitrogen immersed samples than in cryomilled or stamp milled nutmeg for which explanation was not available. He also worked on white pepper and concluded that the absorption of milling heat by cooling was important in order to prevent iron content in cryomilled pepper and nutmeg than in stamp mill processed pepper and nutmeg. The reductions of number of bacteria, mould and yeast were observed by fine cryomilling. Table 2.7 shows the comparative composition of stamp milled and cryomilled spices.

Table .2.7

Comparative composition of stamp milled and cryomilled spices
(Strause, 1967)

Spice	Method of milling	V olatile oil (%)	Moisture (%)
White pepper	Cryomill	3.6	15.8
White pepper	Stamp mill	1.7	14.3
Nutmeg	Cryomill	10.9	8.4
Nutmeg	Stamp mill	9.6	8.0

Pesek *et al.* (1985) and Pesek and Wilson (1986) worked on grinding of spices such as white pepper, nutmeg, cinnamom, cumin and oregano, and compared cryoground and ambient ground samples. Cryoground products were superior to ambient ground spices. The results supported the hypothesis that (a) the light and highly volatile components were more readily retained through cryogrinding than ambient grinding of spices and (b) the high molecular weight components were retained equally well for the two grinding techniques employed. Table 2.8 shows the gas-chromatographic headspace analysis of different spice.volatiles obtained by cryogenic and ambient grinding (Pesek *et.al., 1985).*

Table 2.8

Gas-chromatographic headspace analysis of different spice volatile oils obtained by cryogenic and ambient grinding

(Pesek et al.,1985)

Spice	Volatile oil Compound	Grinding techniques		
		Ambient	Cryogenic	% Increase due to cryo-grinding
White pepper	α-Pinene	4.86	9.50	95.5
	β-Pinene	6.95	10.63	53.0
	Unidentified	9.64	13.36	38.6
	Limonene	5.59	6.76	21.9
Nutmeg	α-Pinene	16.75	19.38	15.7
	β-Pinene	8.84	9.34	5.7
Cinnamon	α-Pinene	1.15	8.32	623.5
	Camphene	0.40	2.53	532.5
	β-Pinene	0.45	2.42	437.8
	Cineole	0.11	0.47	327.3
	Limonene	0.24	0.54	125.0
Cumin	α-Pinene	0.24	0.42	75.0
	β -Pinene	3.23	4.449	39.0
	τ-Terpinene	1.24	1.39	12.1
Oregano	Unidentified	0.62	2.86	361.3
	α-Pinene	1.49	5.71	283.2
	Camphene	0.82	2.44	197.6
	β-Pinene	1.40	4.10	192.9
	Myrcene	0.00	3.98	Very high
	Cymene	8.32	17.31	108.1
	γ-Terpinene	4.92	12.87	16.6

Gopalkrishnan *et al.* (1991) carried out grinding experiments on cardamom at four different temperature conditions viz., ambient (28 C), after freezing seeds in a deep-freezer (-18 C) overnight, by grinding sees along with dry ice, and after pre-cooling the seeds with liquid nitrogen. Ambient grinding of cardamom in a centrifugal mill using 1.00, 0.75, 0.50 and 0.25 mm sieve opening showed 26 to 52% losses of volatile oil and natural aroma. Other grinding methods using a deep freezer (-18C), dry ice and liquid nitrogen brought about noticeable improvement in the product depending on the degree of cooling. Cryogenic grinding using dry ice and liquid nitrogen in the centrifugal mill yielded a superior quality product without the loss of high volatile flavour constituents during grinding.

Anon (1993) reported (in equipment catalogue, *M/s* Hosakawa Alpine, Germany) that the volatile oil retention by cryogenic grinding technique increased by 40% and 64% for black pepper and for white pepper, respectively (Table 2.9).

Table 2.9

Spice	Ambient Grinding (mL/100g)	Cryogrinding (mL/100g)	Increase due to cryo-grinding (%)
White pepper	1.95	3.19	64
Black pepper	2.21	3.09	40
Pimento	2.71	3.08	14
Mace	9.10	14.50	59
Cloves	11.50	16.50	43

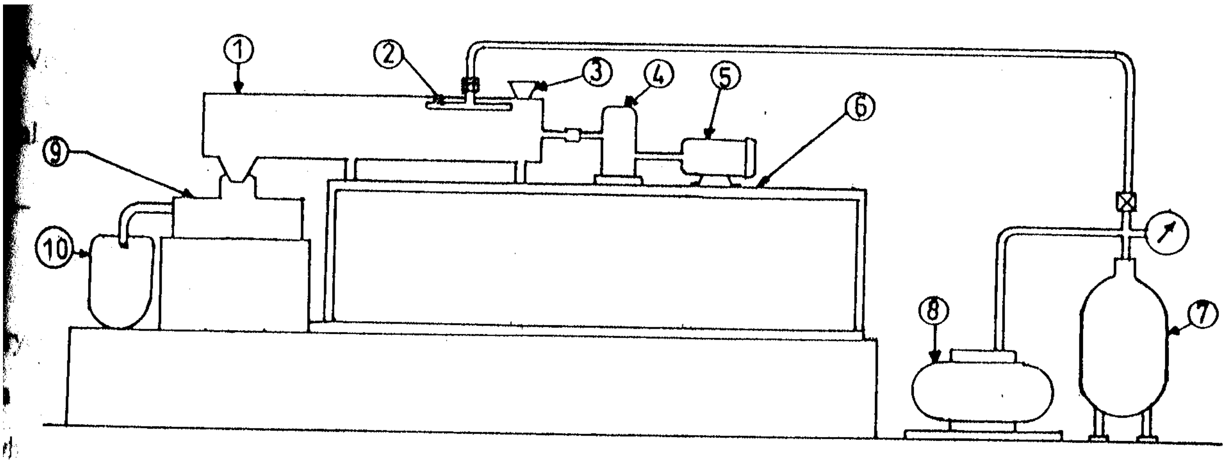
Mckee *et al.* (1993) had studied the effect of different grinding methods at ambient and chilled conditions as well as by using liquid nitrogen on some properties of nutmeg in batches of 6.75 kg each. The highest temperatures of the powder reached during grinding were ambient: 43 C, chilled: 38 C and liquid nitrogen: 33 C. The various parameters of powder viz., modulus of fineness, modulus of powder uniformity, moisture content, volatile oil content, oleoresin content and antioxidant capacity were determined in each of the grinding methods. They found the steam volatile oil contents to be in the order of 5.8, 5.4 and 5.3 g/100g for ambient, chilled and liquid nitrogen grinding, methods, respectively. They also observed that none of the three grinding methods evaluated was clearly superior under the conditions of the study. However, the liquid nitrogen method tended to produce ground nutmeg with more consistent results across the batches than those at ambient and chilled conditions. Overall, nutmeg ground by using liquid nitrogen had a higher oleoresin colour equivalent and a higher percentage of resin. Further, they observed that since a higher oleoresin colour equivalent and a higher percentage of oleoresin imparted the colour and flavour provided by nutmeg to food products, the liquid nitrogen method might provide benefits in terms of reducing the cost of the process. They also observed a potential antioxidant capacity improvement in nutmeg ground by liquid nitrogen method. Table 2.10 shows grinding characteristics of nutmeg powder ground using ambient, chilled and liquid nitrogen grinding methods.

Table 2.10

Grinding method against grinding characteristics of nutmeg powder
(Mckee *et al.*, 1993)

Grinding method	Modulus of fineness	Moisture (g/100g)	Volatile oil (g/100g)	Oleoresin colour equivalent (g/100 mL)
Ambient	3.4	6.9	5.8	0.90
Chilled	3.4	6.8	5.4	0.75
Liquid nitrogen	3.5	6.8	5.3	0.97

Recently, Singh and Goswami (1999a) have designed a laboratory scale (200 g capacity) cryogenic grinding system (Fig. 2.11). They have also reported' results of cryogenic grinding of spices such as cumin and clove (Singh and Goswami, 1999b and 2000). The details are discussed in the subsequent sections.



1. Conveyor; 2. LN_2 distributor; 3. Hopper; 4. Gear box
5. Motor; 6. Plat form; 7. LN_2 cylinder; 8. Compressor
9. Grinder ; 10. Collecting bag

Fig. 2.11 Block diagram of Laboratory cryogenic grinding system.

Table 2.11

Amount of volatile oil present in cumin powder ground under cryogenic and ambient conditions (Singh and Goswami. 1999b)

	Cryogenic grinding				Ambient grinding				
Temperature (C)	-160	-130	-100	-70	40	55	65	75	85
Volatile oil content (mL/100g, db)	3.30	3.28	3.28	3.26	2.86	2.73	2.55	2.36	2.26

Singh and Goswami (1999b) studied the grinding of cumin seed at various cryogenic and ambient temperatures. They have reported that an increase in temperature in cryogenic range (-160 to -70 C) had no significant effect on volatile oil content, whereas increase in temperature in ambient range (40 to 85 C) significantly reduced the volatile oil content from 2.86 to 2.26 mL/100g (Table 2.11). Further, they have reported that the components of volatile oil were not significantly affected by grinding temperature in the cryogenic range. However, these components decreased significantly with increase in grinding temperature under ambient condition. With increase in temperature from - 160 to -70 C for 12 number of rotor ribs, the volume mean diameter of cumin powder increased from 129 to 164 /lm and the specific energy consumption increased from 72 to 108 kJ kg^{-1}.

Singh and Goswami (2000) also studied the grinding of clove at various cryogenic and ambient temperatures. They have reported similar results for grinding of clove as that for cumin. It has been reported that the clove was successfully ground at temperature below -50 C without any deposition over sieve surface. They have reported that an increase in temperature in cryogenic range (-110 to -50 C) had no significant effect on volatile oil content, whereas an increase in temperature in ambient range (55 to 85 C) significantly reduced the volatile oil content from 11.0 to 9.3 mL/100g (Table 2.12).

Table 2.12

Amount of volatile oil present in clove powder ground under cryogenic and ambient conditions (Singh and Goswami, 2000)

	Cryogenic grinding				Ambient grinding			
Temperature (C)	-110	-90	-70	-50	55	65	75	85
Volatile oil content (mL/100g, db)	13.3	13.3	13.2	13.2	11.0	10.3	9.9	9.3

There was about 30% more volatile oil content in cryogenically ground powder amples in comparison to that of ambient grinding. The volume mean diameter of clove powder increased from 119 to 153 μm and the specific energy consumption during, rinding also increased from 62 to 81 kJ kg-^{1} with increase in temperature from -110 to -50 C at constant feed rate of 1.5 kg h-^{1}, rotor speed of 69 IJ1 S-l and sieve opening size of 0.5 mm (Singh and Goswami, 2000).

2.5.5 Advantages of Cryogenic Grinding

Advantages of cryogenic grinding or cryogrinding over ambient temperature grinding have been summerised by Wistreich and Schafer(1962), Anon (1962), Pesek *et al.,* (1985), Pesek and Wilson (1986) and Pruthi (1991). The salient points are as follows:

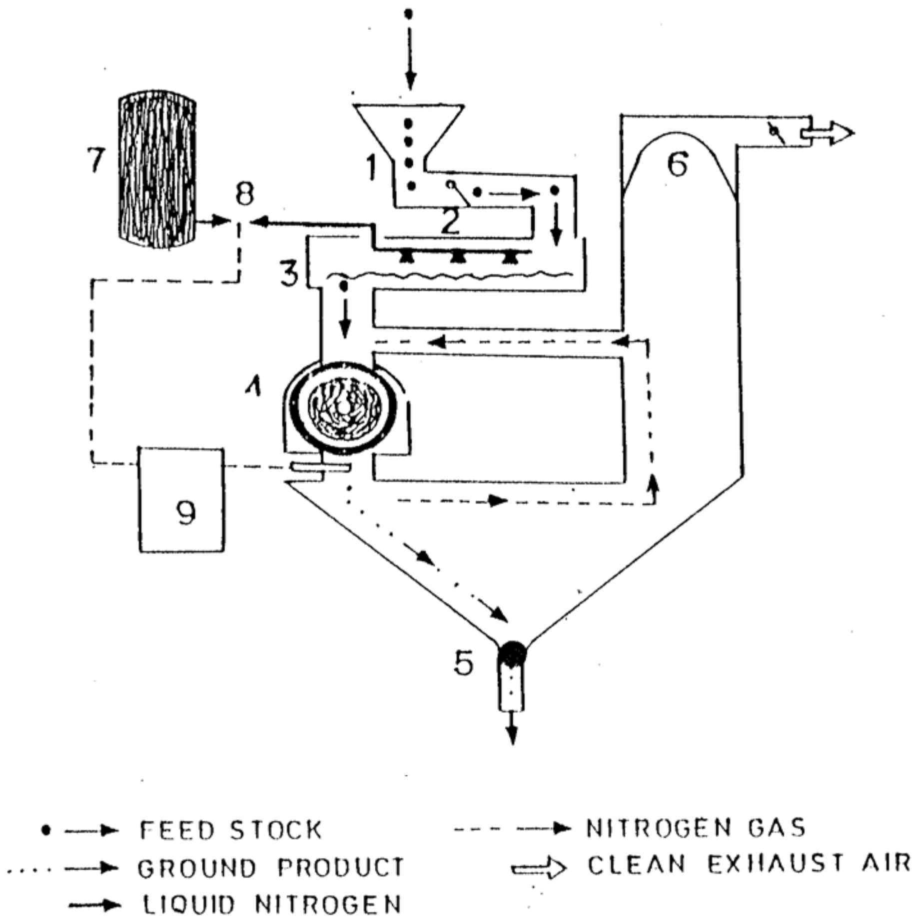
a) Cryogrinding curbs the usual losses of spice aromatics (volatile oils) as well as moisture during the grinding process. The ground products retain their original flavour strength and weight. On an average, 7 g of freeze-ground spices have the same flavouring potential as with 10 g of ambient ground counterparts.
b) Cryogrinding cuts down the oxidation of spice oils because as the liquid nitrogen evaporates in the grinding zone thereby expelling any air in the mill and retaining flavour.

c) It also permits extremely fine grinding, as spices become very brittle and spice oils solidify at very low temperature. Such finely ground spices disperse flavour uniformly throughout the final products. It virtually eliminates specking problems as encountered in sausages.
d) In liquid preparations, freeze-ground spices disperse flavour better and uniformly.
e) Freeze-ground spices have proved to be considerably more stable than ambient ground products. Possibly, spices absorb or retain some quantity of the nitrogen.
f) Grinding rate is increased because the mill's low-temperature operation minimises the ‘gumming up' of grinding surfaces and screens.
g) The actual costs of cryoground spice are lower "than those of conventional products when the increased quality i.e., the flavour strength is taken into account. In addition fine grinding and greater stability are bonus points to food processors and
h) The process is applicable to a variety of other foods, such as cocoa, coffee, tea, coconut and dehydrated meats.

A typical cryogenic grinding system (Fig. 2.12) consists of controlled injection of liquid nitrogen on the spice to be frozen in a cryo-screw-freezer. The liquid nitrogen frozen spices are fed to an universal mill through the cryo-screw-freezer conveyor. If required, liquid nitrogen may also be directly injected into the grinding zone. Instantaneous evaporation of liquid nitrogen quickly chills both the spice and the mill. It absorbs the frictional heat of grinding. By suitably adjusting the liquid nitrogen supply, it is possible to control the temperature of the ground material (Anon, 1994).

2.5.6 Cryogenic Grinding of Other Food Materials

Cryogenic grinding is also applicable to a wide variety of food materials viz., cocoa and chocolate, vanilla-sugar, coconut, coffee, tea, dehydrated meats, etc. It has been found that there is a large gain in flavour when vanilla-sugar is pulverised. The product has interesting possibilities and advantages as a replacement for liquid extract. Coconut can be ground to eliminate objectionable fibres, while improving its aroma and flavour as high fat content gets solidified and fibres become brittle. This offers applications in syrups, cakes, and confectionery. Ground cocoa and chocolate retain their natural flavour and aroma.



1. Vibratory feeder
2. Liquid nitrogen inlet
3. Screw conveyer
4. Universal mill
5. Rotary valve
6. Filter bag
7. Liquid nitrogen tank
8. Temperature control
9. Control Panel

Fig. 2.12 Typical cryogenic grinding system, Pilot scale

Cryoground coffee appears to have longer lasting freshness of particular interest in instant-coffee processing (Wistreich and Schafer, 1962).

2.5.7 Miscellaneous Applications of Cryogenics in Food

Cryogenics is finding new applications in various fields of food processing and storage. The subsequent sections briefly discusses those areas.

2.5.7.1 Liquid Nitrogen in Packaging

Liquid nitrogen injection system can be used for both pressurisation and for creating an inert environment (Anon, 1990). In pressurisation, a drop of liquid nitrogen is injected into a filled can just before sealing. When liquid nitrogen changes phase, it expands and the can gets pressurised, increasing its strength and stackability. Liquid nitrogen is added to an empty container before filling for creating an inert atmosphere; nitrogen expands to about 700 times its original volume, displaces oxygen from the packaging area, thereby increasing the shelf life of the product. The system is useful for the packaging of oxygen-sensitive products such as coffee, sauces, olives and cooking oil.

2.5.7.2 Liquid Nitrogen Peeling of Fruits and Vegetables

Weaver *et al.,* (1980) reported that liquid nitrogen could be used for peeling of fruits and vegetables. For example, tomatoes are immersed in liquid nitrogen for 5-15 seconds and then thawed in warm water to loosen the peel. Since this method involves no cooking, there is a removal of only skin tissue with small amount of internal tomato pulp. Skin removal occurs with a tissue loss of about 5-8%. This technique may also be applied for peeling of other fruits and vegetables.

CHAPTER 3: MATERIALS AND METHODS

CHAPTER 3

MATERIALS AND METHODS

The present chapter describes the details of materials used and the methods employed for determining various physical and mechanical properties as well as the grinding characteristics by ambient and cryogenic grinding of whole black pepper.

3.1 Engineering Properties of Black Pepper

The details of the materials and methods used for determining the various engineering properties of black pepper are described in this section.

3.1.1 Materials

Black pepper (variety *Malabar)* seeds were procured in bulk from the local market. After cleaning, they were stored at room temperature (25 C) for one month for moisture equilibration. The moisture content of the seed, after equilibration, as determined by the ASTA (1985) method, was observed to be 11.1% (dry basis).

3.1.2 Preparation of Seeds at Different Moisture Contents

To obtain seeds with different moisture contents, a fine spray of water was applied using a spray gun, commonly used for spray-painting on wooden or metallic surfaces. The time of spray was varied to obtain seeds with different moisture contents. These seeds were kept in covered glass bottles, at 4 C, for 48 hours with occasional gentle shaking to ensure uniform moisture distribution. A part of the seed-lot was also dried in a tray dryer at 40 C for 2 hours to obtain seeds having a moisture content less than that of the original seeds. The moisture contents of the dried or sprayed samples were obtained by knowing the initial and final weights of the treated seeds using the following equation (Eq. 3.1).

$$W_1(100 + M_1) = W_2(100 + M_0) \qquad (3.1)$$

Where Mo is Initial moisture content, M_1 is final moisture content of the dried and sprayed sample, W_1 is initial weight of the seeds at M_0, W_2 is final weight of the seeds at M_1.

3.1.3 Size, Shape and Weight

The size (diameter) of the black pepper seed was measured to ±0.01 mm accuracy using a dial-type thickness gauge at five different orientations of 100 seeds. The size distribution at 0.20 mm intervals was reported. As the individual black pepper seed was apparently spherical in shape, the sphericity and roundness were determined using Eqs. (2.1) and (2.2) (cited in review of literature), respectively (Mohsenin, 1986); the corresponding values being rep0l1ed as a fraction and percentage basis, respectively. The weight of 1000 seeds was also determined with four replications.

3.1.4 Bulk Density

The bulk density was determined by weighing a container (A 2 Y2 can, capacity 895 mL, commonly used for canning of fruits and vegetables having a diameter of 11.4 cm and a depth of 10.1 cm) filled with black pepper seeds (two gentle tappings were employed). The reported values were the mean ± standard deviation (SD) of five such determinations.

3.1.5 Dynamic Angle of Repose

The dynamic angle of repose depends on the way in which the material heap is formed. For black pepper seeds in bulk, this was determined following the compacted angle of repose method (Thomson, 1984), commonly used for testing bulk solids. The basic principle behind this determination is the property of the seeds to form heap, while stacking.

3.1.6 Flowability

From a physical point of view, the gravitational flow of powder is equivalent to solid failure in shear, and the measurement of flowability is fairly straightforward (Peleg, 1983). This principle was adopted for measuring the flowability of black pepper seeds. The time (in seconds) for 1 kg of seeds to flow through a conical plastic funnel (diameters 150 and 30 mm and height 200 mm) under gravity was reported as funnel flow time. Hence, an increase in funnel flow time means a decrease in flowability. The reported values were the mean ± SD of five determinations.

Uniaxial Compression and Failure Behaviour

A Universal testing machine (Model No 4301, Instron Corporation, Buckinghamshire, UK) was used for the compression of the seeds at a crosshead speed of 50 mm min^{-1} using a load cell with a maximum capacity of 500 N. The seeds were compressed to 75% of their original size for estimation of failure characteristics. A typical uniaxial compression curve along with the different parameters estimated (please see Results and Discussion) is shown in Fig. 4.1.7. These were,

1) failure force, F_f (force in Newton when the seed undergoes failure during compression);
2) failure strain (the strain, expressed as percentage of the original height of the seed, at the time of failure);
3) linear strain limit, E, (the extent of strain up to which the force versus deformation curve was linear, and expressed as percent);
4) failure energy, E_f (energy needed for the failure of the seed during compression, calculated from the area under the curve till the point of failure, and expressed in Joules);
5) deformation modulus, E_d (equivalent to elasticity and was obtained from the slope of the initial linear portion of the force-deformation curve (Szczesnaik, 1983), and expressed in N mm^{-1}).

According to Mohsenin (1986), the failure energy can be denoted as the work required to cause rupture or failure, and is a rough measure of toughness of the sample. The number of seeds tested at each moisture level was 20 with two replications.

3.1.8 Statistics and Data Analysis

Regression analysis using the method of least squares (Snedecor and Cochran, 1968) was adopted to obtain curve fitting equations. The significance of the correlation coefficient (r) was judged at a probability (p) of 0.01. The Duncan's multiple range test (DMRT) was applied to verify if there was a statistical difference between the groups at a p level of 0.05 (Little and Hills, 1978).

3.2 Ambient Grinding of Black Pepper

3.2.1 Performance Study of a Grinding Mill at Various Feed Rates

Black pepper (variety: *Malabar),* procured from the local market, was cleaned using an air classifier. Samples were ground using a micro pulveriser (Swing hammer mill, capacity 10 kg hr^{-1} HP motor, 3 phase, 440 V, 1440 rpm) at feed rates of 3.6,4.8 and 9.5 kg hr^{-1} and these feed rates were maintained by using 0.5, 1.0 and 4.0 mm sieve opening. The temperature of the ground material and the corresponding time were recorded. Geometric mean particle diameter of the powder was determined by sieve analysis. The ground material was drawn at different time intervals/temperatures during grinding for the estimation of moisture and volatile oil contents.

3.2.1.1 Sieve Analysis

Particle diameters of powder samples were measured by sieve analysis technique. Sieve analysis of the powdered samples were conducted using a set of US standard sieves, mounting one above the other, with the sieve having the highest sieve opening at the top and pan (without sieve) at the bottom. These sieve-sets were placed in a mechanical sieve shaker. Powdered black pepper sample of 100 g was spread on the first top sieve of the sieve-set and the top lid was placed. The sieve shaker was operated for 5 minutes. The quantity retained on each sieve (W_i) was determined.

The geometric mean particle diameter (d_{ga}) was determined assuming *log normal* distribution, using Eq. (3.2) (Farrel, 1976).

$$\log(d_{ga}) = [\Sigma\{W_i * \log(d_g)\}/\Sigma\, Wi] \quad (3.2)$$

where d_{ga} is geometric mean particle diameter of powder, d_g is geometric average of two successive sieve openings and W_i is weight fraction of powder retained on i^{th} sieve and the surface mean diameter was calculated using (Coulson and Richardson, 1978) using Eq. (3.3):

$$d_{sa} = [\Sigma(W_i \ d_m^3) / \Sigma (W_i \ d_m^2)] \tag{3.3}$$

where d_{sa} is surface mean diameter of powder and dill is arithmetic mean of two successive sieve openings.

In all the grinding experiments, the above mentioned sieve analysis technique was used. The geometric mean particle diameter was used for defining the powder particle size, while the surface mean particle diameter was used for determining theoretical energy for size reduction and also for diffusion coefficients in the distillation process.

3.2.1.2 Moisture Content of Black Pepper Samples

The toluene distillation method for the determination of moisture is applicable to all spices by co-distillation with toluene, with the exception of capsicums, red peppers, paprika, chillies, saffron, dehydrated garlic, onion and dehydrated vegetables. This method is also known as Dean and Stark technique (Pruthi, *1998).*

The principle behind this measurement is that the amount of water is determined by first distilling the material with an organic liquid not miscible with water and then collecting the distillate in a graduated tube. All glass distillation apparatus with ground glass joints were constructed and assembled (Fig. *3.1).* It can be seen that it consists of 500 mL or 1000 mL round bottom, short neck flask with T.S.24/40 joint, wet condenser with drip tip, 400 mm in length with a T.S.24/40 joint and a Bidwell-Sterling trap T.S.24/40 joint (5 mL capacity, graduated in 0.1 mL intervals).

Usually, an electric heating mantle as the heating source with a variable power control and magnetic teflon covered stirrer could be used to reflux toluene in the above apparatus. Alternatively, an oil bath at temperature of 110 ± 1 C could also be used. Nylon brittle burette brush of 12 mm diameter or a wire loop was used. It was long enough to extend through the condenser (about 450 mm). Alternatively, a long copper

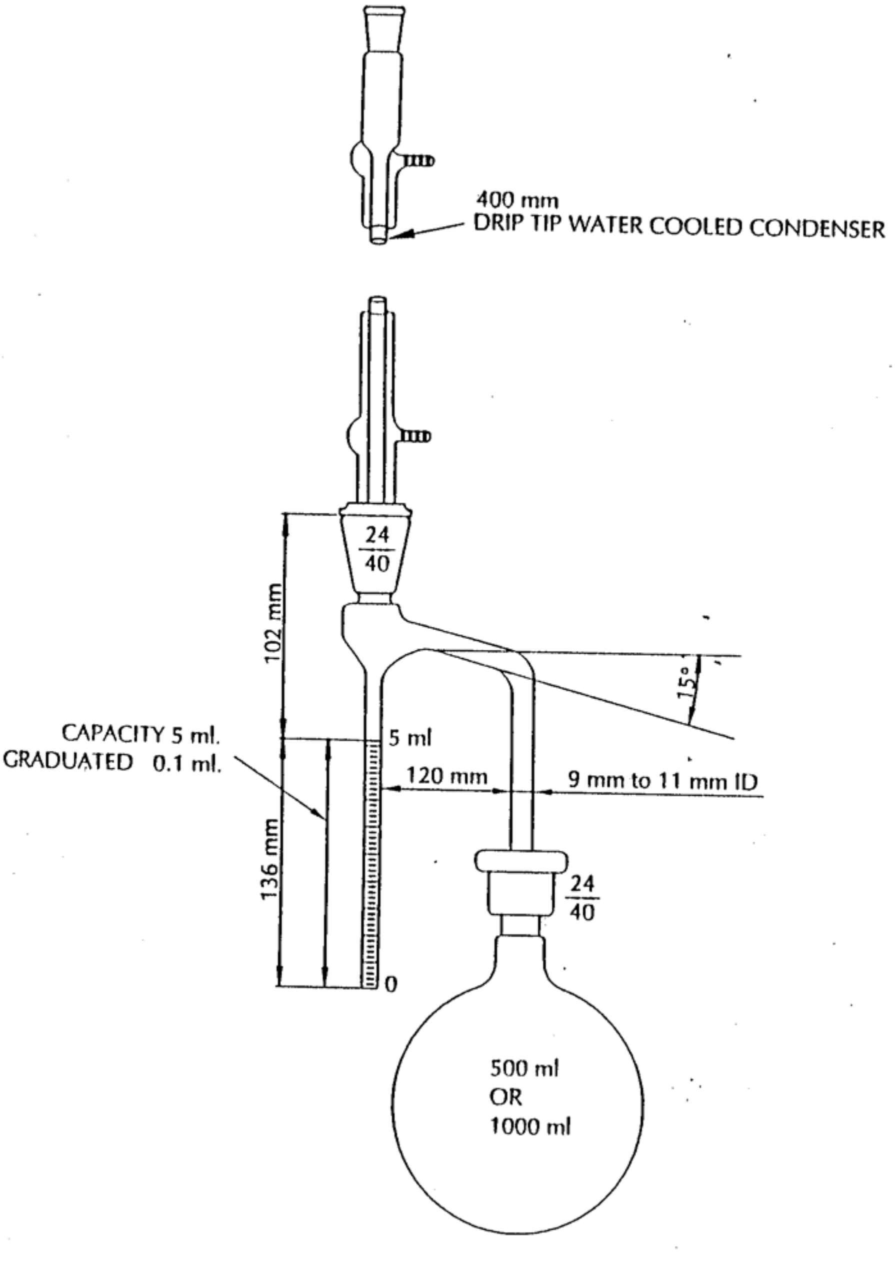


Fig. 3.1 Distillation apparatus for determination of moisture content in black pepper powder

wire extending through the condenser with one end twisted into a spiral could be used. The diameter of the spiral was such that it fitted snugly within the graduated portion of e entrainment distillation apparatus, which compring a glass flask heated by suitable means and provided with a reflux condenser, discharging into a trap and connected to the flask. The connections between this trap and the condenser and flask were interchangeable ground glass joints. The trap served to collect and measured the condensed water, and to return the solvent to the flask. The assembly of the apparatus is shown in Fig. 3.1 and the various components are described below.

A water-cooled glass reflux condenser having a jacket approximately 400 mm long and an inner tube of 9.5 to 12.5 mm outside diameter was employed. The tip of the condenser to be inserted in the trap was ground at an angle of 30 degrees from the vertical axis of the condenser. When inserted into trap, the tip of the condenser was 6 to 7 mm above the surface of the liquid in the trap after distilling conditions had been established.

Receiver (otherwise called the trap) of 5 mL capacity made of high resistance glass, well annealed and free from defects provided with ground glass joints with the shape, dimensions and tolerances was used. This consisted essentially of the upper chamber, together with the tube and ground joint leading to the flask, and the graduated tube. The graduated portion had a capacity of 5 mL when filled to the highest graduation mark. The scale range of 0 to 5 mL and graduated at intervals of 0.1 mL. The graduation marks corresponding to each mL were numbered and carried completely round the tube. The graduation marks mid way between the numbered marks were carried three-quarterway and the remaining marks were carried half way round the tube. The error at any indicated capacity did not exceed 0.05 mL

Powder of black pepper (40 g, enough to yield 2 to 5 mL water) was placed in a distillation flask. Solvent was added to cover sample completely (not less than 75 mL). The receiving tube was filled with solvent (toluene), pouring through top of condenser. Loose cotton plug was inserted through the top of the condenser to prevent condensation of atmosphere moisture in the tube. The flask was heated to boil and distill slowly at the rate of 2 drops/see, until most of water distilled over. Then, the rate of distillation was increased to about 4 drops/sec. The distillation was continued till two consecutive readings at 15 minutes intervals, showed no change. IT there was any water held upon in condenser it was removed with brush of wire loop. The condenser was rinsed carefully with about 5 mL toluene. Distillation was continued for 3 to 5 minutes, after which the receiver was cooled to room temperature (about 25 C) by immersing it in water. Solvent and water layers became clear. The volume of water collected was noted to the nearest 0.01 mL and the moisture content (percent) was calculated on wet as well as dry basis using the following equations, respectively.

$$\text{Moisture content (\% wet basis)} = [V_w/W_s] * 100 \quad (3.4)$$

$$\text{Moisture content (\% dry basis)} = [V_w/(W_s - V_w)] * 100 \quad (3.5)$$

where V_W is volume of water (mL) and W_s is weight of sample (g). The reported values were the mean of triplicate observations.

3.2.1.3 Volatile oil Content by Clevenger's Method

Spices and condiments are valued for their exotic aroma which is due to the presence of natural volatile oil or essential oil mostly comprising volatile organic compounds such as monoterpenes, sesqueterpenes and their oxygenated derivatives. A special Clevenger's apparatus (Fig. 3.2) with minor modifications, is universally accepted for use to obtain volatile oil that is insoluble in water is obtained by steam distillation process (Pruthi, 1998).

The apparatus consists of a flask (shortneck, 1 or 2 L round-bottom) with an T.S.24/40 ground joint, an electric heating mantle or oil bath, variable voltage transformer to control heat, volatile oil traps, Clevenger with T.S. 24/40 ground joints, wet condenser, 400 mm length with drip tip and T.S. 24/40 ground joints (Fig. 3.2).

Powder of black pepper (50 g) was weighed and transferred to a flask. About 500 mL of distilled water was added to the flask and antifoaming beads were also added. The flask was heated to boiling and maintained a reflux rate of 1 to 2 drops per second. Refluxing was continued until two consecutive readings taken at 1 hour interval, showed

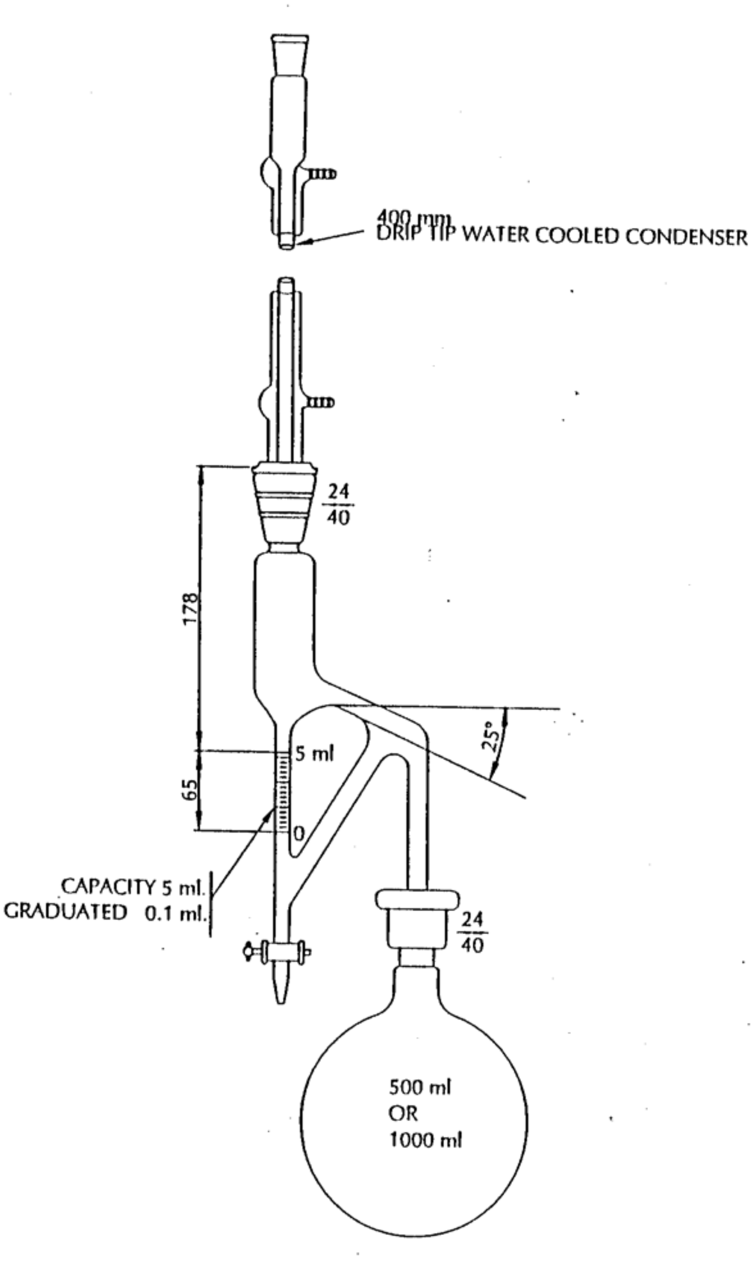


Fig. 3.2 Clevenger's distillation apparatus for determination of volatile oil content in black pepper powder

no change of oil volume in the trap. It was cooled to room temperature by immersing in a water bath. The volatile oil content (moisture free basis, mL/l00g) was calculated using the following equation (Eq.3.6).

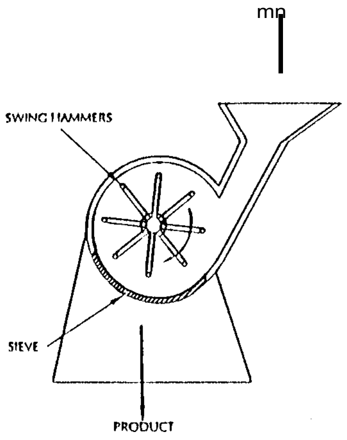
$$\text{Volatile oil content} = \text{Volume of volatile oil} \times 100 / (\text{Dry weight of sample}) \tag{3.6}$$

where volume of volatile oil was measured in mL. Analyses were carried out in triplicates. Average value of volatile oil content, on moisture free basis, expressed in the unit of mL/100g of sample was reported along with standard deviation values.

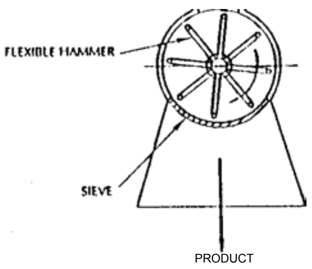
3.2.2 Performance Studies of the Grinding Mills of Various Capacities

In these studies, cleaned black pepper samples were used. The grinding zones of the machines were cleaned thoroughly using hot water and machines were dried, followed by cleaning with acetone. The samples were ground continuously in various mills until the temperature of the ground material reached stabilisation. These samples were then, drawn at the stabilised temperature for determination of volatile oil and gas chromatographic (OC) analysis. Mills employed were Swing Hammer Mill (capacity 5 kg hr^{-1}), Hammer Mill (APEX make, capacity 5 kg hr^{-1}, Plate mill (DIAF type, capacity 5 kg hr^{-1}, Plate Mill (10 kg hr^{-1}) and Roller Mill (about 100 kg hr^{-1}). In swing hammer mill, a sieve with 1 mm opening was used, while in hammer mill 0.025 inch (0.625 mm) sieve was used. Plate (DIAF) mill and Plate mill did not have any provision to introduce sieves for control of size reduction, but there was provision to vary the gap between stationary and movable plates. In the roller mill, the raw material was passed thrice between the same rollers. The samples were compared with hand pounding (mortar & pestle) using traditional method of impact forces. In all the cases, the powder obtained was visually observed to be of nearly uniform size. The schematic diagrams of these machines are given in Fig. 3.3.

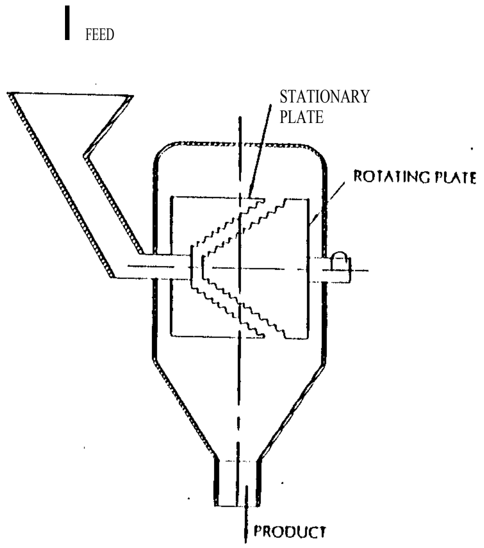
i)



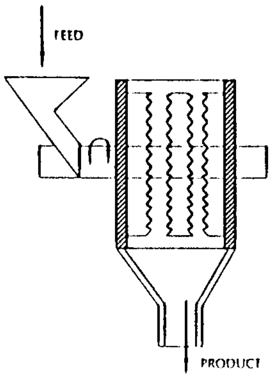
(a) SWING TYPE HAMMER MILL



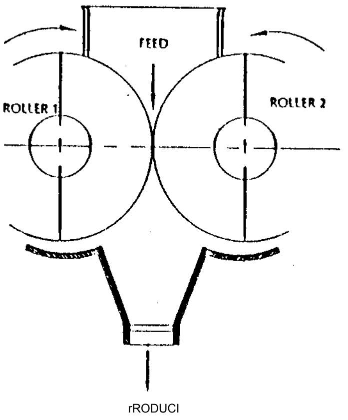
(B) HAMMER (APEX) MILL



(C) PLATE (DIAT) MILL



(d) PLATE MILL



(e) ROLLER MILL.

Fig. 3.3 Schematic diagrams of grinding machines employed for ambient grinding

3.2.2.1 Analysis of Volatile oil by Gas Chromatography

Analysis of volatile oil obtained from powdered black pepper sample was carried out using Hewlett Packard GC 5730a, fitted with a stainless steel column (3 m x 3 mm) packed with 10% SE-30 on Chromosorb W. Nitrogen (30 mL min^{-1}) as the carrier gas. The injection port and detector (FID) temperatures were maintained at 200 and 250 C, respectively. The column temperature was programmed from 75 C (2 minutes) to 220 C (8 minutes) with an increment of 4 C/minute. The volatile oil samples were diluted 5 times with acetone (10 /μL oil in 40 μL acetone), and an aliquot of 1 μL was injected.

3.2.3 Ambient Grinding Characteristics at Different Particle Sizes

Black pepper samples procured from a local market were cleaned using an air classifier and a sifter and graded to uniform size of approximately 5 mm. Four samples (500 g each) were ground in a swing hammer mill, employing 0.5, 1, 4 and 6 mm sieve openings. Another two samples (viz., PD 1, PD2) of 500 g each were ground in a plate mill (DIAF type) to different particle sizes without using sieves, while varying the gap between the plates. The mills were cleaned, and allowed to reach ambient temperature before each sample was ground. The temperature of the ground material at mills' exits was recorded using a mercury-in-glass thermometer. The speed of the mill was maintained constant for each trial in the respective mill. Ground samples were packed in metallised polyester/polyethylene laminate (Met. PET/PE) pouches and were stored in a refrigerator at 4 C till further analysis.

3.2.3.1 Energy Estimation for Grinding

The theoretical energy input (Es) for size reduction to each particle size (geometric mean particle diameter) was estimated using Bond's energy equation (Eq. 2.11) assuming a constant work index (E_o) of 60 kJ kg^{-1} (Loncin and Merson, 1979) and initial average particle diameter of 5 mm. The initial (d_i) and the final particle sizes (d_{sa}) were in μm for determining energy, and the energy equation became as follows (Eq. 3.7).

$$E_s = E_o\,[(100/\,d_{sa})^{1/2} - (100/\,d_i)^{1/2}] \qquad (3.7)$$

Where E_s is theoretical energy required for size reduction, E_0 is work index, d_{sa} is surface mean diameter and d_1 is average particle diameter of black pepper berries.

3.2.3.2 Volatile oil at Various Time Intervals

The total volatile oil contents of the powders were determined by ASTA (1985) method employing Clevenger's apparatus with 50 g powder as mentioned in Section 3.2.1.3. Whereas in this Section, the volatile oil distilled was measured at intervals of 30 minutes. The heater of the apparatus was turned off for 2 minutes before taking each reading of the volatile oil distilled. The distillation was continued until two consecutive readings, were almost the same. However, for samples PD1, PD2 and PD3, the distillation was terminated after 390, 360 and 360 minutes, respectively as prolonged distillation did not yield much oil. Analyses were carried out in triplicate. Average value of volatile oil content, on moisture free basis, measured mL/l00g was reported with standard deviation.

3.2.3.3 Physical Properties of Volatile oil

The volatile oils obtained from the black pepper samples were analysed for their physical properties viz., specific gravity (AOAC method 30.022, 1980), refractive index (AOAC method 30.023,1980) and optical rotation (AOAC method 19.080,1980).

3.2.3.3.1 Specific Gravity or Relative Density

Specific or relative density at 27 C means the ratio of the densities of the liquid material at 27 C to that of distilled water at 27 C. The specific gravity bottle (10 mL capacity) was washed and cleaned with alcohol and diethyl ether. It was then dried in a current of dry air. The empty specific gravity bottle was weighed (md accurately and was filled with distilled water at about 27 C, taking care to avoid the presence of air bubbles. It was then immersed in water bath maintained at 27 ± 0.2 C for 30 minutes. The temperature of the water bath was checked and the level of distilled water was adjusted to the mark. The specific gravity bottle was closed by using a stopper and the outer side was wiped carefully with a dry filter paper: It was then weighed (m_2) in the same balance. Then, the specific gravity bottle was emptied, washed with alcohol followed by diethyl ether, and finally dried by means of a current of dry air. The bottle was filled with volatile oil at about 27 C, avoiding the presence of air bubble. The bottle was immersed again in water bath maintained at 27 ±·0.2 C for 30 minutes. The volatile oil was adjusted to mark, and the procedure was repeated as stated for distilled water. The bottle with the volatile oil was then weighed (m3) accurately. Specific gravity was calculated as equal to (m3- mi)/(m2- mi) at a temperature of 27 C.

3.2.3.3.2 Refractive Index

Refractive index is the ratio of the sine of the angle of incidence to the sine of the angle of refraction when a ray of light of defined wavelength passes from air into test material kept at constant temperature. The wavelength normally used is 589.3±0.3 nm corresponding with 01 and 02 lines of sodium spectrum. The reference temperature is 27 C except those, which are not liquid at those temperature in which case a higher temperature (say 30 C) depending on the melting point of the material should be used.

Here, a recognised type of refractometer allowing direct readings of refractive indices between 1.3000 to 1.7000 with an accuracy of ±0.0002 was used. The instrument was calibrated with benzyl benzoate to obtain a refractive index of 1.5678 at 27 C. Sodium light, diffused day light or light from an electric lamp may be used for instruments fitted with an achromatic compensator.

3.2.3.3.3 Optical Rotation

The angle through which the plane of polarized light is rotated by a layer of 100 mm thickness of the material under test at a specified temperature is called optical rotation. The wave length of radiation used should be 589.3 ± 0.3 nm.

In this study, polarimeter of precision within ±0.03 degree was used after calibration with reference material by employing a monochromatic light source of wavelength at 589.3 ± 0.3 nm. The light source was switched on and it took a few minutes to get the full luminosity. Zero error of the instrument was determined. The polarimeter tube was filled with material previously brought to the temperature specified, ensuring the absence of air bubbles. The tube was placed in the polarimeter and reading dextrorotatary (+) or laevorotatory (-) optical rotation on the scale of the instrument was taken. The analyser was carefully adjusted in such a way that both halves of the filled when viewed through the telescope was showing illumination of equal intensities. Three readings were taken and the average was reported. The optical rotation values were expressed in circular degree to the nearest 0.0 1 degree.

3.2.3.4 Gas Chromatographic - Mass Spectrometric (GC-MS) Analysis

The volatile oil samples were analysed using Shimadzu 17 A-GC Chromotograph equipped with a QP 5000 (Quadrapole) mass spectrometer. The oil samples were diluted 20 times with acetone (10 µL oil in 190 µL acetone) and 1 µL was injected. The following column along with the conditions was employed in the analysis. Fused silica capillary column, SPB -1, 30 m x 0.32 mm (i.d) coated with poly dimethyl siloxane (0.25 /lm film thickness) was used. The other conditions were carrier gas: helium (1.0 mL/minute), injection port temperature: 150 C, detector (FID) temperature: 250 C, temperature programme: 60(2) -250 (5) C @ 2 C/minute.

3.2.3.5 Diffusion Coefficient in Volatile oil Distillation

The volatile oil present in the powered black pepper samples was distilled using Clevenger's (glass) apparatus. When the mixture of distilled water and black pepper powder (50 g) was heated, the volatile oil components in black pepper shall be diffused into water at 100 C during distillation. As there was sufficient agitation of water-powder mixture (due to buoyant forces) while boiling in the Clevenger's apparatus, the surface resistance becomes small. Further, it can be assumed that the total resistance is due to only the 'internal resistance' and the phenomenon was modeled using Fick's second law (Selman et al., 1983).

Assuming the powdered particles to be spherical in shape, and using the unsteady transfer equation, Fick's second law (Crank, 1970) may be depicted as

$$(\partial u/\partial t) = D_e\, (\partial^2 u/\partial r_l^2) \qquad (3.8)$$

with boundary conditions;

$u = 0,\ r_l = 0,\ t > 0$

$u = a_r\, Co,\ r_l = a_r,\ t > 0$

$u = r_l f(r_l),\ t = 0,\ 0 < r_l < a_r$

where D_e is effective diffusion coefficient of oil from powder to water and C_o is the constant concentration at the surface.

The solution to Eq. (3.8) (Crank. 1970) is given by

$$M_t/M_f = 1- [(6/\Pi^2)\, \sum n=_{1 \text{ to } \infty} \quad \{(1/n^2)\exp(-(D_e n^2 \Pi^2/r_s^2)t)\}] \qquad (3.9)$$

where M_t is the total amount of diffusing substance leaving the sphere in time t, M_f is initial volatile oil content in the powder sample, rs is surface mean radius of powder sample and n varying from one to infinity.

With n=l and neglecting higher order terms, Eq. (3.9) can be rewritten as,

$$\text{In}(M') = - K.\ t$$

(3.10)

where $M' = (\Pi^2/6M_f).\ (M_r-M_t))$ and

(3.11)

the slope, $K = D_e\, (\Pi^2/\, r_s^2)$

(3.12)

Plotting of Eq. (3.10), with In(M') versus t, would give a straight line, from where the diffusion coefficient (D_e) could be evaluated.

3.3 Cryogenic Size Reduction or Grinding of Black Pepper

3.3.1 Cooling, Chilling and Cryogenic Freezing Methods

Black pepper samples procured from the local market, was cleaned and graded to have an uniform size using a sifter. The samples of 100 g each were used for grinding experiments. In all the cases, the temperatures of raw material before grinding and after grinding were recorded. A stainless steel domestic mixer jar (2 litre capacity) was slightly modified by providing a water jacket (Fig. 3.4) for cooling purpose. The outer wall of the jacket was thermally insulated. The grinding experiment was repeated three times in each condition.

Sample CAI was packed in a polythene bag and sealed. It was stored in a cold room maintained at + 10 C, for 8 hours, after which the same was immediately ground after removing them from the cold room. Sample CA2 was also packed in a polythene bag and sealed. It was placed in a Plate freezer chamber for 4 hours for chilling. After removing from the plate freezer, the sample was immediately ground Sample CA3, was immersed in a liquid nitrogen tank for I minute. It' was ground immediately after removing them from the liquid nitrogen tank. Sample CA4 was separately taken in the jar and about 200 mL of liquid nitrogen was poured on to the samples. The sample was then ground immediately in the bath of liquid nitrogen. Sample CA5 was ground under ambient conditions (25 C). The schematic diagrams of the cooling, chilling and freezing methods are shown in Fig. 3.5.

3.3.2 Cryogenic (LN_2) grinding and Volatile oil Content on a Laboratory Set-up

The raw material was cleaned using an air classifier and a sifter. A sample of black pepper (l50g) was placed in a domestic grinder jar and about 300 mL of liquid nitrogen was mixed with black pepper. Grinding was conducted using a constant motor speed of 14500 rpm for 3 minutes. The temperatures of raw material after mixing with liquid nitrogen, and after grinding were recorded with the help of a copper-constantan probe thermometer. The experiment was repeated four times. The other sample was

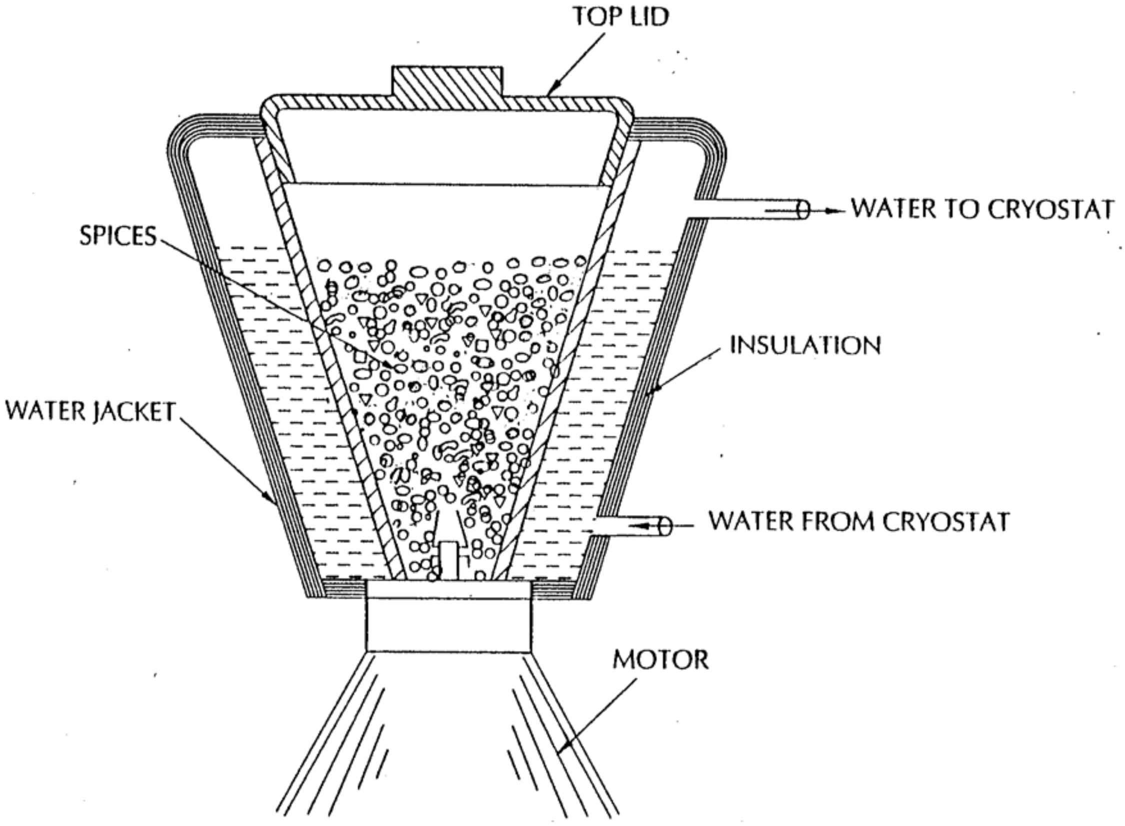
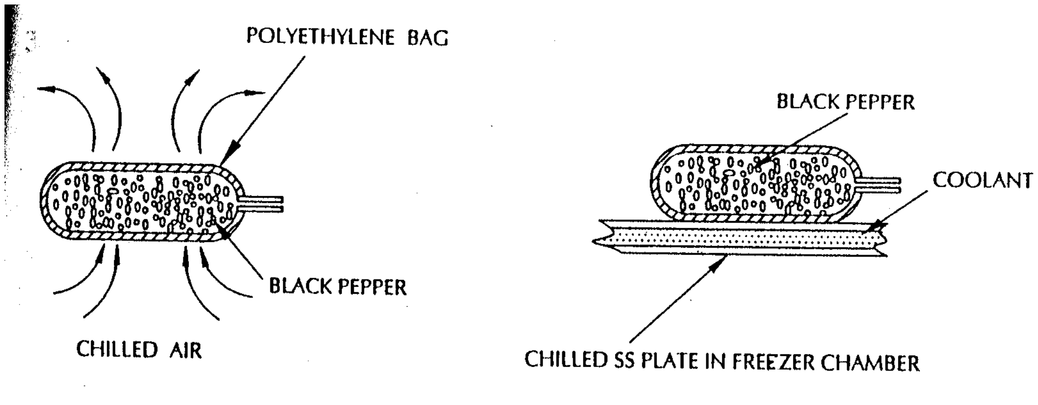
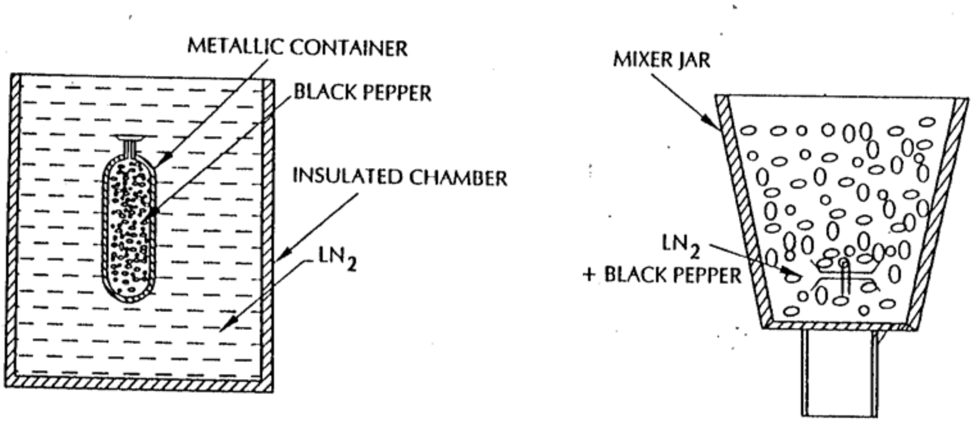


Fig. 3.4 Experimental set-up for grinding of black pepper (laboratory scale)



(1) COLD ROOM(CA1)

(2) PLATE FREEZER(CA2)



(3) LN2 (INDIRECT) FREEZING
(CA3)

(4) LN2(MIXING) FREEZING
(CA4)

Fig. 3.5 Schematic diagrams of cooling, chilling and cryogenic freezing systems ground using ambient condition (25 C), with the same speed and the grinding time as mentioned earlier. The volatile oils in the samples were distilled using Clevenger's method.

3.3.3 Effect of Cryogenic, Chilled, Ambient and High Temperature Grinding Methods on Grinding Characteristics

A domestic mixer jar (Waring blender type) was used for grinding black pepper. The stainless steel mixer jar (2 litre capacity) was slightly modified by providing a water jacket. The outer wall of the jacket was thermally insulated (Fig. 3.4).

For attaining the chilled (10 C) temperature of raw material, black pepper was placed in the mixer jar and chilled water was circulated through the jacket while maintaining the temperature by connecting the jar to a cryostat. The system was allowed to reach the set equilibrium temperature by running the cryostat for about 3 hours. Similarly, for attaining the high temperature (40 C) of raw material, hot water was circulated through the jacket.

For cryogenic grinding, about 200 mL of liquid nitrogen was poured on to the material taken in the mixer jar prior to grinding of sample and a feed temperature of -120 C was attained. Sample which was at the ambient temperature of 24 C, was also ground. The samples were stabilized at a pre-set feed temperature, prior to grinding. A grinding time of 3 minutes with a motor speed of 14500 rpm and samples of 150 g were used for all the experiments. The ground powder was packed in metallised polyester/polythene laminate (Met. PET/PE) pouches and stored in a refrigerator at 4 C for subsequent analysis. The different unit operations of the process are depicted in Fig. 3.6.

3.3.3.1 Sieve Analysis

Fineness of the product was determined by standard sieve analysis, using 60 mesh sieve (Taylor series, with an opening of 0.250 mm) as per British standard method of test for spices and condiments (BS 4585:Part 8: 1977/ISO-3588-1977). Weight of particles passing through the sieve of 60 mesh with 5 minutes of shaking time was recorded.

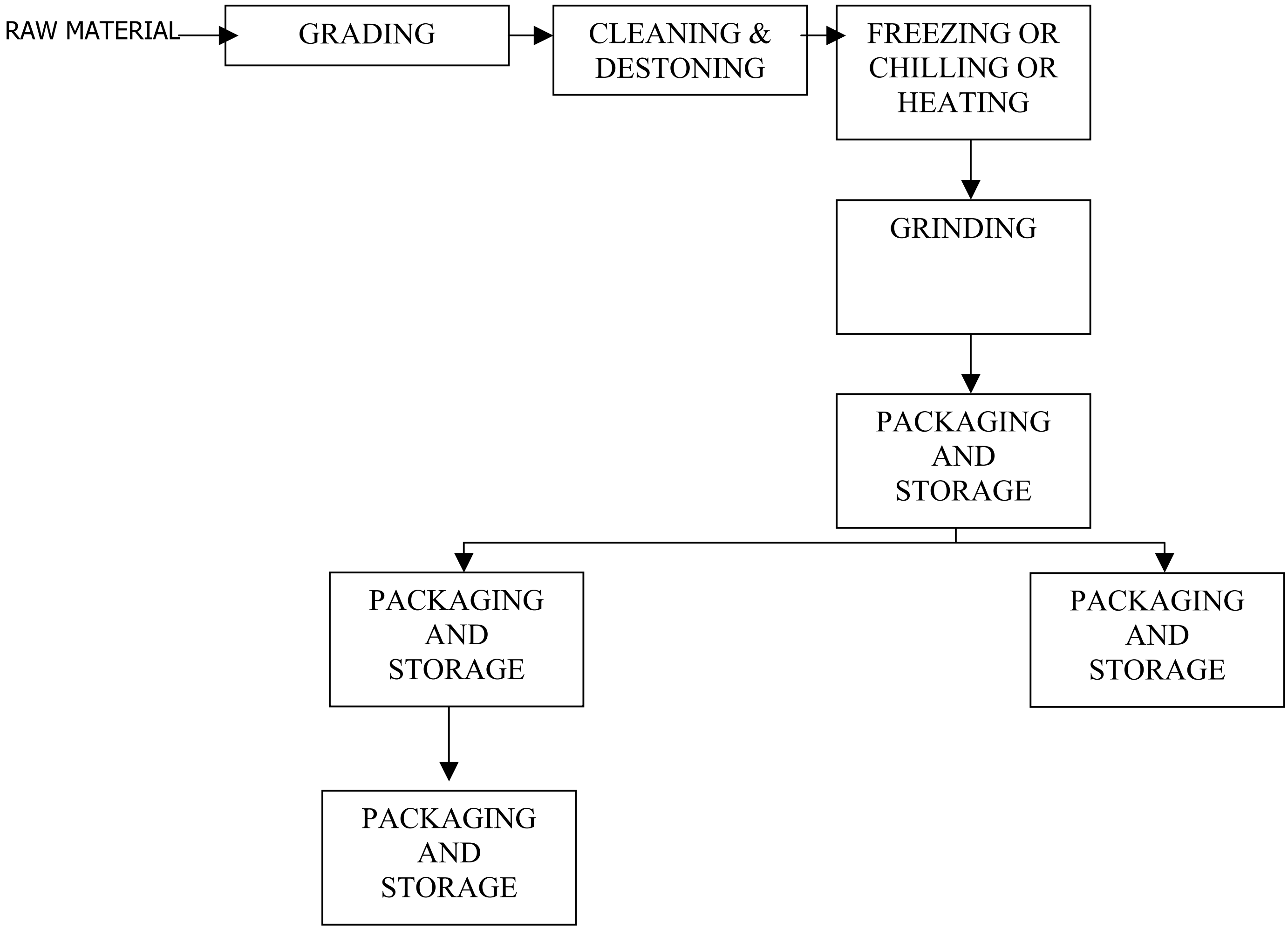


Fig. 3.6 Flow chart of unit operations used in grinding

3.3.4 Cryogenic Grinding in Pilot Scale

The samples of black pepper were obtained from a local spice processor. The variety was *Malabar* with low oil content and medium size (about 4.1 mm in diameter). These were cleaned for brokens and immature seeds, and- foreign matters.

The experiments were conducted using a pin mill (Hosokawa Alpine, Germany, capacity 80 kg hr^{-1}, 3.7 kW motor, 3 phase, 440 V, stainless steel construction) as pin mills are employed for very fine grinding and higher capacity (Pruthi, 1980). The schematic diagram of cryogenic grinding set up is shown in Fig. 3.7.

The compressor was run before starting the experiments. The outlet valve of the compressor was opened slightly so as to get the required pressure in the liquid nitrogen *dewar* flask depending upon the grinding temperature to be maintained according to the experimental design. The valve of transfer line was opened to enable the liquid nitrogen flow into the grinding zone. Black pepper (4 kg) was loaded on to the hopper which was connected to the grinding zone through a vibratory sieve. Feed rate was adjusted to the desired value as per the experiment design. Temperature sensor was located immediately below the mill's outlet in such a manner that it could measure the temperature of the ground product just before coming out after grinding. The grinding trials were carried out by directly introducing liquid nitrogen into the grinding zone of the pin mill at a controlled rate to maintain the desired range temperature (-15 to 60 C) with a variation of about ± 4 C during experimentation. The grinding temperature was maintained by controlling the flow of liquid nitrogen manually by operating the transfer line valve. The feed rate of black pepper into the mill was varied as per the experimental design. All the experiments were repeated twice.

3.3.4.1 Design of Experiments and Response Surface Methodology

A 2 variable (5 levels each), central composite rotatable experimental design (CCRD) with 4 replications at the center points (0,0,0,0) (Myers, 1971) in coded levels of variables was employed wherein the independent variables were the feed rate of black

pepper (X_1) and the product temperature of black pepper powder (X_2). The coding of the variables were done according to the Eq. (3.13):

j)

$$x_i = \frac{X_i - X_i}{Interval} \qquad (3.13)$$

where i = 1 to 2; the interval refers to the difference in actual levels of variables (corresponding to the difference between 1 and 0 in coded level of variables. The term $\overline{X_i}$ is the mean of X_i

The experimental design in the actual (X) and coded (x) levels of variables are shown in Table 4.3.7 (Please see Results & Discussion). The response function y, I.e. and quality of volatile oil, geometric mean particle diameter and energy expenditure, contents of monoterpenes and sesqueterpenes, is expressed in terms of the independent variables as

$$y = f(x_1, x_2) \qquad (3.14)$$

The response function was approximated by a second degree polynomial (Eq.3.15) with linear, quadratic and interaction effects using the methods of least squares (Little and Hills, 1978).

$$y = b_o + \sum_{i=1}^{n} b_i x_i + \sum_{\substack{i=1 \\ i \leq j}}^{n} \sum_{j=1}^{n} b_{ij} x_i x_j + \varepsilon \qquad (3.15)$$

The number of variables is denoted by n, i & j are integers. The coefficients of the polynomial are represented by b_o (constant), b_i (linear effect), b_{ij} (quadratic effect when $i = j$ and interaction effect when $i < j$) and ε is the random error.

The effect of individual linear, quadratic and interaction terms was determined (Khuri and Cornell, 1989). The significance of the terms in the polynomial was judged by F test at a probability (p) level of 0.0 1, 0.05 or 0.10. The significance of the multiple correlation coefficient (r) was judged at a probability level of 0.01. The analysis of variance (ANOVA) table is reported for the response function (y). The regression equation is also expressed in the actual levels of variables (X) for convenience in use. The response surface graphs were obtained from the regression equations, keeping the response function on the Z axis with X and Y axes representing two independent variables.

The levels of the variables (X_1, X_2) (within the experimental range) to obtain a maximum volatile oil were determined by employing canonical analysis (Khuri and Cornell, 1989; Myers, 1971). In brief, the analysis consisted of the translation of the response function (y) from the origin to the stationary points (x_o). Then the response function was expressed in terms of new variables, the axes of which correspond to the principal axes of the contour system. The optimization of the variables were conducted by superimposing the contour plots of more than one desired response function.

3.3.4.2 Energy Expenditure for Grinding

The energy expenditure for grinding of black pepper was determined by measuring the current using an ammeter, using the following Eq. (3.16);

$$P = (\sqrt{3})\, V\, (I - I_o)\, \eta\, \mathrm{Cos}\phi \tag{3.16}$$

where P is power (W), V is voltage (V), I is the measured current (A), 10 is the no load current (A), ll is the motor efficiency (0.95) and Cosθ is the power factor. No load current was subtracted from the total current to arrive at the actual energy consumed during grinding. The energy expenditure for grinding (E_G) was then calculated at different feed rates according to the following equation (Eq. 3.17).

$$E_G = (3.6\, P \,/\, \text{mass feed rate}) \tag{3.17}$$

where EG is energy expenditure (kJ kg^{-1}), P is power (W) and mass feed rate is in kg hr^{-1}. The energy values of cryogenic grinding were statistically compared with DMRT test. All tests were repeated twice.

3.3.4.3 Sensory Studies of Powdered Samples

Odour profiles were carried out by, 12 trained panel of age group 28-50 years from both sex. The training sessions were conducted with the reference chemicals that gave the odour notes present in top notes and secondary notes of ground black pepper. The reference chemicals are shown in Table 3.1. These sessions were followed by further training with a fresh harvest to stored ground black pepper. The samples were presented to panellists after sufficient accumulation of head space volatile in room temperature.

Table 3.1

Reference chemical compounds and their odour notes used in sensory analysis of ground black pepper

Serial No.	Compound	Odour note
1	α-terpineol	Floral
2	Acetophenone	Irritant, sharp
3	Hexanal	Green, green apple
4	Nerol	Fresh floral, herbal
5	Nerolidol	Mild spicy/rooty
6	1,8- cineol	Camphory
7	Dihydrocarveol	Warm, woody
8	Citral	Citrussy
9	α-pinene	Terpenic, oxidised
10	Piperonol	Sweet, floral

The panellists were trained to mark the intensity of the perceived odour on a horozontal line scale of 10 cm score card, anchored at two ends as low and high. The tests were carried out in three repetitions of all the experimental samples and as sets of four to eliminate panel fatique. Coded duplicate samples were presented each time to check the consistency of panel performance. The panellists examined the top notes, basic notes and defective notes followed by overall quality.

The data accumulated were collected as the measured distance on the line scale in centimeters from the beginning up to the point where the horizontal line is cut. These data points were further edited for total out layers. The mean and standard error were calculated for further analysis. The attributes were plotted on a 10 point scale. The overall quality grading indicate that the mean score of up to 2 is not usable, 3 and 4 is poor, 5 is average, is fair, 7 and 8 is good, 9 and 10 is very good (Narasimhan *et al., 1990).*

CHAPTER 4: RESULTS AND DISCUSSION

CHAPTER 4

RESULTS AND DISCUSSION

This chapter has been divided into three Sections for presenting results, followed by discussion. The physical and mechanical properties of spices have been classified under the Sections on engineering properties of black pepper. Conventional grinding aspects have been classified under the Section on ambient grinding. Cryogenic grinding aspects have been classified under the Section on cryogenic size reduction.

4.1 Engineering Properties of Black Pepper

Engineering properties of foods are important from the points of view of storage design, processing and handling/conveying systems (Mohsenin, 1986). However, the engineering properties are topics by themselves comprising of physical properties, relating to size, shape, etc., thermal properties, aerodynamic properties, mechanical properties, etc.

4.1.1 Moisture Dependent Engineering Properties

The study on engineering properties of black pepper has been restricted only to selected properties or characteristics related to grinding. The physical properties such as size, shape etc., and mechanical properties such as angle of repose, flowability, uniaxial compression, etc., have been studied at different moisture contents as black pepper processing industries invariably receive materials with different moisture levels. The material used for this study is cited in Section 3.1.1, whereas methods employed to determine these properties are described in Section 3.1.2 to 3.1.7 of Materials and Methods (Chapter 3).

4.1.1.1 Size

Sizes of spices decide the sieve to be used for screening and handling. The frequency distribution for the dimension (maximum and minimum) of the seeds (at 11.1 % moisture content, dry basis), at an interval of 0.2 mm, is shown in Fig. 4.1.1, whereas, Fig. 4.1.2 shows the cumulative frequency distribution. About 20% seeds had the maximum dimensions between 5.20 and 5.39 mm, whereas, 24% seeds had minimum dimensions between 4.80-4.99 mm (Fig 4.1.1). A nearly bell shaped curve was obtained in both the cases. The mean size of the seed obtained was 5.12 ± 0.48 mm at a moisture content of 11.1 % (dry basis). On the other hand, when the curhulative frequency was plotted (Fig. 4.1.2) against size intervals, a sigmoid type curve was obtained for the maximum size but an exponential curve resulted when the frequency data were plotted against minimum size. The 1000-seed weight was 60.5 ± 2.4 g at this moisture level. The change in size (Fig. 4.1.3) of the sample with increase in moisture content, though showed a slight increasing trend, was not statistically significant ($p \leq 0.05$) according to Duncan's multiple range test (DMRT). This might be due to the absorption of moisture in the pore spaces of the fibrous structure of black pepper seed, and so, the size remained fairly constant.

4.1.1.2 Sphericity and Roundness

Sphericity can be defined as the ratio of the surface area of a sphere (Eq. 2.1), which has the same volume as that of the solid, to the surface area of the solid. On the other hand, roundness (R_d) of a solid (Eq. 2.2) is a measure of the sharpness of its corners (Mohsenin, 1986). A minimum Rd value of one is for a perfect sphere, and an increase in the same shows even more sharpness in the seed. Both these values (Fig. 4.1.3) were not affected by the change in moisture content. The experimental roundness and sphericity values were in the neighbourhood of 1.1 and 95%, respectively indicating a near spherical shape of the seed. The variations in the experimental results, as indicated by the error bars in Fig. 4.1.3, are expected as biological materials usually show such variations due to maturity and other agronomical factors.

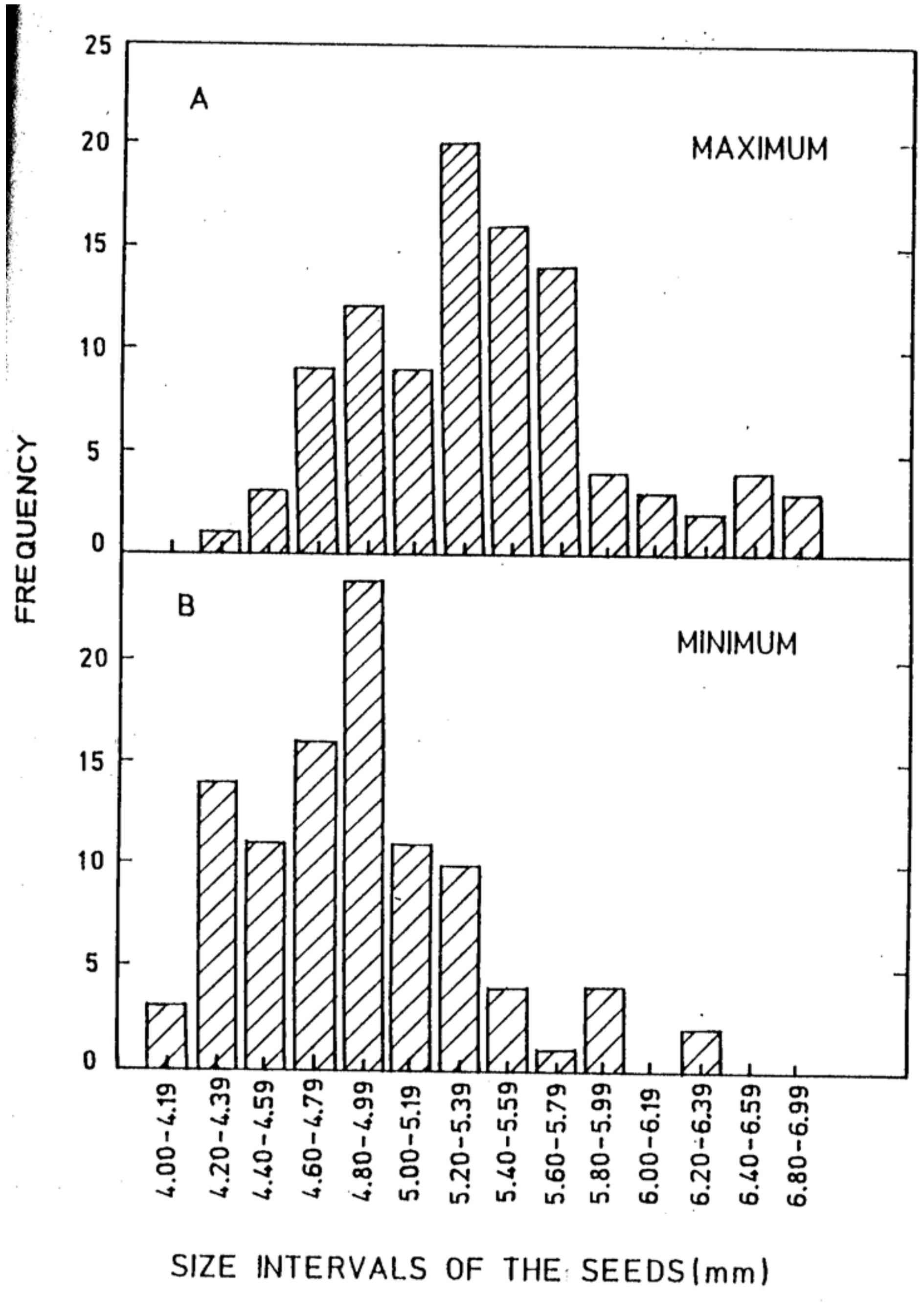


Fig. 4.1.1 The frequency distribution for the dimension of the black pepper seeds (A) Maximum dimension; (8) Minimum dimension

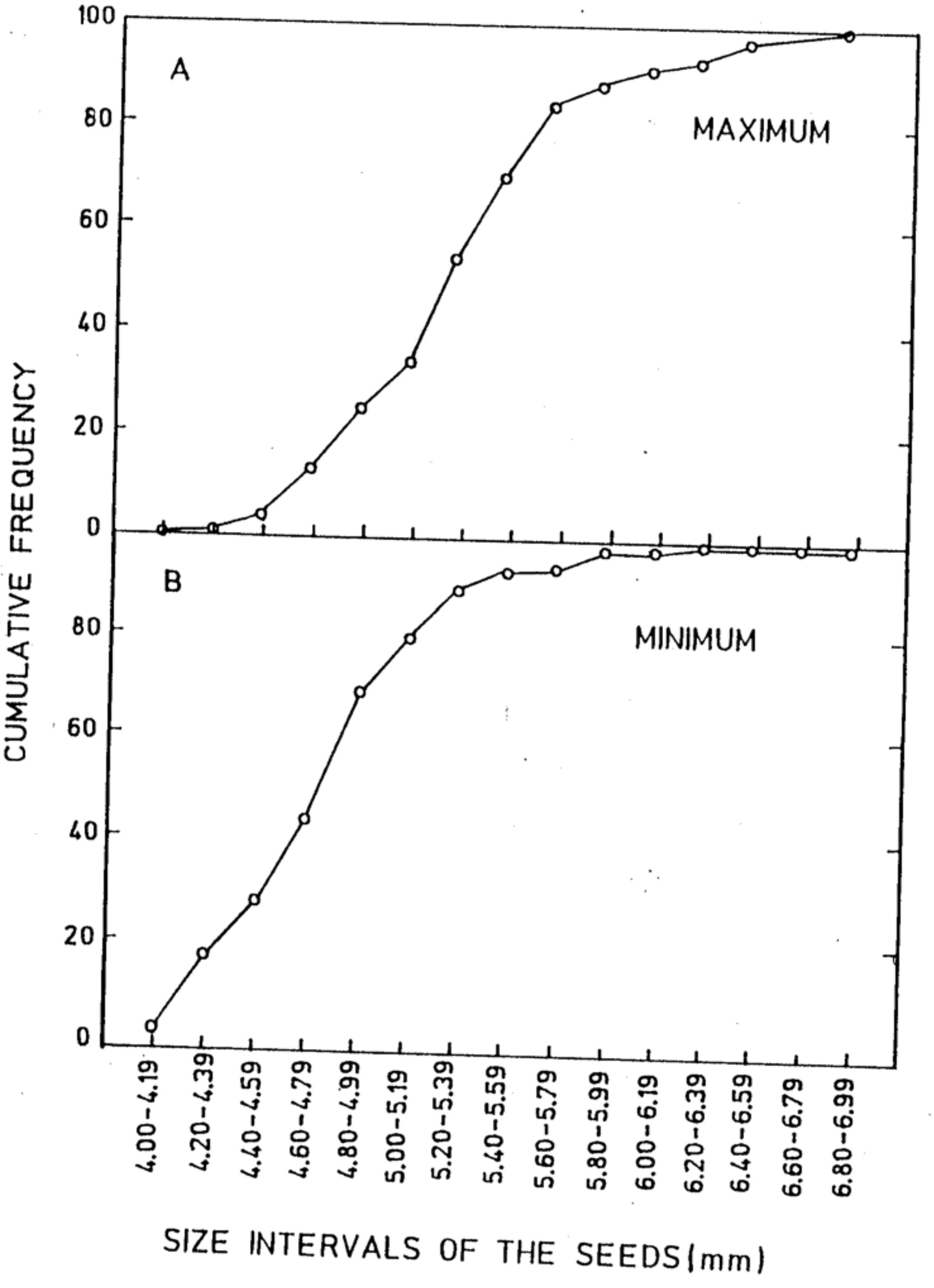


Fig. 4.1.2 Cumulative frequency for the dimension of black pepper seeds, plotted against size interval. (A) Maximum dimension; (B) Minimum dimension

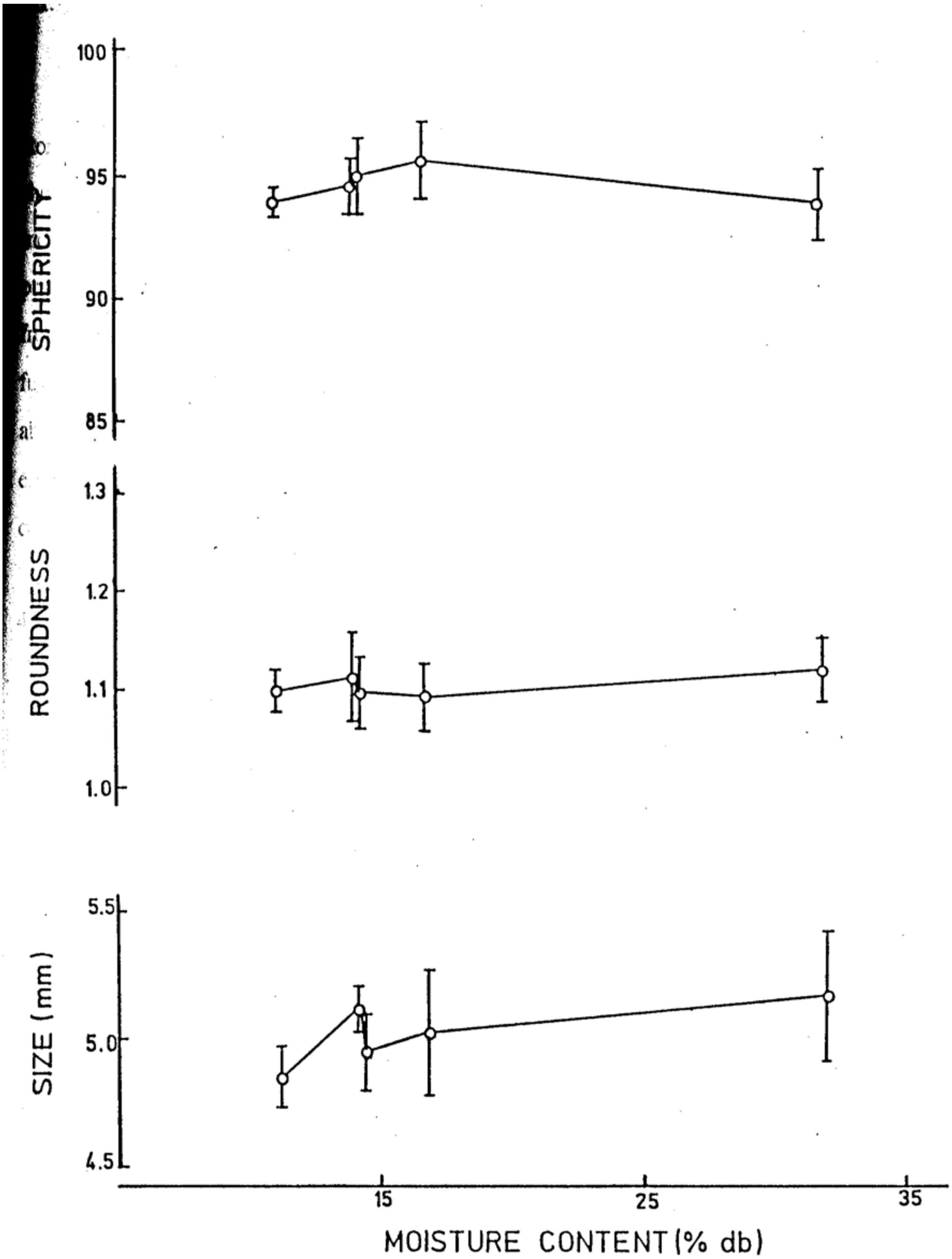


Fig. 4.1.3 Variations of mean size, roundness and sphericity of black pepper seed with moisture content

4.1.1.3 Bulk Density

Bulk density (P_b), is particularly important from the point of view of designing the 'age system of black pepper seeds prior to processing. The bulk density of the seeds showed a complex behaviour with respect to moisture content (Fig. 4.1.4). Initially, it reased marginally with an increase in moisture content. This was due to the filling of the pores and surface cracks by moisture without increasing the volume. According to Fig. 4.1.4, from about 14% moisture onwards, there was an increasing trend in size (diameter). A further increase in moisture (above 14%) led to visible (but erratic) decreases in ρ_b-values about which no explanation would be given. The present findings did not conform with the earlier reports that their existed simple negative linear relations between ρ_b and moisture content for millets (Visvanathan *et al.,* 1990), and for chick pea (Dutta et al., 1988).

14.1.1.4 Dynamic Angle of Repose and Flowability

The movement of material largely depends on angle of repose. In addition, the design of funnels and hoppers are mainly based on angle of repose. The movement of seeds during conveying is also equally important when they are allowed to fall under gravity. Therefore, the flowability of seeds was determined in terms of funnel flow time (Section 3.1.6).

The angle of repose (θ) (Fig 4.1.5) and funnel flow time (a measure for flowability) (Fig 4.1.6) varied between 35.4 ° and 48.2°, and between 5.2 and 7.7 s, respectively; both showing an uniform increasing trend with the moisture content. This was expected as cohesiveness would increase with an increase in moisture content for many food products and particulate foods, such as, moist grain and powders, and even for highly inert inorganic substances, e.g., sand. In the initial stage, an increase in moisture content from 8 to 14% hardly affected these indices but a marked increase was observed when the moisture content exceeded 14%. An increase in 8-values with an increase in moisture content was reported for different seeds (Visvanathan *et al.,* 1990; Dutta *et al.,* 1988). The former researchers reported a linear relationship ($r \geq 0.97$), whereas, the latter mentioned a quadratic equation ($r = 0.99$) to suit their results. The results of the present study showed a linear equation as θ

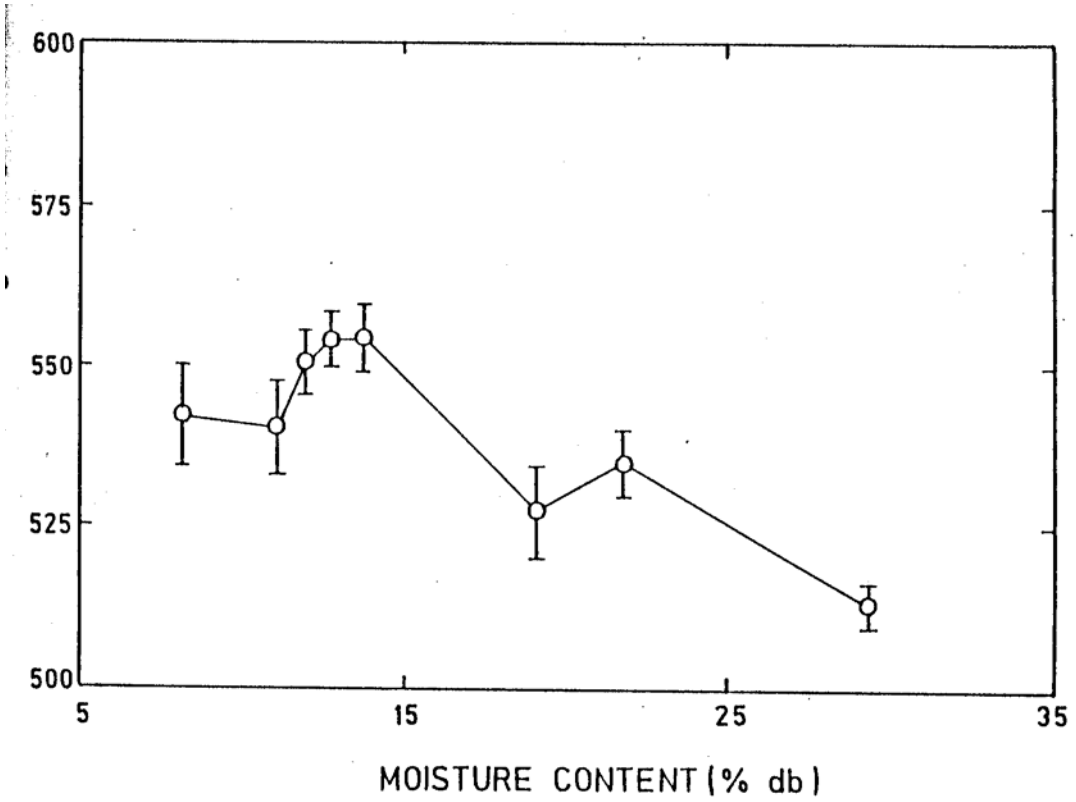


Fig. 4.1.4 Bulk density at different moisture contents of the seeds

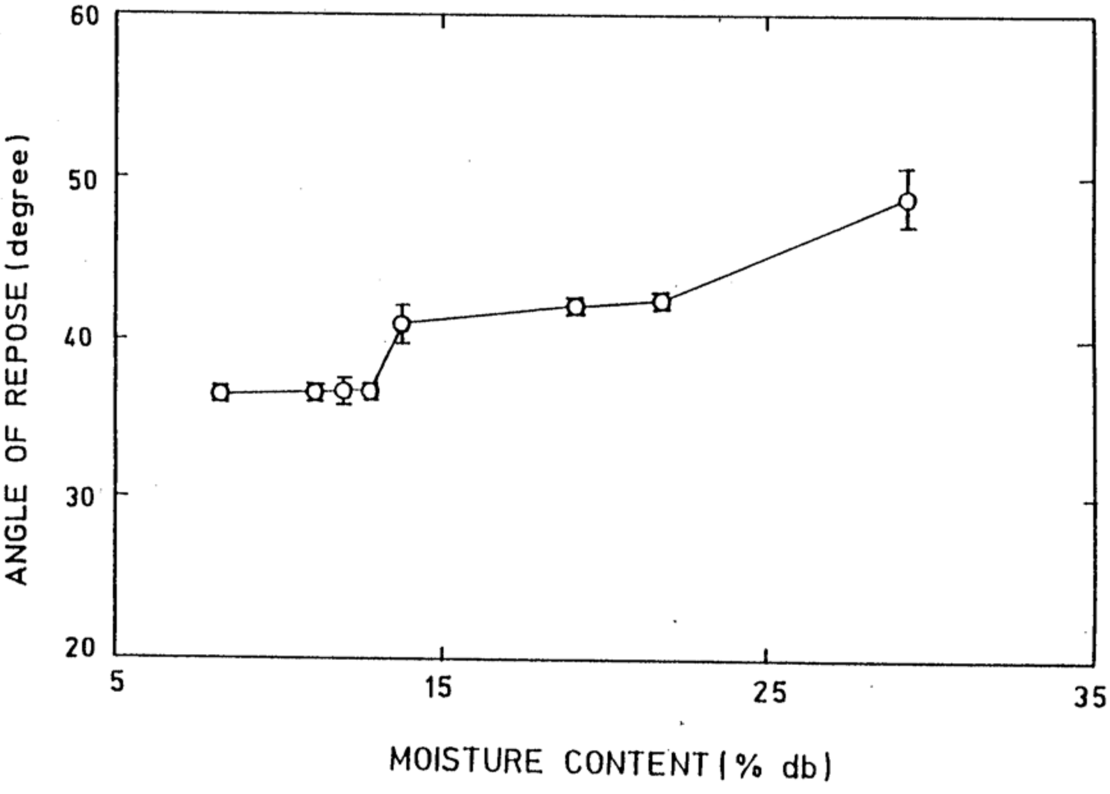


Fig. 4. I .5 Angle of repose at different moisture contents of the seeds

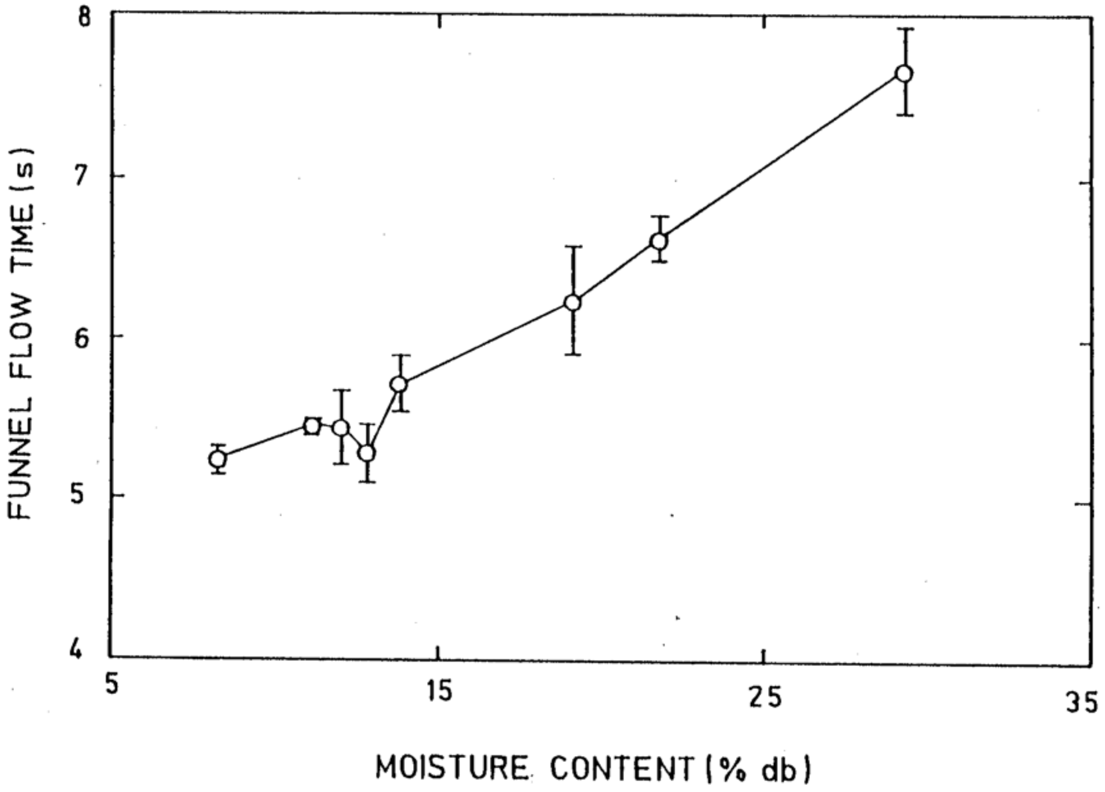


Fig. 4.1.6 Funnel flow time at different moisture contents of the seeds

= 30.45 + 0.60 M, with a r-value of 0.96 ($p \leq 0.01$) where 8 is dynamic angle of repose and M is the moisture content. The r-values did not improve even when the order of the equation was increased to second or third.

4.1.1.5 Uniaxial Compression and Failure Behaviour

When· black pepper seeds are subjected to grinding compression is the most common force employed (Section 2.3.1, Loncin & Merson, 1979 and Prasher, 1987). Hence, compression of the seeds at different moisture contents was studied employing the technique of uniaxial compression. The failure characteristics were also determined.

The different parameters (failure force: F_f, failure strain: ε_f, linear strain limit: failure energy: E_f and deformation modulus: E_d), derived from the uniaxial compression study on black pepper seed at various moisture contents, are shown in Table 4.1.1. The generalised force-deformation curve (Fig. 4.1.7) shows the visco-elastic nature of the whole seed during compression (till failure). Initially, at low compression force, the seed offered little resistance towards compression, and exhibited a linear relationship that could be designated as the elastic behaviour of the seed. The soft outer coat possibly could offer little resistance during the initial stages of compression. Once the outer coat was compressed, the inside hard core offered considerable resistance, resulting in a line with large gradient thus denoting plastic behaviour. As the extent of compression was increased, the seed suddenly ruptured into two segments (this was the failure point) and thus the force decreased drastically. The portion of the curve beyond the failure point would have little importance.

An increase in moisture content reduced F_f and E_f values (Table 4.1.1); the decrease in F_f being uniform, whereas, the decline in E_f was noticed only at high moisture content of the seed (31.9%, db). At a low moisture content, it was the outer coat that mostly absorbed moisture, whereas, increased moisture addition allowed the inner core to absorb moisture gradually. Thus, with the increase in the moisture content, the inner core became markedly soft only when the moisture was high (31.9%, db). This was expected as the whole seed becomes soft at high moisture level. Further, moisture altered the mechanical strength of the product by plasticising and softening the starch/protein matrix.

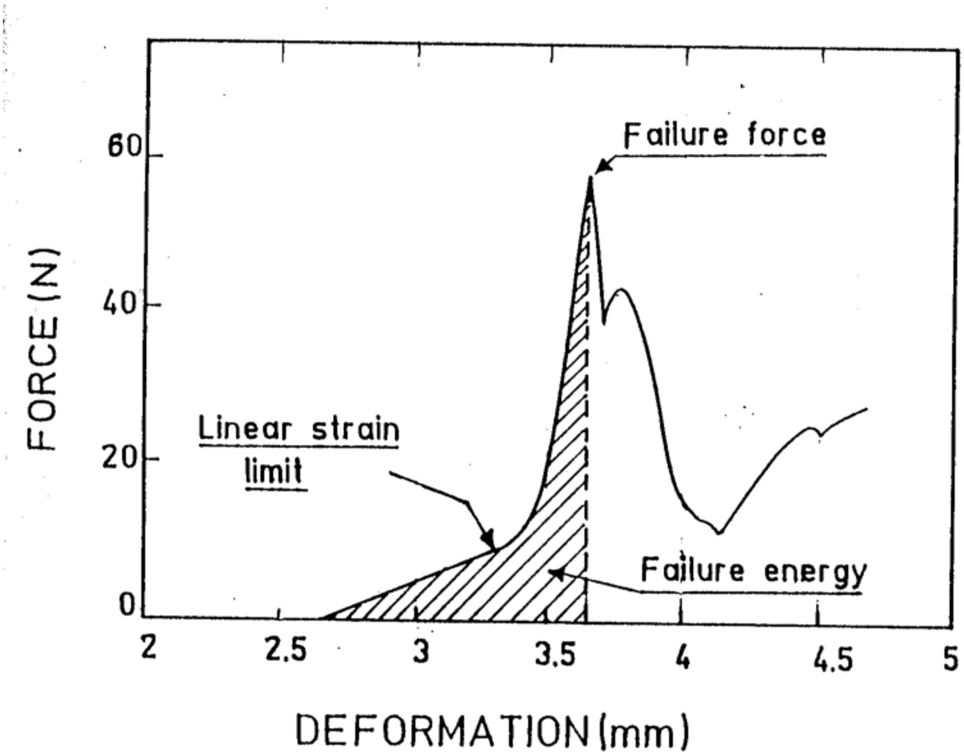


Fig.4.1.7 Uniaxial compression curve for black pepper seed showing the different parameters

Table 4.1.1

Parameters derived from uniaxial compres~ion testing of black pepper

Moisture content M (%, db)	Failure force Fr (N)	Failure strain Er (%)	Linear strain limit EI (%)	Failure energy Er (J)	Deformation modulus Ed (N mm-^{l})
11.1	70.0 ± 15.3	16.6 ± 3.3	.7.9 ± 1.2	0.022 ± 0.003	44.5 ± 15.4
14.0	66.8 ± 12.3	18.5 ± 4.2	8.6 ±0.9	0.025 ± 0.006	40.3 ± 13.5
14.6	66.5 ± 10.6	18.5±2.1	8.3 ± 1.7 .	0.022 ± 0.004	39.7 ± 10.8
16.8	55.6 ± 8.9	20.9 ± 3.4	8.7 ± 1.2	0.021 ± 0.003	28.6 ± 6.5
31.9	38.9 ± 8.1	29.1 ± 4.4	12.2 ± 0.8	0.014 ± 0.002	14.1 ± 3.9

There are conflicting reports on the effect of moisture content on these parameters. Paulsen, (1978), Hoki and Tomita (1976) and Liu *et al.* (1990), reported decrease in F_f values for soybean with increase in moisture contents. This phenomenon was found to be true for the present work also. On the other hand, the compressive strength for snap bean *(Phaseolus vulgaris* L.) was reported to increase (Bay *et al.,* 1996) with elevation in moisture content. Therefore, in addition to the above, other compression properties (failure strain, linear strain limit and deformation modulus) as a function of moisture content were also determined (Table 4.1.1). The results showed that the linear strain limit increased with an elevation in moisture indicating that the seeds would exhibit an enhanced extent of elastic behaviour at high moisture levels. It thus would fail only at a high level of compression (i.e., failure strain increases). The values for deformation modulus decreased markedly. Therefore, it was easy to break or fracture black pepper seeds at a high moisture content with the application of low compressive force. The failure energy of seeds was fairly constant to a value of about 0.02 J when the moisture content was between 11 and 17% (db). As the moisture content was increased beyond 17%, the failure force was decreased markedly (Table 4.1.1) with simultaneous decreases in the slopes of both the zones (elastic and plastic behaviour), leading to a notable decrease in deformation modulus.

4.1.1.6 Conclusions

The study on the determination of selected moisture dependent engineering properties relating to grinding gave the following conclusions:

1) Black pepper seeds had a near spherical shape as reflected by roundness values (close to 1) and high sphericity values (close to 100%).

2) An increase in the moisture content would increase the angle of repose but decrease the flowability, particularly when the moisture content was above 14%.

3) Uniaxial compression of seeds showed two different zones (elastic and plastic behaviour). An increase in the linear strain limit but decrease in deformation modulus showed that the seeds of black pepper could be deformed to higher extent particularly at high moisture contents. The failure energy remained same when the moisture contents of black pepper was in the range of 11 and 17% (dry basis).

It is worth mentioning here that the present study basically generated design data, relating to grinding and handling of black pepper seeds. Data on this important area were earlier missing though the importance of engineering properties was well realised. It is hoped that future design system would be able to utilise these values to have specific handling and grinding systems of black pepper.

4.2 Ambient Grinding of Black Pepper

Spices, including black pepper, are ground conventionally and commercially in mills which usually do not have any facility for temperature control and/or cooling system. Hence, before initiation of any work on cryogenic grinding, it is logical to have studies and data on conventional or ambient grinding of black pepper. The term 'ambient grinding' means that the grinding operations are carried out (truly speaking, the grinding starts at room temperature) without any cooling of mill or cooling of material to be ground.

In the first study, a commonly used size reduction unit was selected. The only variable that was studied was the feed rate. The results are presented and discussed in the following sections with an intention to understand the phenomenon when black pepper was commercially ground.

4.2.1 Performance Study of a Grinding Mill at Different Feed Rates

The objective of this experiment was to study the effect of feed rate on the rise of temperature during grinding, and on particle size and as well as volatile oil content of black pepper powder on grinding.

Black pepper was ground using a swing type hammer mill (capacity 10 kg h^{-1}, 430 Volts) at three different feed rates viz. 3.6,4.8 and 9.5 kg h^{-1}. The temperature of the ground pepper powder was monitored at an interval of one minute for all the three feed rates, and results are shown in Table 4.2.1. The initial temperatures of the feed material in bulk were 27, 31 and 27 C, respectively (when sample 2 was ground on different days the initial temperature of the material was also different, whereas samples 1&3 were ground on the same day). The samples of black pepper powder were collected during grinding for further analysis. All grinding trials were repeated twice.

4.2.1.1 Temperature Rise During Grinding

The rise of temperature of black pepper powder during grinding indicates the dissipation of mechanical (frictional) energy into thermal energy which affect the quality the ground product. The temperature reported in Table 4.2.1 had a standard deviation (SD) values less than 1 C.

The highest temperature of ground material reached was 76 C in case of the feed rate of 3.6 kg h^{-1} and the least was 36 C in case of 9.5 kg h^{-1}. If the feed rate was less, the ground material temperature was high, as the feed spent more time within the grinding, zone receiving more energy for size reduction which was dissipated as heat. The product (powder) temperature increased initially with time of grinding but later the curves (Fig. 4.2.1) flattened, indicating the attainment of equilibrium condition. The maximum rise in product temperatures (viz., the difference of product temperature and corresponding ambient temperature, at a grinding time t) were 49, 29 and 9 C for the feed rates of 3.6, 4.8 and 9.5 kg h^{-1}, respectively.

The temperature of product during grinding followed an empirical polynomial of third order (r^2>0.95, p<0.0l) with grinding time (t_g). The corresponding equations at different feed rates were as follows:

At 3.6 kg hr^{-1}:

$$T=0.010\, t_g^{3} - 0.475\, t_g^{2} + 7.998\, t_g + T_i \tag{4.2.1}$$

At 4.8 kg hr^{-1}:

$$T=0.005\, t_g^{3} - 0.216\, t_g^{2} + 3.421\, t_g + T_i \tag{4.2.2}$$

At 9.5 kg hr^{-1}:

$$T=0.010\, t_g^{3} - 0.259\, t_g^{2} + 2.361\, t_g + T_i \tag{4.2.3}$$

where T is the product temperature in C at grinding time t_g and T_j is the ambient temperature. The coefficients of determination were (r^2) were 0.99, 0.99 and 0.95 respectively. The predicted product temperatures at different feed rates by using Eqs. 4.2.1, 4.2.2 and 4.2.3 are shown in Table 4.2.1 for comparison. The predicted values by regression analysis compared well with the experimental ones.

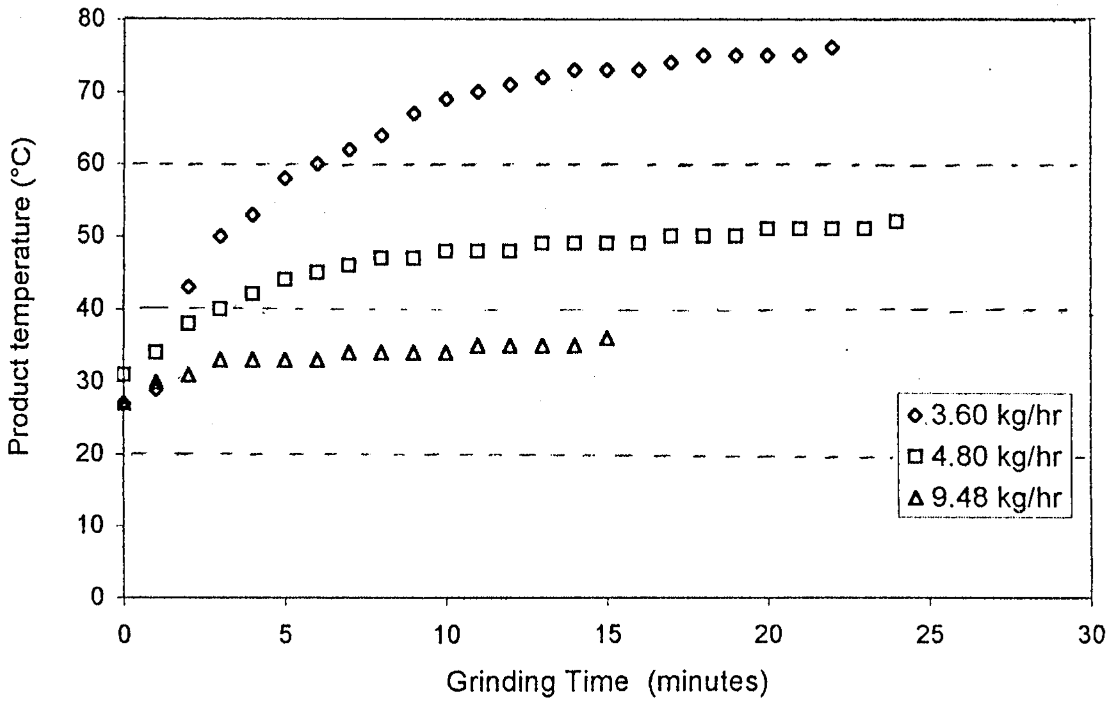


Fig. 4.2.1 Effect of feed rates on the product temperature and grinding time

Table 4.2.1

Effect of feed rate on product temperature at different grinding time during grinding of black pepper using a swing hammer mill

Grinding time (min)	Experimental value of product (powder) temperatures (C) at different feed rates of			Rise in product temperatures (C) at different feed rates of			Predicted value of product temperatures (C) at different feed rates of		
	3.6 (kg h(l)	4.8 (kg h(l)	9.5 (kg h(1)	3.6 (kg *h(')*	4.8 (kg *h(')*	9.5 (kg h(1)	3.6 (kg h(1)	4.8 (kg 111·-1)	9.5 (kg h(1)
0	27	31	*17*	0	0	0	27.0	31.0	17.0
1	29	34	30	2	3	3	34.5	34.2	29.1
2	43*	38	31	16	7	4	41.2	37.0	30.8
3	50*	40*	33	23	9	6	47.0	39.4	32.0
4	53	42	33	26	II	6	52.0	41.5	32.9
5	58	44	33	31	13	6	56.3	43.3	33.5
6	60	45	33	33	14	6	60.0	44.7	33.9
7	62	46	34	35	15	7	63.1	45.9	34.1
8	64	47	34	37	16	7	65.6	46.9	34.2
9	67*	47	34	40	16	'7	67.6	47.6	34.2
10	69	48	34	42	17	7	69.2	48.2	34.2
11	70	48*	35	43	17	8	70.5	48.6	34.3
12	71	48	35	44	17	8	71.4	48.9	34.5
13	*72*	49	35	45	18	8	*72.1*	49.1	34.8
14	73	49	35	46	18	8	*72.6*	49.2	35.4
15	73	49	36*	46	18	9	73.0	49.2	36.2
16	73	49	-	46	18	-	73.2	49.3	-
17	74	50	-	47	19	-	73.5	49.3	-
18	75	50*	-	48	19	-	73.8	49.4	-
19	75	50	-	48	19	-	74.2	49.5	-
20	75	51	-	48	20	-	74.8	49.8	-
21	75	51	-	48	20	-	75.6	50.1	-
22	76*	51	-	49	20	-	76.6	50.6	-
23	-	51	-	-	20	-	-	51.3	-
-	-	52*	-	-	21	-	-	52.2	-

* Indicates ambient temperature

** Coefficient of variation (CY) < 15%

- Data were not collected as grinding temperature reached equilibrium

4.2.1.3 Volatile oil Content of Powder

Volatile oil content in the spice powder is a measure of its aroma and flavour, and hence its quality. Higher the volatile oil content in spice powder, the higher is its market value in financial terms since spices are valued for their aroma and flavour (Gopalkrishnan *et at.,* 1991). Therefore, in order to have a better quality of the ground spice, it is desirable that the volatile oil content should be as high as possible. It is thus desirable to determine the volatile oil content with a detailed analysis of the volatile oil.

4.2.1.2 Particle Size of Powder

The particle size of the ground material affect the consumer acceptability and, hence is an important quality attribute. The particle size' of powder was determined by 'sieve analysis technique (method cited in Section 3.2.1.1). Table 4.2.2 shows that the three feed rates viz., 3.6, 4.8 and 9.5 kg h(l yielded the powders (when the mill attained stabilized condition) having geometric mean particle sizes of 0.13, 0.20 and 0.61 mm, respectively. The feed rate of 9.5 kg h(l (highest feed rate) reached the equilibrium temperature at the earliest (15 min). Fine particle size could be achieved with low feed rate because of longer residence time of the sample inside the grinding system.

Table 4.2.2

Effect of feed rate on particle size and on rise in product temperature at the time of stabilisation of grinding mill

Sl No.	Feed rate (kg hr'l)	Temperature of feed* (C)	Rise in product temperature (C)	Time for stabilization of hlill** (min)	Geometric mean particle size of powder after grinding ** (mm)
1	3.6	27	49	22	0.14
2	4.8	31	29	24	0.20
3	9.5	27	09	15	0.61

Volatile oil content as determined by distillation (method cited in Section 3.2.1.3) has been reported as volatile oil content of black pepper powder throughout the present research. The moisture content of spice samples are reported in a similar way. The coefficient of variation (CY) was less than 10%.

The volatile oil contents (moisture free basis) of black pepper powder drawn at different temperatures and feed rates are shown in Table 4.2.3. The volatile oil content in the powder varied with both particle size and the temperature. The loss of volatile oil in comparison to the hand pounding (control sample) is reported in Table 4.2.3, which shows that as the temperature of the product increased, the volatile oil content decreased and hence the loss of volatile oil as compared to control sample increased markedly. These two indices also varied with feed . rate, and a high feed rate (and hence, low grinding or residence time) reduced the loss of these important quality parameters. The closest value of 1.91 mL/100g, as compared to control sample (2.15 mL/100g), was obtained only with highest feed rate of 9.5 kg h(1 because the rise in temperature during grinding was hardly 9 C. In other words, the loss of volatile oil was the lowest (11.2%) at a feed rate of 9.5 kg hr-^{1} and highest (50.7%) at a feed rate of 3.6 kg hr^{-1}. The corresponding geometric mean particle sizes were 0.61 and 0.14 mm respectively (Table 4.2.2). It was observed in the present study (Section 4.2.1.2) that low feed rate gave a powder of fine particle size, and high powder temperatures (at equilibrium during grinding) but with highest loss of volatile oil. Similar results have been reported by Gopalkrishnan *et ai.* (1991) for ambient grinding of cardamom, wherein the loss of volatile oil varied from 26% to 52% for particle size of 1.00 to 0.25 mm, respectively.

The volatile oil content in the black pepper samples followed a negative relation with product temperature analysis, according to the following empirical equations at different feed rates of 3.6 and 4.8 kg hr-^{1} (regression equation was not possible for 9.5 kg h(l due to insufficient data points):

At 3.6 kg hr^{-1}:

$$V_o = - 0.011\ T + 1.898 \tag{4.2.4}$$

2) At 4.8 kg hr^{-1}: (4.2.5)

$$V_o = - 0.024\ T + 2.781$$

where V_o is the volatile oil content (mLl100g) and T is the corresponding product temperature (C). The coefficients of determinations were 0.99 and 0.96, respectively.

The predicted product temperatures at different feed rates by using Eqs. 4.2.4 and 4.2.5 are given in Table 4.2.3. The predicted values by regression compared well with the experimental ones.

Table 4.2.3

Effect of feed rate on temperature, moisture and volatile oil content of the ground black pepper powder samples

(Initial volatile oil content by hand pounding (control) sample = 2.15±0.04 mL/100g)

Feed rate (kg h{l)	Ground material temperature (C)	Moisture content (%) wet basis	Volatile oil content (moisture free basis) (mL/100g) Experimental values	Predicted from the regression equation	Loss of oil due to grinding* (%)
3.6	43	8.0	1.43 ± 0.09	1.42	33.5
	50	7.4	1.32 ± 0.03	1.34	38.6
	67	7.3	1.15 ± 0.05	1.15	46.5
	75	6.0	1.06 ± 0.08	1.06	50.7
4.8	40	8.0	1.82 ± 0.09	1.83	15.3
	48	8.0	1.65 ± 0.07	1.64	23.3
	50	7.9	1.62 ± 0.05	1.59	24.6
	52	7.2	1.51±0.12	1.54	29.7
9.5	36	8.2	1.91 ± 0.10	-**	11.2

* Loss of oil was calculated in comparison to the control sample

** Could not fit an equation due to insufficient data points

Similar results have been reported by Singh and Goswami (1999b) during ambient grinding of cumin seed. In their study, the volatile oil content decreased from 2.86 to 2.26 mL/100g with grinding temperature increasing from 40 to 85 C. Further, the statistical analysis of the data obtained by these researchers revealed the decrease in volatile oil content was significant at all the grinding temperatures ($p \leq 0.01$) under ambient condition. This was because of the fact that during the ambient grinding process, the mass transfer rate increased due to an increase in vapour pressure at higher temperatures which resulted in a loss of volatile oil at corresponding temperatures (Wolf and Pahl, 1990). The empirical equation ($r^2=0.99$, $p \leq 0.01$) obtained by regression analysis using the experimental data of Singh and Goswami (1999b) for ambient grinding of cumin seeds is represented as:

$$V_o = - 0.014\, T + 3.460 \qquad (4.2.6)$$

where V_o is the volatile oil content (mL/100g) and T is the corresponding product temperature. It is observed that the empirical Eq. 4.2.6 was similar to the empirical equations (Eqs. 4.2.4 and 4.2.5) obtained in the present study.

The moisture content of the ground samples varied from 6.0 to 8.2 %, and higher the powder temperature lesser was the moisture content of the samples. The highest moisture loss (moisture content was 6%) was observed at a product temperature of 76 C which was expected because of high rate of vaporisation of moisture from the powder sample at a high temperature.

4.2.1.4 Conclusions

From the foregoing results and discussion on performance study of swing type hammer mill at different feed rates, it was concluded that

1) The product (black pepper powder) temperature reached a temperature of as high as 76 C at the lowest feed rate of 3.6 kg h(l. The product temperature during grinding followed a polynomial of third order with grinding time. The rise in product

temperature was of the order of 49, 29 and 9 C at the feed rates of 3.6,4.8 and 9.5 kg hr^{-1} respectively.

2) The geometric mean particle sizes of the products were 0.14, 0.20 and 0.61 mm at the feed rates of 3.6, 4.8 and 9.5 kg hr-^{l}, respectively. The lower the feed rate the finer was spice powder and vice-versa.

3) The volatile oil contents of black pepper samples at the stabilisation temperatures of 75, 52 and 36 C were 1.06, 1.51 and 1.91 mL/lOOg, respectively. The volatile oil contents varied negetively with the product temperature at different feed rates. The loss of volatile oil due to grinding was calculated with respect to the control sample (hand pounding) and the values varied from 11.2 to 50.7% depending on feed rate and product temperature. Volatile oil content also varied with both powder temperature and average particle size. Lower feed rate gave a powder of finer particle size, higher powder temperatures but highest loss of volatile oil whereas the high feed rate gave a powder of coarse particle size, low powder temperature but lowest loss of volatile oil.

3)

4.2.2 Performance Study of Different Types of Mills of Various Capacities

Based on grinding trials (Section 4.2.1) in a particular size reduction unit at different feed rates, and determining the temperature rise during grinding and loss of volatile oils in ground samples, the second set of experiment was planned, to study the performance of different types of commonly used grinding mills. The objective of this investigation was not only to confirm the earlier results reported in Section 4.2.1, but also carry out further detailed studies on the ~haracteristics of grinding vis-a-vis volatile oil components in five commonly used grinding mills.

Black pepper seeds were ground in five different grinding mills VIZ., Swing hammer mill, Hammer mill (APEX make), Plate (OlAF make) mill, Plate Mill, Roller Mill which are commonly used for grinding of spices in India. These mills were of different capacities (Table 4.2.4) as it was extremely difficult to obtain commercial mills of similar capacities. The results of the study are discussed in the subsequent sections.

4.2.2.1 Particle Size of Powder

The geometric mean particle sizes of the ground powders were determined from the sieve analysis technique using Eq. 3.1. Swing hammer mill and Hammer (APEX make) mill had the provisions to introduce sieves to roughly control the particle size, whereas other mills did not have the provisions to introduce any sieve. The geometric mean particle sizes obtained by grinding in Swing hammer mill, Hammer (APEX) mill, Plate (DIAF) mill, Plate type, Roller mill and hand pounding, were 0.20, 0.25, 0.38, 0.16, 0.50 and 0.63 mm, respectively Cfable 4.2.4). The raw material (black pepper) had a geometric mean particle diameter of about 5 mm. Fine particle 《0.2 mm) was obtained when ground in Plate mill, whereas coarse particles (> 0.5 mm) resulted by to hand pounding (Table 4.2.4).

Table 4.2.4

Performance evaluation of commonly used grinding mills during ambient grinding of black pepper

(Ambient temperature = 30 C)

Parameters	Type of Mill					
	Swing hammer Mill	Hammer (APEX) Mill	Plate (DIAF) Mill	Plate Mill	Roller Mill	Hand pounding (control)
Capacity of mill (kg/hI')	10	25	10	60	100	-*
Quantity of material ground (kg)	5.0	5.0	5.0	10.0	5.0	0.1
Volatile oil content # (mL/100g)	1.61 t 0.08	2.58 to.09	2.65 to.07	1.24 to. 10	2. 15tO.08	2.15 t 0.04
Product Temperature## (C)	52	43	47	68	30+	30+
Moisture content (%, wet basis)	11.0	10.6	11.2	8.6	11.6	10.0
Particle size (mm)**	0.20	0.25	0.38	0.16	0.50	0.63

* Not determined.
# Moisture free basis ##
SD is less than 1 C
**Geometric mean particle diameter +
+Indicates ambient temperature

4.2.2.2 VolatHe oil Content of Powder

The volatile oil contents (moisture free basis) from Swing hammer mill, Hammer (Apex) mill), Plate (DIAF) mill, Plate type and Roller mill from Swing hammer mill, Hammer (Apex) mill), Plate (DIAF) mill, Plate type and Roller mill were 1.61,2.58,2.65, 1.24 and 2.15 rnL/100g, respectively (Table 4.2.4). The results were comparable *with* those of the control sample obtained by conventional hand-pounding (2.15 rnL/I00g).

swing type hammer mill and Plate mill yielded powders having less volatile oil content. This may be attributed to higher grinding temperature and finer particle size of powder. On other hand Plate (DIAF) type and Hammer (APEX) type yielded powders having higher oil contents than the control sample because of the low temperature attained during grinding in these mills. Seeds ground in both Roller mill and hand pounding (control sample) yielded similar quantities (2.15 mL/lOOg) of volatile oil. In these mills, despite having lower grinding temperature (30 C), the volatile oil content was less than that of volatile oil obtained from Plate (DIAF) mill and Hammer (APEX) mill. This may be due to coarser particle size of powder which resulted in incomplete distillation of volatile oil (Vide Section 4.2.3.4). The temperatures of the powders were 52, 43, 47, 68, 30 and 30 C, respectively in those selected six different systems at stabilised grinding condition, while the ambient temperature was around 30 C. These results indicated that the quality of ground powder in terms of volatile oil content depended on the type of the mill employed for grinding. This indicates to the fact that appropriate mill is needed to have a good quality spice powder.

4.2.2.3 Analysis of Volatile **oil** by Gas Chromatography

The gas chromatographic (GC) analysis of volatile oils is a method of separation and identification of volatile compounds based on their retention time within gas chromatographic column. Clevenger's method of distillation of volatile oil gives the total volatile oil content in the powder sample, whereas the gas chromatography is a tool to identify the various constituents of volatile oil for measuring the quality of the oil.

Hasselstrom *et al.* (1957), Uday Sankar (1989) and Pino *et al.* (1990) have reported the constituents of black pepper oils obtained, by steam distillation and by supercritical carbon dioxide extraction methods, respectively. Pepper oil constitutes mainly monoterpenes (70-80%), sesqueterpenes (20-30%) and a small amount (less than 5%) of oxygenated compounds (Lewis *et al.,* 1969 and Govindarajan 1977). The compounds viz., a-thujene, a-pinene, sabinene, I)-pinene, 1,8-cineole and limonene are the monoterpenes present in the volatile oils of black pepper, whereas the sesqueterpenes are a-copaene, I)-caryophyllene, I)-bisabolene and caryophyllene oxide (which is an oxygenated compound, and is also classified under sesqueterpenes). The chemical

•formula, molecular weights and boiling points of the above compounds are shown in Table 2.2 of Review of Literature. Monoterpenes are the lower molecular weight compounds (molecular weights being 136 to 1~4), having lower boiling points as compared to the sequeterpenes (molecular weights being 204 to 222).

Table 4.2.5

Gas chromatographic analysis of ground pepper samples using different mills (Relative concentrations are shown as percentages)

SI No	Compounds	Mill type					
		Swing hammer type mill	Hammer (APEX) type mill	Plate (OlAF) type mill	Plate mill	Roller mill	Hand pounding
I	Thu jene+a-pinene	6.01	7.60	8.69	2.80	7.04	8.97
2	Sabinene+p-pinene	18.84	22.53	24.31	11.79	21.34	22.19
3	1,8-cineole+ limonene	20.98	23.06	20.13	15.90	22.25	22.01
4	a-copaene	5.24	4.79	4.25	6.25	4.74	4.25
5	p-caryophyllene	8.93	5.33	3.39	10.65	4.58	8.74
6	p-bisabolene	9.61	7.63	5.23	11.14	6.90	8.81
7	Caryophyllene oxide	8.55	10.18	9.14	12.24	9.86	5.49
8	Total	78.16	81.12	75.14	70.77	76.71	80.46
9	Monoterpenes (I to 3)	45.83	53.19	53.13	30.49	50.63	53.17
10	Sesquiterpenes (4 to 7)	32.33	27.93	22.01	40.28	26.08	27.29
II	Ratio of Monoterpenes to Sesquiterpenes	1.42	1.90	2.41	0.76	1.94	1.95
12	Monoterpenes (%)*	58.64	65.57	70.71	43.08	66.00	66.08
13	Sesquiterpenes (%)*	41.36	34.43	29.29	56.92	34.00	33.92

* Percent present in total oil

The ratio of monoterpenes to sesqueterpenes in the volatile oil is an important quality attribute. Hubert (1991) observed that the ratio of monoterpenes to sesquiterpenes of more than 1.74 would give strong peppery note in oil. According to Salzer (1977), the ratio of monoterpenes to sesquiterpenes represents the quality of the volatile oil and . indicates aroma value. Monoterpenes provide the odour and body to the volatile oil whereas the sesquiterpenes provide the spicy note to the volatile oil. In other words, while the powder is fresh, it contains more of monoterpenes in the volatile oil. Hence, it is desirable to have more monoterpenes in the volatile oil.

The concentrations of black pepper volatile oil compounds obtained in the present study are shown in Table 4.2.5. Pino *et al.* (1990) identified a total of 46 compounds (Table 2.1) present in the volatile oil which included, trace elements. In present research, however, only nine major volatile oil compounds were chosen and used for analysis. The quantity of monoterpenes viz., a-thujene+a-pinene, sabinene+~-pinene, 1,8cineole+limonene, present in the volatile oil were analysed by gas chromatography technique. The quantity of sesqueterpenes viz., a-copaene, ~-caryophyllene, ~-bisabolene and caryophyllene oxide (an oxygenated compound), present in the oil were also analysed by gas chromatography technique. The total relative' percentage concentrations of black pepper volatile compounds used in all the selected mills varied roughly between 70% and 80% in the present study. Among the mills, Hammer mill (APEX), Plate (DIAF) mill, Roller mill and hand pounding gave ratios of monoterpenes to sesqueterpenes as 1.90, 2.41, 1.94 and 1.95, respectively, which indicated that the volatile oils had a strong peppery note. The oils obtained from samples ground in these mills had more concentrations of monoterpenes. The oil obtained from Swing type hammer mill gave a ratio of monoterpenes to sesqueterpenes of the order of 1.,42, whereas that from Plate mill gave a least value of 0.76, which indicated that oil obtained from these two mills had more concentration of sesqueterpenes. This might be due to high volatility of monoterpene compounds at higher temperature, as grinding temperatures in Swing type hammer mill and Plate mill were 52 C and 68 C, respectively. Table 4.2.6 shows the vapour pressure and temperature data available for a few monterpene compounds of volatile oil (Perry, 1950). It can be seen from Table 4.2.6 that if the vapour pressure of the compound was reduced below atmospheric pressure then the boiling point of that particular compound also reduced. During grinding, the high rotational speed of mill reduced the pressure in the grinding zone to less than the atmospheric pressure (760 mm Hg). At this point, the boiling point of the volatile oil compound came down depending on the pressure drop in the grinding zone (Table 4.2.6). If the temperature gradient (the

Idifference between the grinding temperature and boiling point) was reduced considerably then there was an increase in mass transfer of that piuticular compound from powder to (the surrounding atmosphere. The temperature gradient was much high in case of Swing type hammer mill and Plate mill due to increased grinding temperature (52 and 68 C). Singh and Goswami (l999b) have also ob'served loss of highly volatile components with low boiling points during ambient grinding of cumin at a temperature of 85 C.

Figures 4.2.2 - 4.2.4 show the contents of, various compounds present in the distilled volatile oil (expressed as mL/I00g) as determined by combining Table 4.2.4 and Table 4.2.5. For example, in case of Swing type hammer mill, the content of ~caryophyllene was calculated as (8.93*1.61/100) = 0.14 mL/I00g. The total volatile oil (all the nine compounds) content was calculated as (78.16*1.61/100) = 1.25 mL/100g; the content of monoterpenes as (45.83* 1.61/100)= 0.74 mL/100g; the content of sesqueterpenes as (32.33* 1.61/100)= 0.52 mL/ 100g. Though the total volatile oil content was 1.61 mL/I00g (Table 4.2.5) in case of grinding in Swing type hammer mill, the total of all nine major compounds of volatile oil was only 1.25 mL/100g. The rest of volatile oil of about 0.36 mL/100g accounted for unidentified and trace compounds. The above method of determining the volatile compounds in mL/100g was followed throughout the present work.

Figure 4.2.2 shows the plot of total oil content, quantities of monoterpenes and sesqueterpenes for different grinding mills. The content of monoterpenes was lowest in samples ground in Swing type hammer mill and Plate mill. This was basically due to the fact that the powder temperatures were high (52 and 68 C) and powder particles were too fine (0.20 and 0.16 mm) for these mills which had resulted in the loss of light and highly volatile components viz., the monoterpenes (Pesek *et ai.,* 1985; Pesek and Wilson, 1986). On the other hand, the total content of monoterpenes was dependent upon the type of mill. The maximum content of monoterpenes was observed in the powder obtained by grinding in Hammer (APEX) mill and Plate (DIAF) mill where the powder temperatures were slightly low (43 and 47 C) with powder particle size of 0.25 and 0.38 mm, respectively. The samples of Roller mill and by hand pounding did not yield highest quantity of monoterpenes despite having a low powder temperatures (30C) as the powder particle sizes were coarser viz., 0.50 and 0.63 mm,. respectively (this phenomenon was

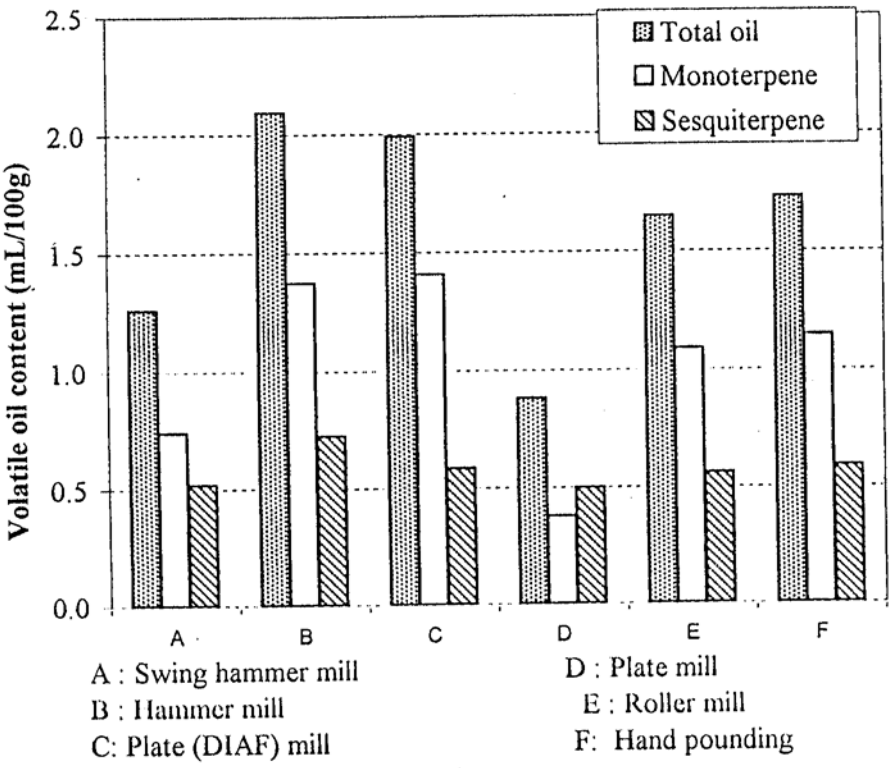


Fig. 4.2.2.. Variation of total, monoterpene and sesqucterpenes contents in black pepper volatile oil obtained by different grinding mills

Ilso discussed in Section 4.2.3). However, the mean content of sesqueterpenes in the oil amples obtained from all mills was fairly constant (0.58 mL/100g). This content did not ~epend on the type of mill as compounds having higher molecular weight i(sesqueterpenes) were not affected by grinding temperature (Pesek *et at.,* 1985; Pesek and

!

fWilson, 1986) and particle size.

Table 4.2.6

Boiling points (C) of volatile oil compounds of black pepper at different vapour pressure (Perry 1950)

Compound	Pressure mm Hg										Melting ---..P.0int (C)
		5	10	20	40	60	100	200	400	760	
	Temperatures (C)										
a-pinene	-1.0	24.6	37.3	51.4	66.8	76.8	90.1	110.2	132.3	155.0	-55.0
~~-pinene	4.2	30.0	42.3	58.1	71.5	81.2	94.0	114.1	136.1	158.3	
cymene	17.3	43.9	57.0	71.1	87.0	97.2	110.8	131.4	153.5	177.2	-68.2
limonene	14.0	40.4	53.8	68.2	84.3	94.6	108.3	128.5	151.4	.175.0	-96.9
myrcene	14.5	40.0	53.2	67.0	82.6	92.6	106.0	126.0	148.3	171.5	

—

- Indicates data not available

Figure 4.2.3 shows the distribution of three different sets of monoterpene compounds viz., a-thujene+a-pinene, sabinene+~-pinene, 1,8-cineole+limonene. The distribution pattern of these compounds was similar in samples from all the mills except for Plate (DIAF) mill, where the quantity of (sabinene+~-pinene) was the highest. Figure 4.2.4 shows the distribution of four sesqueterpenes compounds viz., a-copaene, ~caryophyllene, ~-bisabolene and caryophyllene oxide. Though the total quantity of sesqueterpenes in the oil was nearly same, content of caryophyllene oxide was higher for samples ground in Plate mill (Table 4.2.5). It might be due to the oxidation of ~caryophyllene into caryophyllene oxide at higher temperature (62 C). Hand pounding (control) sample yielded low quantity of caryophyllene oxide as there was a little chance of oxidation of ~-caryophyllene in the grinding process.

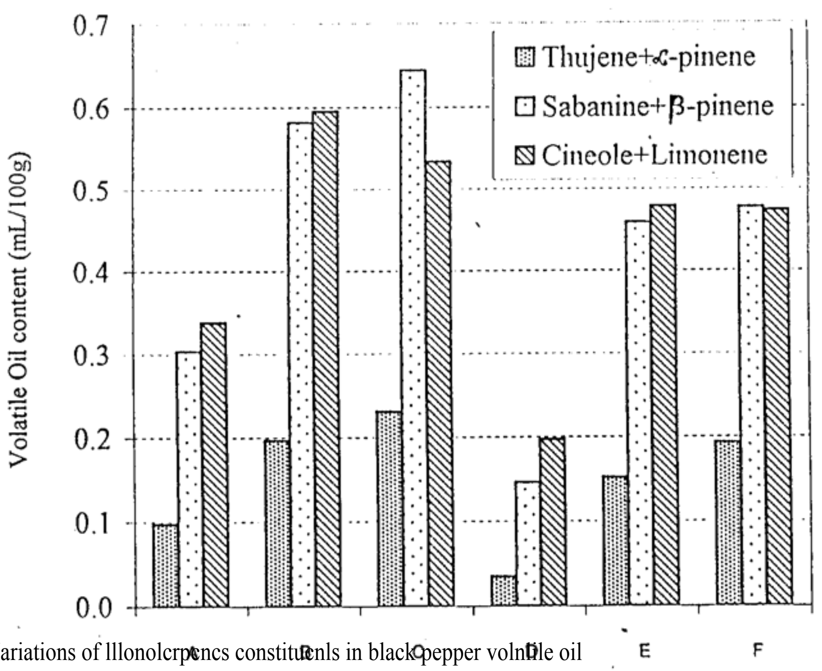


Fig. 4.2.3 Variations of lllonolcrpcncs constitutcnls in black pepper volntile oil obtained by difTerent grinding mills

A : Swing hammer mill
B : Hammer mill
C: Plate (DIAF) mill
D : Plate mill
E : Roller mill
F: Hand pounding

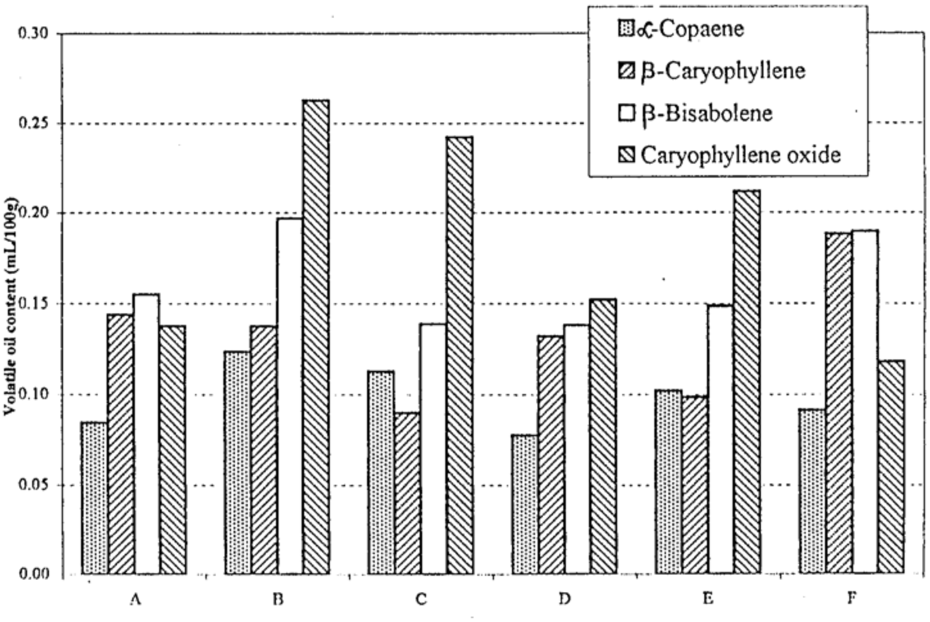


fig. 4.2.4 Variation of sesqueterpenes constitutcnts in black pepper volatile oil obtained by different grinding mills

4.2.2.4 Conclusions

The following conclusions can be drawn based on the results reported in the present section.

1) Among the mills employed for grinding, fine powder could be obtained using Plate mill, with a geometric mean particle diameter of 0.16 mm.
2) The volatile oil contents (moisture free basis)· of samples ground in Swing type hammer mill, Hammer (APEX) mill, Plate (D1AF) mill, Plate Mill, Roller mill and hand pounding were 1.61,2.58,2.65,1.24,2.15 and 2.15 mL/lOOg, respectively The corresponding product temperatures were 52, 43, 47, 68, 30 and 30 C. These results indicated that the quality. of ground powder in terms of volatile oil content depended on a few factors such as the type of the mill employed for grinding, the product temperature, and the average particle size of the ground material.
3) The gas chromatographic (GC) analysis data of the volatile oil showed that grinding Hammer (APEX) mill, Plate (DIAF) mill, Roller mill and hand pounding gave oil with high quantity of monoterpenes. Monoterpenes were sensitive to grinding temperatures and their volatility increased with an increase in grinding temperature. The overall content of sesqueterpenes in the oil samples obtained from all the mills was fairly constant and it did not depend on the type of mill.

ƒ4.2.3 **Ambient Grinding** Characteristics **at Different Particle** Sizes

Generally, spices are ground either for direct consumption as powder or for making value-added products like essential or volatile oils or as oleoresins. Grinding facilitates the release of aroma and flavour principles from the spices for mixing with food materials (Gopalkrishnan, *et at.,* 1991). During grinding, most of the energy input to the grinder is converted into heat, whereas only a small portion is used for actual size reduction (Loncin and Merson, 1979). if the particle size of powdered product is low (fine powder), enormous quantity of heat is generated within the mill raising the temperature of the ground product to as high as 93 C (Wistreich and Schafer, 1962).

As observed in the previous sections, the grinding of black pepper at high temperatures and to low particle sizes (fine powder) resulted in the higher loss of volatile oil. At the same time, it was observed that even if the particle size obtained was high (coarse powder), the loss of volatile oil was also high though the powder temperature was low. Energy laws for grinding indicates that to obtain low particle size (fine powder), more grinding energy is required and grinding to' high particle size (coarse powder) consumed less grinding energy. However, the low particle size (fine powder) consumed less time in the distillation process for the extraction of volatile oil from the powdered samples, while high particle size (coarse powder) consumed more time for distillation. As volatile oils are critical components of spices, and spices are valued according to their volatile oil content, a detailed investigation was undertaken to find the optimum mean particle size (diameter) of powder at a point in which the loss of volatile oil would be minimum, and to study the corresponding conditions of grinding energy and distillation times.

The black pepper samples were coded as POI, P02, PD3, PD4, PD5 and P06 for easy identification and they were ground to different particle sizes as explained in Section 3.2.3 (Chapter 3, Materials and Methods). The powder obtained by grinding of sample PO 1 was the coarsest particle size and that of sample P06 was the finest particle size. The other samples (P02, P03, PD4 and PD5) were in the range from coarser to finer particle sizes; number increased with a decrease in particle size. (Table 4.2.7). Separate grinding trials resulted in powdered samples of different particle sizes viz., PO 1 to P06. For

Table 4.2.7

Grinding Characteristics of Black pepper by ambient grinding

Ambient Temperature = 30C

Codes for Samples	Mean particle size (mm)	Moisture content (%, wb)	Mill's discharge rate (g. min $^{-1}$)	Product temperature (C)	Maximum oil content (mL/100g)	Distillation on time (h)	Grinding energy (kJ.kg^{-1})	Fourier Number F_0	Diffusivity Dx10^{11} (m^2-s^{-1})
PD1	2.10	9.5	255	30	2.54±0.04	6.7	4.61	0.17	1.70
PD2	1.23	9.5	210	30	2.72±0.06	6.0	8.62	0.20	1.50
PD3	0.70	9.5	165	31	2.92±0.03	6.0	14.19	0.29	1.10
PD4	0.61	9.5	158	31	2.65±0.05	4.0	15.81	0.31	1.23
PD5	0.20	9.0	80	45	2.02±0.09	3.5	33.94	0.28	0.14
PD6	0.14	7.0	60	65	1.48±0.03	3.0	42.22	0.29	0.03

obtaining the different particles sizes of PD 1 and PD2, the gap between the plates in the Plate (DIAF) mill was varied, whereas in case of other samples viz., PD3 to PD6, the sieves of different sizes were employed in the Swing hammer mill. The subsequent sections discuss the results of this study.

4.2.3.1 Temperature Rise during Grinding

The product (powder) temperatures of the samples PD 1, PD2, PD3, PD4, PD5 and PD6 measured at the outlet of grinding mill, were 30, 30, 31, 31, 45 and 65 C, respectively, whereas the feed material temperature was 30 C (ambient temperature) (Table 4.2.7). The ground products obtained from samples PD5 and PD6 (fine samples) had temperature rise of 15 and 35 C, respectively, whereas for the other samples, the rise in temperature was marginal. This was expected as fine particles could be obtained only with enhanced level of energy input.

4.2.3.2 Particle Size of Powder

The average particle sizes of the powders were determined from the sieve analysis data using equations (3.2) and (3.3) and are shown.in the Table 4.2.8. The geometric mean diameters were 2.10, 1.23,0.70,0.61,0.2 and 0.14 mm for ground samples PDl, PD2, PD3, PD4, PD5 and PD6, respectively. The corresponding surface mean diameters of the above samples were 3.12, 2.52, 1.81, 1.50, 0.50 and 0.21 mm, respectively. The surface mean diameters of the powders were- determined for the purpose of estimating the effective diffusion coefficient of the distillation process (discussed later in Section 4.2.3.9).

4.2.3.3 Estimated Energy for Grinding

The gririding of spices is an energy intensive process. The energy needed for grinding of solids is a function of surface area of particles produced. There are several energy laws for grinding (Section 2.3.3 of Review of Literature) of which three of them viz., Kick's law, Rittingers law and Bond's law are cOIpmonly used for estimation of energy for grinding. However, Kick's law is best suited for small initial particle sizes ereas Rittinger's law is best applicable for larger initial particle sizes. As the Bond's 'W.is best suited for medium particle sizes (which is true here), Bond's equation was plied for the estimation of energy in the present study.

The estimated energy required for size reduction or grinding from an initial article size of 5 mm (initial average size or diameter of a black pepper seeds) to different article sizes (PD1, PD2, PD3, PD4, PD5 and PD6) using Bond's Eq. 3.4 is shown in Table 4.2.7. As expected, the highest estimated energy (42.22 kJ kg-I) was consumed for 'obtaining fine powder (PD6) of geometric mean particle size of 0.14 mm and lowest energy (4.61 kJ kg-I) was consumed for obtaining coarse powder (PD1) having geometric mean particle size of 2.10 mm.

Table 4.2.8

Sieve analvsis data of ground black pepper powder to different particle sizes

51 No.	Mesh size	Mean sieve Diameters		Weight fractions (Wi) ofdlf't'erent samples					
		d_m	d_g	PD1	PD2	PD3	PD4	PD5	PD6
1	4/5	4.375	4.359	0.058	0.010	-	-	-	-
2	5/10	3.000	2.828	0.683	0.231	0.044	0.012	0.003	-
3	10/20	1.425	1.304	0.157	0.582	0.438	0.392	0.016	-
4	20/30	0.725	0.714	0.020	0.017	0.092	0.096	0.167	-
5	30/40	0.513	0.505	0.032	0.048	0.130	0.144	0.209	-
6	40/60	0.338	0.326	0.026	0.034	0.098	0.120	0.088	0.057
7	60/80	0.215	0.212	0.010	0.052	0.055	0.097	0.108	0.084
8	80/100	0.165	0.164	0.016	0.024	0.066	0.054	0.1 04	0.218
9	100/120	0.138	0.137	-	-	0.040	0.036	0.043	0.215
10	120/140	0.116	0.115	-	-	-	-	0.106	0.160
11	140/200	0.091	0.089	-	-	-	-	0.098	0.101
12	200/270	0.064	0.063	-	-	-	-	-	0.091
Geometric mean diameter (Eq.3.2)				2.10	1.23	0.70	0.61	0.20	0.14
Surface mean diameter (Eq.3.3)				3.12	2.52	1.81	1.50	0.50	0.21

dm arithmetic mean sieve diameter
dg – geometric mean sieve diameter

Table 4.2.9

Cumulative volatile oil content of powdered samples obtained by Clevenger's distillation at different time intervals

Distillation time (min)	Volatile oil content of different samples (mL/100g)						Volatile oil content to the total volatile oil different distillation time (%)					
	PDI *	PD2	PD3	PD4	PD5	PD6	PD1	PD2	PD3	PD4	PD5	PD6
0	0	0	0	0	0	0	0.0	0.0	0.0	0.0	0.0	0.0
30	1.08	1.10	1.13	0.97	1.01	0.88	42.5	40.6	38.7	36.6	50.0	59.5
60	1.41	1.49	1.57	1.55	1.45	1.03	55.5	54.8	53.8	58.5	71.8	69.6
90	1.61	1.71	1.81	2.12	1.63	1.27	63.4	62.9	62.0	80.0	80.7	85.8
120	1.71	1.92	2.14	2.34	1.80	1.38	67.3	70.8	73.3	88.3	89.1	93.2
150	1.83	2.06	2.30	2.52	1.89	1.41	72.0	75.9	78.8	95.1	93.6	95.3
180	1.97	2.28	2.59	2.56	1.98	1.48	77.6	83.8	88.7	96.6	98.0	100.0
210	2.10	2.39	2.70	2.61	2.02	1.48	81.9	87.9	92.5	98.5	100.0	-
240	2.17	2.45	2.72	2.65	2.02	-	85.4	89.9	93.2	100.0	-	-
270	2.23	2.49	2.76	2.65	-	-	87.8	91.7	94.5	-	-	-
300	2.41	2.62	2.83	-	-	-	94.9	96.3	96.9	-	-	-
330	2.48	2.67	2.87	-	-	-	97.6	98.3	98.3	-	-	-
360	2.52	2.72	2.92	-	-	-	99.2	100.0	100.0	-	-	-
390	2.54	-	-	-	-	-	100.0	-	-	-	-	-

4.2.3.4 Volatile oil Content of Powder

The content of volatile oil or the yield of volatile oil distilled using Clevenger's apparatus at an intervals 30 min was determined to know the quality of ground spice samples. The cumulative contents of volatile oils for different samples (PDl, PD2, PD3, PD4, PD5 and PD6) are given in Table 4.2.9. Figure. 4.2.5 (a and b) shows the plot of volatile oil contents versus the distillation times for the different particle sizes of samples (PDl, PD2, PD3, PD4, PD5 and PD6). Table 4.2.7 shows the maximum volatile oil contents of powders ground to different particle sizes. The volatile oil contents of samples PDl, PD2 and PD3 were 2.54, 2.72 and 2.92 mL/lOOg, respectively. The volatile oil contents of samples P04, PD5 and PD6 are 2.65, 2.02 and 1.48 mL/lOOg, respectively. Figure 4.2.5 (a) shows that quantity of volatile oil released increased asymptotically with

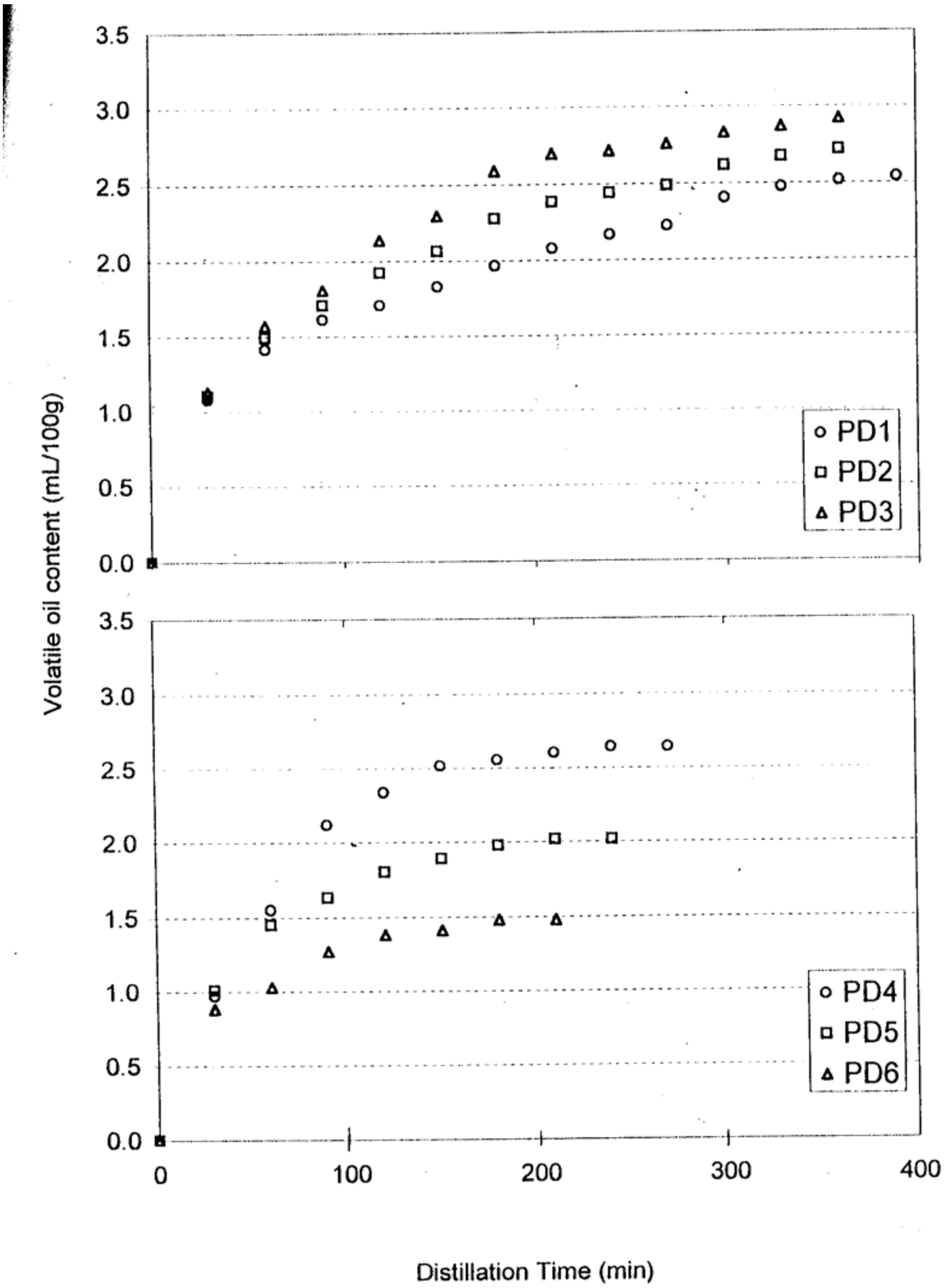


Fig. 4.2.5 Volatile oil yield versus distillation time at different particle sizes of black pepper powder (a) For samples of POI, P02 and P03 (b) For samples of PD4, P05 and PD6 .

the distillation time for all the three samples of PO 1, P02 and P03, indicating that the complete volatile oils present in these powdered samples were not removed in the distillation process as the curves were not flattened even at the end of 350 minutes. On the other hand, Fig. 4.2.5 (b) shows that as the entire quantity of oil present in the powdered samples (P04, P05 and P06) was distilled, as the curves flattened at the end of distillation process. This meant that there was a definite loss in the volatile oil content due to grinding in case of samples P04, P05 and P06 (finer powders) as these samples yielded less volatile oil when compared with the content of volatile oil of sample P03. The lowest content of volatile oil was found to be in P06, which had a very fine geometric mean particle diameter of only 0.14mm. There results indicate that particles with low average mean diameter possess low quantity of volatile oil.

4.2.3.5 Distillation Time

The distillation time for distillation of volatile oil from the samples changes due to the particle size of the powder (Table 4.2.9). The time for the complete distillation of volatile oil samples of PD1, P02, PD3, P04, PD5 and PD6 were 390,360,360,240,210 and 180 min, respectively. Table 4.2.9 shows that the content of volatile oil was about 40% of the total volatile oil in first 30 min of distillation for samples of PO 1, P02, PD3 and P04, whereas the contents were 50 and 60% in case of P05 and PD6, respectively. The mean volatile oil content at the end of 90 min of distillation time was about 63% for samples of PD1, P02, PD3, and about 80 to 86% in case of PD4, PD5 and P06. It indicated that if coarser were the particles slower was' the rate of volatile oil distillation but finer the particles faster was the distillation of volatile oil. This might be because, if coarser were the particle size, the resistance offered by the particle for the movement of volatile oil from the core of the particle to the surface was higher and hence the mass transfer was slower. In the case of finer particle size, however, this resistance was relatively low, and hence, the mass transfer was faster, thereby reducing the distillation time. It was thus concluded that distillation time of Hfe particles depended on the mean diameter of the powder particles.

4.2.3.6 **Optimization of Particle** Size

The foregoing discussions indicated that during ambient grinding of spices, very fine particle sizes had yielded less of volatile oil due to the volatile oil loss during grinding. On the other hand, if the powder was coarse, volatile oil content was also less as the complete volatile oil present in the powder was not released easily during distillation. Hence, there might exist a particle size between coarse and fine which could offer the highest content of volatile oil. The present section thus deals with finding of the best particle size of black pepper suitable for commercial purpose.

The optimal particle size of the powder is defined as the geometric mean particle diameter at which percentage recovery of volatile oil is maximum or the loss of volatile oil is minimum. Figure 4.2.6 shows the plot of volatile oil loss, distillation time and input energy for grinding versus geometric mean particle (d_{ga}) diameter. The loss of volatile oil was minimum at geometric mean particle diameter (size) of about 0.7 mm. If the particle size was less than 0.7 mm, the loss of oil was more (due to high temperature during grinding and due to enhanced surface area of the particles exposed to the atmosphere during grinding), the energy for size reduction was also high, though the distillation time was less. On the other hand, if the particle size was more than 0.7 mm, the content of oil was less as the oil present in the powder could not be completely distilled even after 6 hours of extraction, though the energy required for size reduction reduced. Hence, the particle size of about 0.7 mm (US 25 mesh) can be taken as optimum (Fig. 4.2.6) and the corresponding grinding energy and distillation time were 14.19 kJ kg-^{1} and 6 hours, respectively. Gopalkrishnan *et al.* (1991) reported that the volatile oil content is maximum for particles obtained with sieve size of 0.75 mm in case of grinding of cardamom.

This optimal particle size (about 0.7 mm) would be of commercial importance in the large scale industrial grinding operations where black pepper is ground for the production of volatile oil by distillation process.

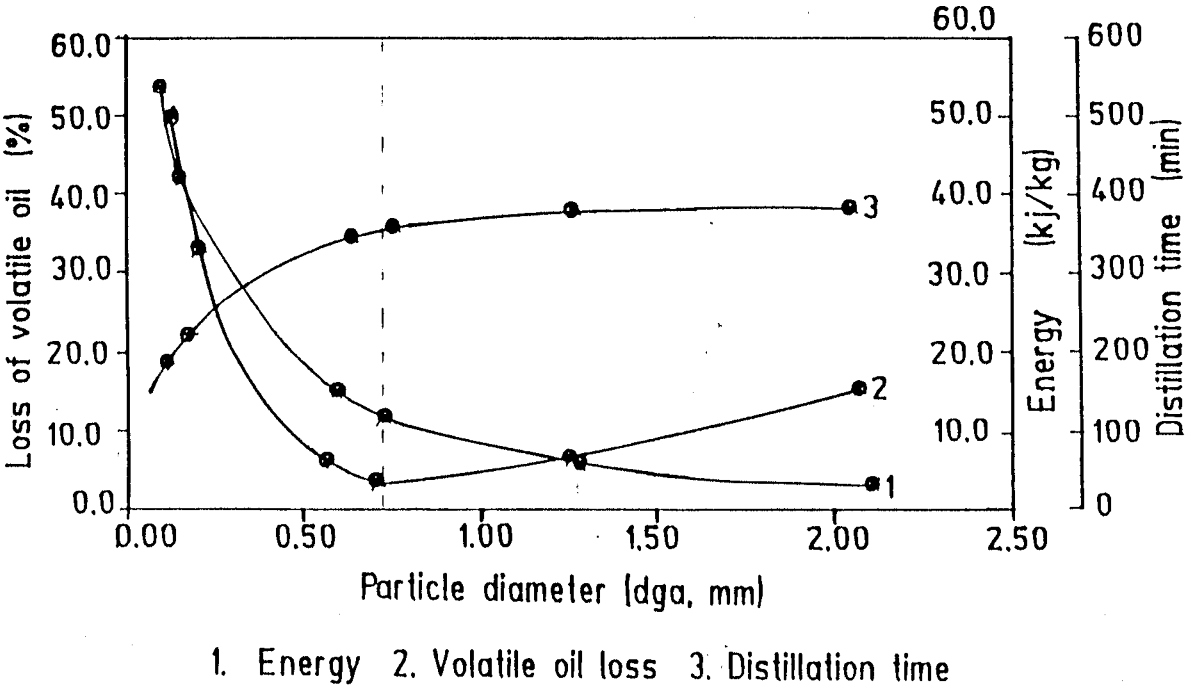


Fig. 4.2.6 Optimization of parameters in grinding of black pepper

4.2.3.7 Physical Properties of Volatile oil

The properties of volatile oil of black pepper samples were determined in order to determine the quality of ground samples (PO 1, P02, P03, P04, PD5 and P06). The physical properties of volatile oil measured were specific gravity, refractive index and optical rotation Cfable 4.2.10). No significant changes (p S 0.05) in the physical properties of oils at different particle sizes were observed. The average values of specific gravity, refractive index and optical rotation of oils were 0.94, 1.49 and -2.40°, respectively. The values indicated that these properties could not be used to differentiate the quality of ground black pepper. In other words, it indicates that in range of particle sizes studied, these selected physical properties of volatile oil remains unaltered.

Table 4.2.10

Physical properties of volatile oils of black pepper ground to different particle sizes in various mills.

	Plate Mill →		Hammer mill →			
Sample	POI	P02	P03	P04	P05	P06
Particle Diameter (mm)	2.08	1.23	0.70	0.61	0.20	0.14
Grinding temperature (C)	30	30	31	31	45	65
Volatile oil content *(mL/100*g)	2.54 ± 0.04	2.72 ± 0.06	2.92 ± 0.03	2.65 ± 0.05	2.02 ± 0.09	1.48 ± 0.03
Specific gravity	0.930	0.932	0.941	0.954	0.905	0.942
Refractive index	1.495	1.492	1.487	1.488	1.485	1.490
Optical rotation(degree)	-2.381	-2.340	-2.396.	-2.360	-2.495	-2.393

4.2.3.8 Analysis of Volatile oil by Gas Chromatography

The gas chromatographic analysis of volatile spice oils is a method of separation of volatile compounds based on their retention time within gas chromatographic column. Clevenger's method of volatile oil distillation gives the total volatile oil content in the powdered sample, whereas the gas chromatographic analysis is a tool to identify the various constituents of volatile oil for measuring the quality of the oil. As mentioned in earlier sections, volatile oil constitutes mainly of monoterpenes (70-80%), sesqueterpenes (20-30%) and small amount (less than 5%) of oxygenated compounds.

The Gas Chromatographic-Mass Spectra (GC-MS) analysis of one of the samples of volatile oil (Fig. 4.2.7) was done to identify these components. Based on the retention time, Kovats indices (Jennings and Shibamato, 1980; Davies, 1990) and also matching with the reference mass spectra (Adams, 1989) or by co-injection on GC,' nine major compounds were identified (Table 4.2.11). These were taken as markers to study the flavour quality of the oil. These nine compounds constituted 79 to 90% of the total volatile oil (Table 4.2.12). The absolute recovery data with respect to each component in volatile oil are shown in Fig 4.2.8 and 4.2.9.

The quantities of monoterpenes (Fig. 4.2.8 and 4.2.10) viz., a-thujene, a-pinene, sabinene, 13-pinene and limonene, present in the volatile oil was higher in large and medium sizes of particle. The quantity of monoterpene reached maximum when the particle size was 0.70 mm. At a higher particle size (2.10 mm), the release of monoterpenes was incomplete. At lower particle sizes (0.14 and 0.20 mm), less quantities of monoterpenes indicated that the loss was due to higher temperatures (45 to 65 C)

during grinding.

Table 4.2.11

Identification of flavour compounds in volatile oil of black pepper by GC-MS analysis

Compounds	Peak No.**	Retention time (Min)	Refractive index	Method of identification * * *
α-Thujene*	-	-		Co-GC
α-Pinene	A	3.767	942	RI, GC, MS
Sabinene*	-	-	-	Co-GC
~-Pinene	B	4.867	982	RI, GC, MS
Limonene	C	6.633	1033	RI, GC, MS
a-Copaene	**O**	24.300	1368	RI,MS
~-Caryophyllene	E	26.700	1428	RI, MS, Co-GC
~-Bisabolene	F	32.567	1505	RI,MS
Caryophyllene oxide	G	35.383	1582	RI,MS

* Identified by co-injection in gas chromatography
** Please see Fig.4.2.7 for details of GC peaks
*** GC means Gas Chromatography, Co-GC means co-injection of *GC,*
RI means refractive index, MS means mass spectrography

The quantities of sesquiterpene (Fig. 4.2.9 and Fig. 4.2.10) viz., α-copaene, β-caryophyllene, β-bisabolene and caryophyllene oxide, present in the oil were maximum at the particle size of 0.14 mm. At higher particle sizes, the release of sesquiterpenes was incomplete (Table 4.2.12). The amount of oxygenated compound (major compound: caryophyllene oxide identified from its mass spectrum and Kovats index value) present in volatile oil at various particle sizes varied from 0.20 to 0.26 mL/lOOg. In the present study, no noticiable change was observed except its complete disappearance in. the volatile oil obtained from the powder of particle size 0.2 mm, probably due to its conversion to β-caryophyllene during processing as observed by a rise in its quantity.

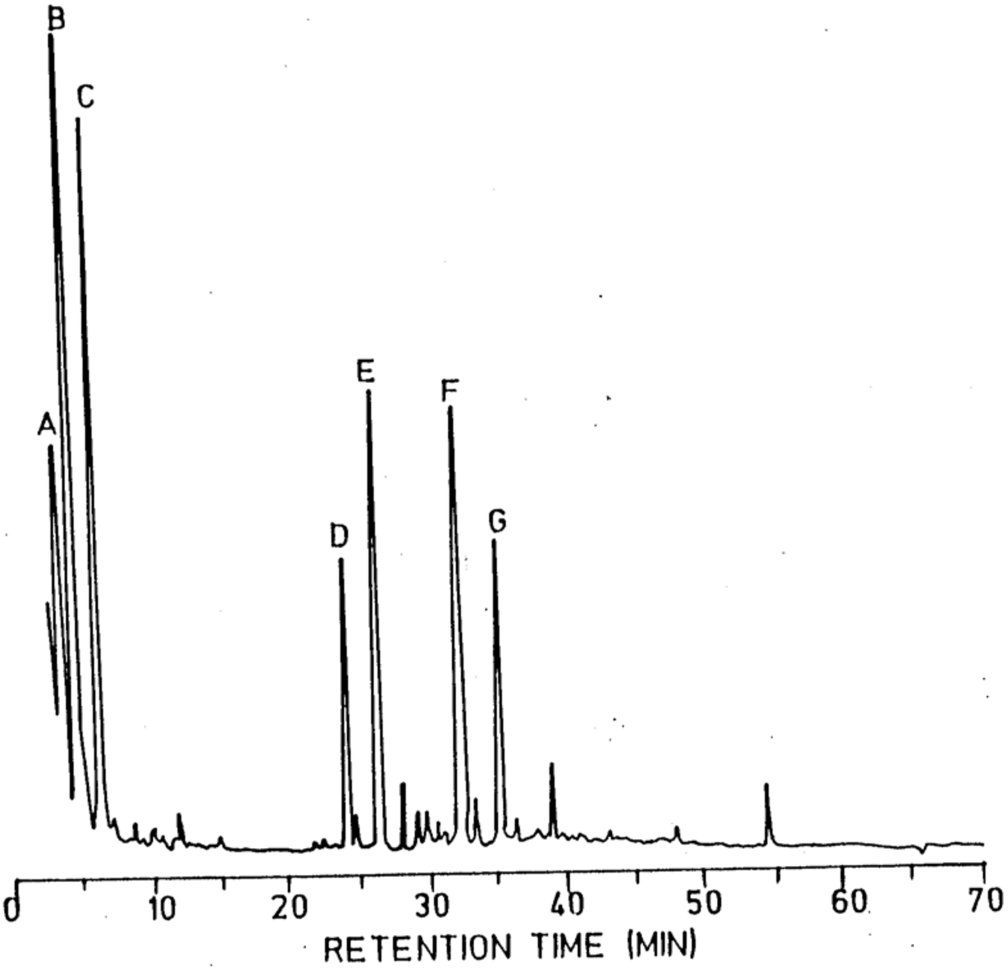


Fig. 4.2.7 GC-MS analysis of volatile oil for identifying constituents

Table 4.2.12

Gas chromatographic analysis data of volatile oil samples of black pepper ground to different particle sizes (% concentrations)

Compounds	Samples of black					
	PD1	PD2	PD3	PD4	PD5	PD6
1. α-Thujene	0.72	1.72	2.00	1.12	1.44	0.41
2. α-Pinene	3.38	5.57	8.58	4.59	4.87	1.65
3. Sabinene	16.68	19.52	24.47	17.23	15.19	7.80
4. β-Pinene	10.53	11.53	14.42	10.63	12.45	5.53
5. Limonene	26.17	24.20	23.31	22.70	23.82	15.62
6. α-Copaene	4.19	3.50	3.55	4.46	5.96	9.30
7. β-Caryophyllene	1.82	1.64	1.58	2.09	15.94	9.44
8. β-Bisabolene	6'(19	5.67	4.35	7.21	10.13	14.20
9.Caryophyllene	9.58	8.73	6.82	9.88	0.00	17.22
Total	79.16	82.10	89.08	79.91	89.80	81.17
Monoterpenes (%)	57.48	62.54	72.78	56.27	57.77	31.01
Sesqui terpenes (%)	21.68	19.54	16.30	23.64	32.03	50.16
Ratio of To Sesquiterpenes	2.65	3.20	4.47	2.38	1.80	0.62

* Particle sizes of. PO I. P02. P03. P04. P05 and P06 are 2.10. 1.23. 0.70. 0.61. 0.20 and 0.14 mm. respectivelv

Hubert (1991) observed that the ratio of monoterpenes to sesquiterpenes more than 1.74 would give strong peppery note to oil. Table 4.2.12, shows that the ratio was greater than 1.74 for oils obtained from particles sizes greater than 0.2 mm, for maximum amount of volatile oil with overall flavour quality. According to Salzer (1977), good amounts of monoterpenes for odour and the body, moderate amounts of sesquiterpenes for spicy note and reasonable amounts of oxygenated compounds should be present in the oil. Accordingly, the particle sizes of 0.6 to 0.7 mm were preferred. If large amounts of sesquiterpenes in the volatile oil are required, the particle sizes of 0.20 and 0.14 mm may be preferred which gives sweet and flowery notes (Lewis *et at.,* 1969). The variation in the content of sesqueterpenes was not significant (in the range of 0.48 to 0.74 mL/100g) as compared to the contents of monoterpenes. which varied from 0.46 to 2.13 mL/ 100g.

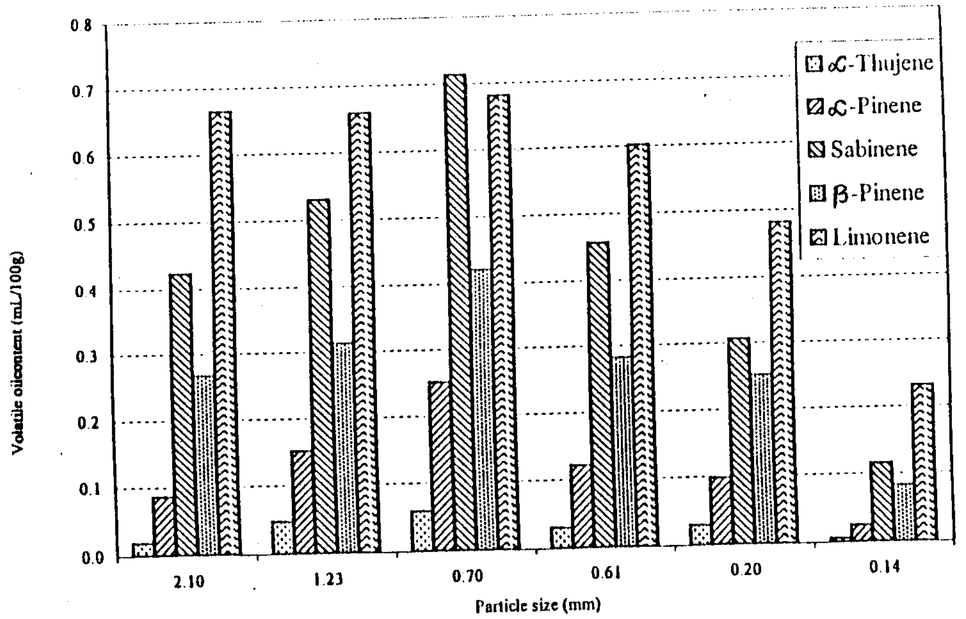
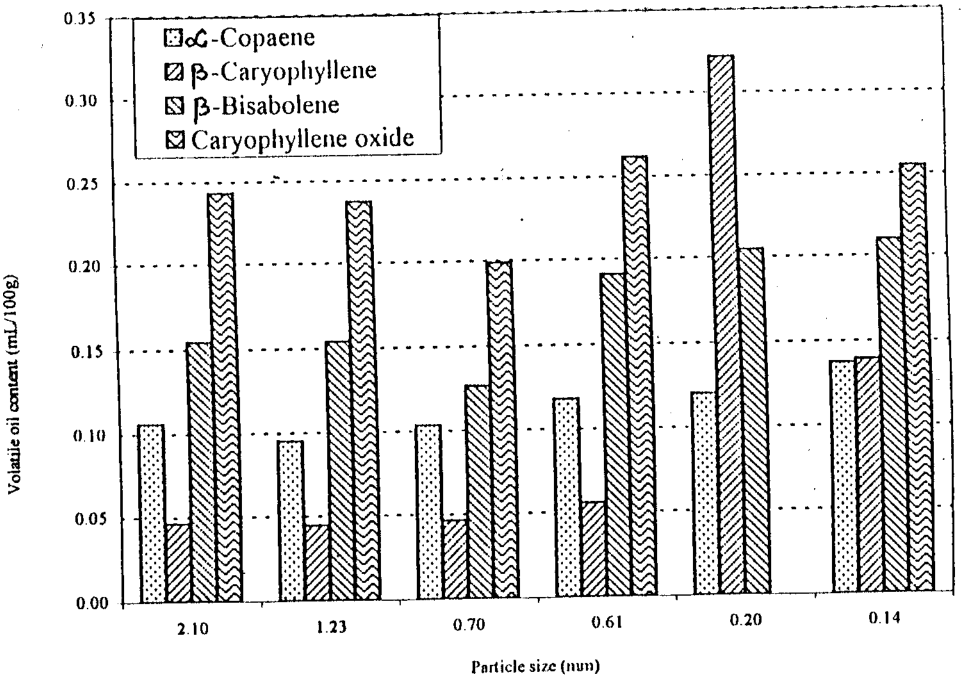


Fig. 4.2.8 Variations of 1lI0noterpenes constituents in black pepper volatile oil ground to different particle sizes



rig. 4.2.9 Variations of sesqucterpencs constituents in black pepper volatile oil ground to different particle sizes

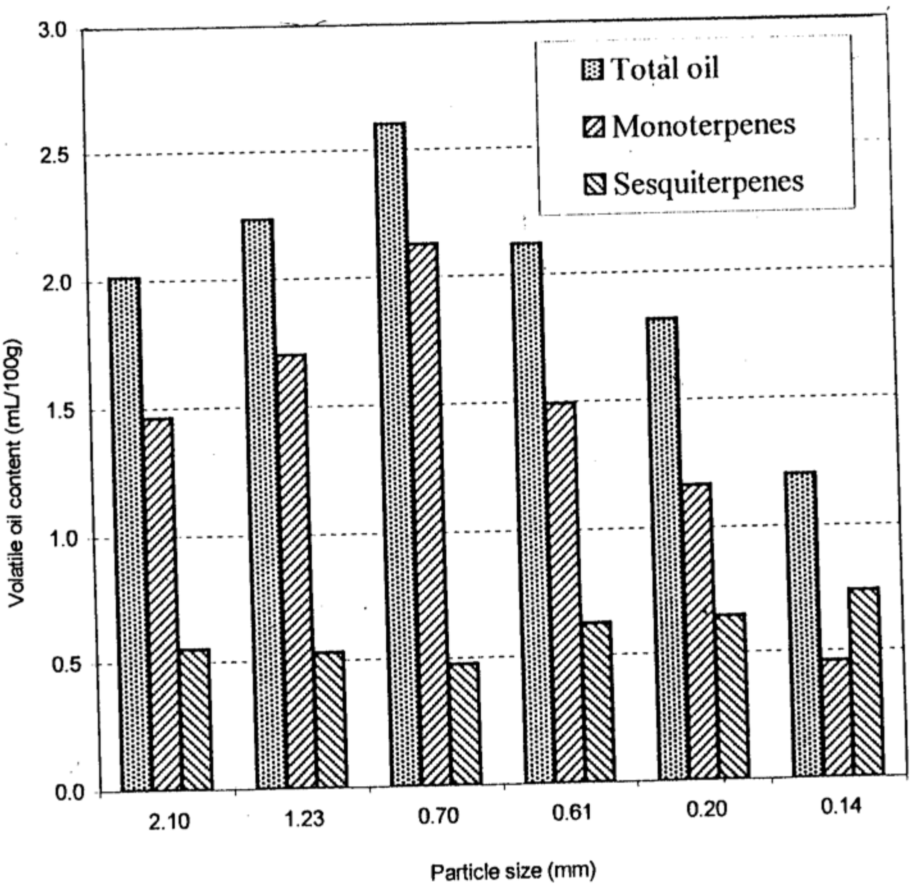


Fig. 4.2.10 Variations of total, l1lonoterpene and sesqueterpenes content in pepper volatile oil ground to different particle sizes

Typical gas chromatographs of PO 1 (2.1 0 mm) and P06 (0.14 mm) are indicated in Fig. 4.2.11 (a) and (b), respectively for comparison of distribution pattern of gas chromatographic peaks in both particle sizes. These graphs indicated that at higher particle sizes (2.10 mm) the contents of monoterpenes (viz., peak numbers 1 to 5) in the volatile oil were higher whereas the contents of sesquete~'penes (viz., peak numbers 6 to 9) were lower. In the case of lower or finer particle sizes (0.14 mm) the contents of sesqueterpenes were relatively higher. This meant that at finer particle sizes, the loss of monoterpenes could be higher due to higher product temperatures.

4.2.3.9 Effective Diffusion Coefficient

Distillation of volatile oil involves removal of volatile oil present in the powdered black pepper samples using Clevenger's apparatus (Section 3.2.3.2 of Materials and Methods). The quantity of volatile oil content per unit distillation time is a function of particle size, as has been mentioned in the earlier sections. If the particle size is very fine then the content of volatile oil is less due to the volatile oil loss during grinding. On the hand, if the particle size of the powder is coarse then volatile oil content is also less as the complete volatile oil present in the powder is not released during distillation. In this section, this phenomenon was analysed employing the diffusion theory (mentioned in Section 3.2.3.5) by determining the effective diffusion coefficients for different particle sizes of samples namely PDI, PD2, PD3, PD4, PD5 and PD6.

The volatile oil from the black pepper powder was distilled using Clevenger's apparatus. When the mixture of black pepper powder and water system was heated, the volatile oil constituents of the powder were be diffusing into water at 100 C during the distillation process. As there was sufficient agitation of powder-water mixture system due to buoyant forces while boiling in the apparatus, the surface resistance became small. Therefore, it was assumed that the total resistance was due to only internal resistance, and the phenomenon was analysed using diffusion theory employing Pick's second law (Eq.3.8). The powdered particles were assumed to be spherical in shape and surface mean particle diameters were used in determining the effective diffusion coefficients.

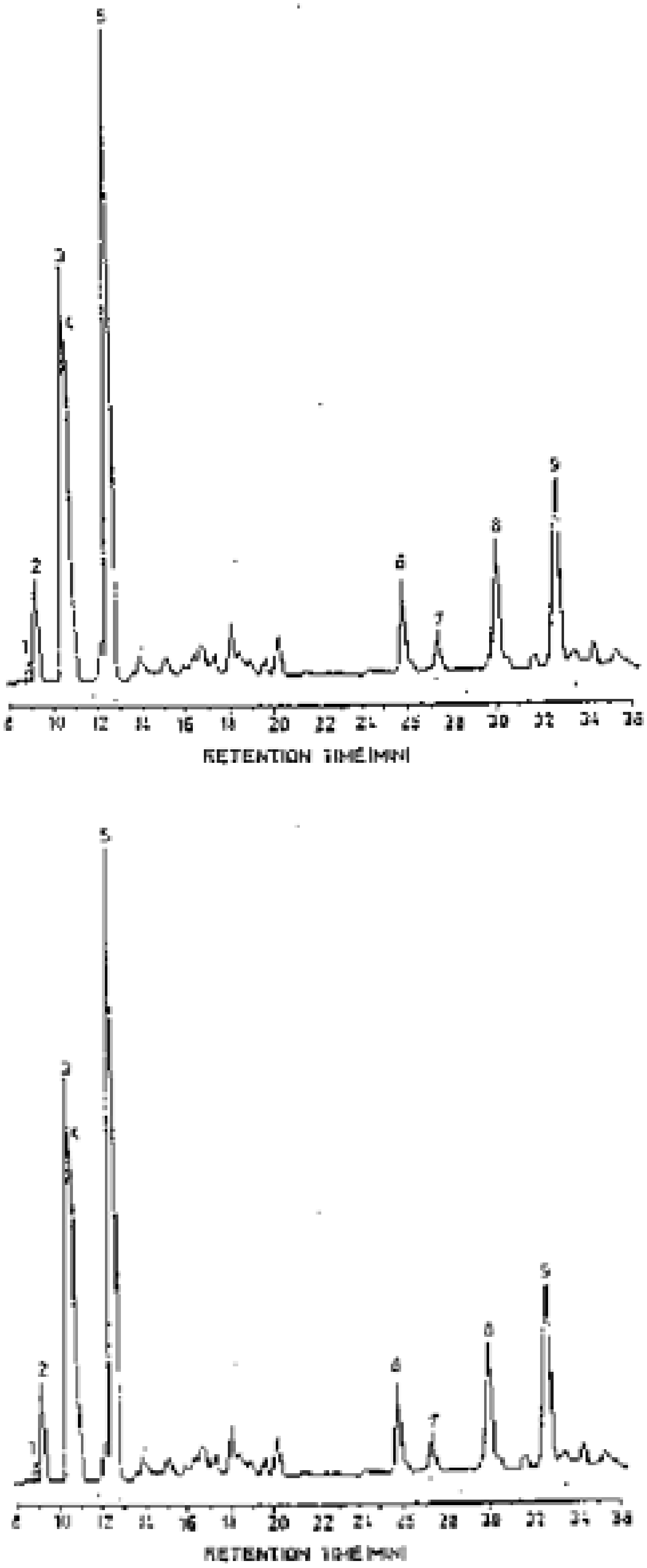


Fig. 4.2.11GC Profiles of black pepper volatile oil (a) at particle size of 2.10 mm and (b) at particle size of 0.14mm

The effective diffusion coefficient of the samples was calculated using Eq. 3.10, from the plots of In M^1 versus distillation time t, employing linear regression technique. However, the significance of the intercepts was overlooked (Spiro and Hunter, 1985). The initial oil content Mr in case of PDI, PD2 and PD3 was taken as 3.07 ml/100g (assuming 95% distillation efficiency of sample PD3). In the case of PD4, PD5 and P06 the initial oil contents were 2.80, 2.13 and 1.56 mI/100g, assuming 95% distillation to give their maximum yield. The weighed surface mean particle radius was determined using Eq. (3.3) for the calculation of effective diffusion coefficient.

The experimental data fitted well with the Eq. 3.6, as evidenced by high correlation coefficients (0.96 to 0.99) and the plots are shown in Figs 4.2. 12(a & b). The values of effective diffusion coefficients are shown in Table 4.2.7. The values of diffusion coefficients for coarser particle samples PO 1, P02, PD3 and P04 were of the same magnitude (1.7 x 10,11, 1.5 x 10,11, 1.1 x 10,11 and 1.2 x 10,11 m^2 S,I, respectively) with an average of 1.38 x 10'11 m^2 S,l. Gekas (1992) reported a value of diffusion coefficient to be 1.08 x lO'IIm^2 S'I for the extraction of oil from soybean flakes (0.43 mm thick) using hexane as solvent. Thus, the values of di~Tusion coefficients obtained in the present study compared well with literature values for coarser particles of higher oil concentrations. For finer powders (P05 and P06), the yalues were very low, 0.14 x 10,11 and 0.03 x 10,11 m^2 S,I, respectively, which might be attributed to low initial oil concentrations in these samples. The latter was in accordance with the observations made by Aguerre *et al.,* (1985) that the diffusion coefficients were not constant for drying and leaching operations at low concentrations.

4.2.3.10 Fourier Number

The Fourier number (F_o) was determined employing Eq. 3.9 which contains a range of values for n that can vary from unity to infinity. The values of effective diffusion coefficients were determined assuming n value as unity for simplification. To check whether this assumption was correct, the Fourier number (Fo= De tl^{r}s2) was determined using effective diffusion coefficients (De), obtained from the experimental data using distillation time (t) and surface mean radius of the powder. ,The values of Fourier numbers for powdered samples of PD1, PD2, PD3, PD4, PD5 and PD6 thus determined were 0.17,

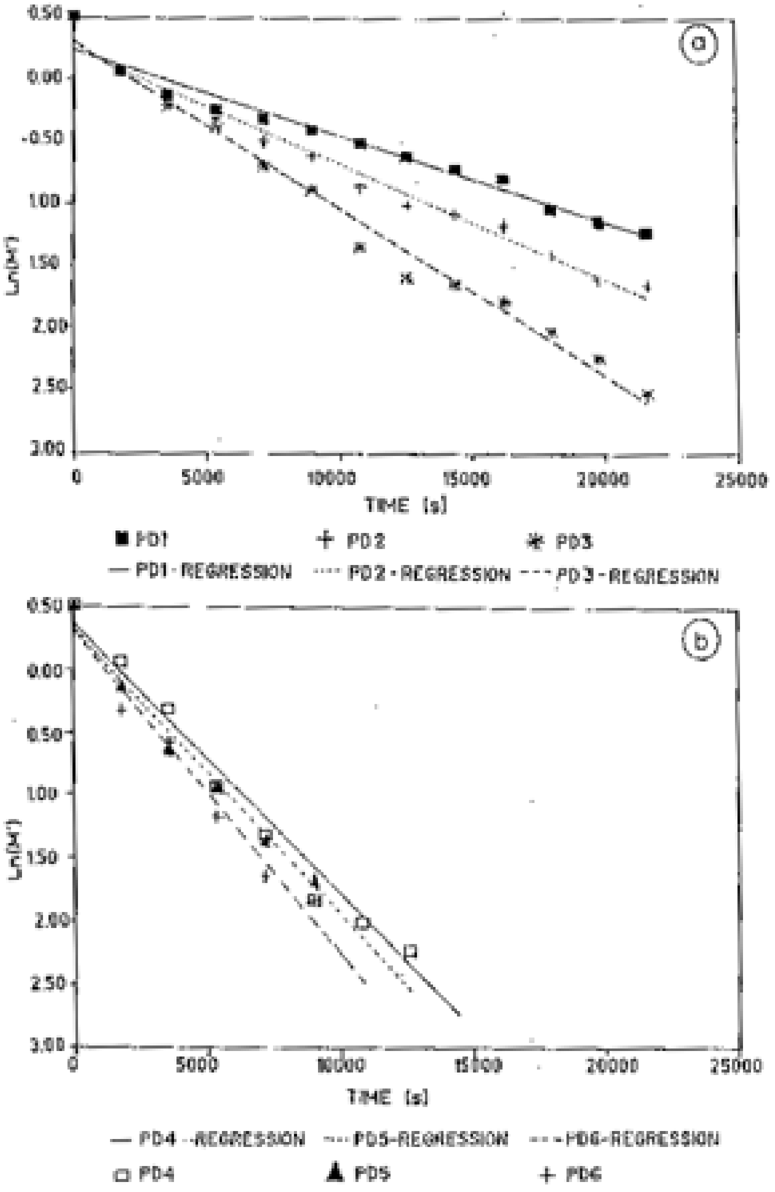


Fig. 4.2.12 Ln (M^l) versus distillation time at different particle sizes of black pepper powder (a) For samples of PD1, PD2 and PD3 (b) For samples of PD4, PD5 and PD6

0.20, 0.29, 0.31, 0.28, and 0.29, respectively. It has been reported (McCabe and Smith, 1976; Aguerre *et al.,* 1985) that if the Fourier number thus obtained is greater than 0.1 then the assumption of n=l in Eq. 3.9 is justified. It was observed in the present study that the Fourier numbers (Table 4.2.7) for all the particle sizes were greater than 0.1, which justified for considering only the first term (n=l) in Eq. 3.9, ignoring the higher order terms.

4.2.3.11 Conclusions

The study on ambient grinding characteristics has led to the following conclusions:

1) The particle size of powdered sample determined using sieve analysis varied from coarse to fine. The powdered sample of PD I, PD2, PD3, PD4, PD5 and PD6 had geometric mean particle diameters of 2.10, 1.23, 0.70, 0.61, 0.20 and 0.14 mm, respectively. The finer the particle size of powder the higher was the temperature of ground powder measured at the mill's outlet at steady condition, and obviously the finer the particle size the higher was the energy expenditure.

2) The time for volatile oil distillation of coarse to fine powdered samples varied from 390 to 180 min, respectively indicating that the finer were the powder particles the faster was the distillation.

3) The volatile oil content of samples of PD1, PD2, PD3, PD4, PD5 and PD6 at the end of distillation were 2.54,2.72,2.92, 2.65,2.02 and 1.48 mL/IOOg, respectively. The lowest volatile oil content was observed with fine particles. The particle mean diameter of 0.7 mm was found to be the optimum particle size which gave the desirable highest volatile oil content.

4) The physical properties of volatile oil viz., specific gravity, refractive index and optical rotation did not change in the range of experimental particle sizes.

5) The study on quality of oil using gas chromatographic analysis showed that higher ratio of monoterpenes to sesqueterpenes was present in coarse particles (> 0.2 mm),

and gave a very strong peppery note. Powdered particle sizes lesser than 0.2 mm contained more quantity of volatile oil that gave spicy, sweet and flowery notes. The content of sesqueterpenes varied marginally (0.5 to 0.7 mL/100g) as compared to the content of monoterpenes, which varied between 0.5 and 2.1 mL/100g for the range of particle sizes studied.

6. The effective diffusion coefficients (determined using Fick's second law) were fairly constant (1.38 x 10-^{11} m^{2} S-I) for powdered samples of POI, P02, P03 and P04 having higher initial oil concentrations. These were low for powdered samples of P05 and PD6 having lower initial oil concentration. The Fourier numbers determined for all the powered samples were greater than 0.1.

4.3 Cryogenic Size-Reduction or Cryogenic Grinding of Black Pepper

The aim of spice grinding was to obtain powder of smaller particle sizes with good quality in terms of aroma and flavour. In the ambient grinding process, heat is generated when energy is used to fracture a particle into smaller sizes. This generated heat IS detrimental to the finished product, as it rises the temperature to as high as 93 C (Wistreich and Schafer 1962), and it may result in considerable loss of aroma and flavour components, resulting in deterioration of quality.

The loss of volatile oil (aroma and flavour) can be significantly reduced by a cryogenic grinding technique (Pruthi, 1980). Liquid nitrogen at -195.6 C provides the refrigeration needed to pre-cool the spices and maintain the desired low temperature by not allowing the heat (generated during grinding operation) to increase the temperature of product. In addition to maintaining the low temperature, vapourisation of liquid nitrogen to the gaseous state, in effect, creates an inert and dry atmosphere for additional protection of spice quality. Pre-cooling of raw spice and continuous low temperature maintained within the mill reduce the losses of volatile oils and moisture contents, thereby retaining most of the flavour strength per unit mass of spice (Singh and Goswami, 1999a). As quantitative data on cryogenic grinding of Indian spices are scarce, this experiment was planned to study the grinding characteristics of black pepper employing the system of cryogenic grinding and to compare it with the conventionally followed ambient grinding method, both in laboratory scale (150 to 200 g) and at pilot scale (4 kg) grinding operations.

4.3.1 Evaluation of Cooling, Chilling and Cryogenic Freezing Methods for Grinding

A comparison of different cooling systems including cryogenic freezing is a prerequisite to know the advantages or limitations of these systems. Low temperature of the spice before grinding can be attained by different methods. The present section deals with four such methods for obtaining low temperature of feed spice prior and after grinding employing domestic mixer grinder (Fig. 3.4), using identical grinding conditions.

Table 4.3.1

Temperature of feed and products obtained by different methods of cooling

Sample Code	Method of cooling*	Temperature of black pepper (C)	
		Before grinding	After grinding
CAI	Cold room	13 ± 1	49 ± I
CA2	Plate Freezer	-11 ± 1	40±4
CA3	LN_2 indirect mixing	-38 ± 3	41 ± 2
CA4	LN_2 direct mixing	-195.6	-32 ± 3
CA5	Ambient	30± 0	61 ± 1

* Details of grinding systems employed are shown in Fig. 3.5 of chapd.er 3.

The following four cooling or chilling or freezing methods were employed. They were: (1) cooling black pepper in a cold room, (2) chilling black pepper using a plate freezer, (3) freezing by dipping black pepper enclosed in a polyethylene pouch in liquid nitrogen and (4) freezing black pepper by directly injecting liquid nitrogen into a known quantity of the spice. These methods of cooling or chilling or freezing are represented by schematic diagrams as shown in Fig. 3.5. The product temperatures were measured immediately after grinding. As expected, the lowest temperature of the product was obtained by directly mixing liquid nitrogen with black 'pepper sample (Table 4.3.1). This was because the heat transfer rate was higher in case of direct mixing of liquid nitrogen with black pepper as small droplets evaporated quickly by absorbing the latent heat of vapourisation from the sample. In other freezing methods, polyethylene cover acted as a barrier (insulating effect) for heat transfer between the spice and liquid nitrogen, and reduced the rate of heat transfer and hence, spice did not attain such a low temperature.

It was observed, from preliminary laboratory experimentation, that among the different methods of freezing (viz., cooling, chilling and cryogenic freezing) the cryogenic freezing method with liquid nitrogen, by direct injection into black pepper, was the most efficient method of freezing and reaching extremely low temperature of spice and spice powder. These results are used in subsequent sections and detailed grinding studies were conducted.

4.3.2 Evaluation of Cryogenic Grinding and Volatile oil Content of Black Pepper on a Laboratory Set-up

A comparison of cryogenic and ambient grinding was needed to judge the quality of the ground samples. Hence, the objective of this study was to compare the two grinding methods viz., cryogenic grinding and ambient grinding. Black pepper samples were ground using domestic mixer-cum-grinder under both cryogenic and ambient grinding conditions keeping other grinding parameters constant. Temperatures of the spice before and after grinding were recorded in both the cases (Table 4.3.2). These temperatures were -195.6 and -54.3 C, respectively for cryogenic conditions whereas for ambient grinding these temperatures were 28 and 36 C, respectively. The cryogenic condition yielded markedly higher volatile oil (3.18 mLlI00g) as compared to ambient sample (2.85 mL/100g).

Table: 4.3.2

Cryogenic (LN_2) grinding and content of volatile 'oil of black pepper as compared to ambient grinding in laboratory scale

Samples	Temperature of black pepper (C)		Content of volatile oil (mL/lOOg)
	Before grinding	After grinding	
Cryogenic grinding	-195.6	-54.3 ± 8	3.18 ± 0.03
Ambient grinding	+28 ± 0	+36.0 ± 2	2.85 ± 0.07

It was concluded from this laboratory scale experiment that cryogenic grinding could yield about 12% higher quantity of volatile oil from black pepper as compared to that of ambient grinding.

4.3.3 Effect of Cryogenic, Chilled, Ambient and High Temperature Grinding Methods on Grinding Characteristics in Laboratory Scale

During the ambient grinding of black pepper, the mill and product temperature might rise to as high as 93 C, and at such high temperature, there will be considerable loss of volatile oil (Wistreich and Schafer, 1962). Section 4.2 also supported this finding that at a high grinding temperature, the loss of volatile oil was considerably high. Cryogenic grinding could overcomes this problem and help in retaining more volatile oils (Section 4.3.2 in the present study, Pruthi 1980 and 1991). It has been reported (Anon, 1993) by a grinding equipment manufacturer (Hosakawa Alpine, 'Germany) that cryogenic grinding increased total volatile oil by 40% (Table 2.9). Mckee *et ai.* (1993) compared three grinding methods viz., ambient, chilled and liquid nitrogen with ground material temperatures of 40, 38 and 33 C, respectively and observed marginal variation in the volatile oil content.

The present section thus deals with studies on the effect of temperature on grinding characteristics of black pepper. The four grinding methods (as described in Section 3.3.3) were the powder samples of black pepper obtained by employing cryogenic, chilled, ambient and high temperature grinding methods. The temperatures of raw materials prior to grinding were maintained at -120, 10,24 and 40 C, respectively. The parameters determined for comparison were particle size, temperature rise, and quantity and quality of volatile oil. These parameters were selected considering the commercial importance of quality of ground spice.

4.3.3.1 Particle Size of Powder

Fineness of the powder is an index for quality of ground spice. It was measured in terms of quantity of powder by weight which passed through a 60 mesh sieve (US sieve) having aperture opening of 0.42 mm (Table 4.3.3). Fineness of powder was found to be greater (72.2 %) in case of LN_2 cooled samples. At cryogenic conditions, the material became brittle and crisp (Pruthi, 1991) making size reduction easy by shattering technique instead of tearing. At high temperature conditions, the fineness was the lowest (62.5%), and at chilled water and ambient grinding conditions, the values were 52.5 and

55.6%, respectively. These values indicate that LN2 ground samples possess the highest fineness which is highly desirable in commercial operations.

4.3.3.2 Temperature Rise During Grinding

The input and output temperatures of black pepper samples when subjected to grinding under different conditions are shown in Table 4.3.3. As expected, the product (powder) temperature was the lowest (-20 C) when liquid nitrogen was used for cooling the feed material, while, the product temperature was very high (62 C) when the feed material was stabilized at 40 C before grinding. At ambient conditions (24 C), the product temperature was 50 C while with chilled water circulation the product temperature was 30 C. The moisture content of the product varied from 11.8 to 13.5%. These results show that high temperature (prior or after grinding) is detrimental to quality of ground spice samples.

Table 4.3.3

Effect of grinding conditions on the volatile oil content and fineness of ground black pepper

Grinding Condition	Feed temperature (C)	Product temperature (C)	Moisture content (%)	Volatile oil content (mL/I00g)	Retention" of oil (%)	Fineness[b] (%)
High Temperature	40	62	11.8	2.65 ± 0.07		62.5
Ambient	24	50	13.5	3.]0 ± 0.09	17.0	55.6
Chilled water	10	30	13.4	3.56 ± 0.05	34.3	52.5
LN$_2$ cooling	-120	-20	12.5	3.60 ± 0.04	35.9	72.2

a - Percentage increase in retention of volatile oil as compared to high temperature condition
b- Percentage of powder by weight passing through a 60 mesh US sieve

4.3.3.3 Volatile oil Content of Powder

The volatile oil content of a ground spice is the primary index for quality of product. It was (Table 4.3.3) the highest (3.6 mL/100g) in the case of cryogenically (liquid nitrogen) frozen-ground sample and was least (2.65 mL/I00g) at the high product temperature of 62 C. The volatile oil content in chilled pepper sample and in liquid nitrogen frozen samples were close (3.56 and 3.6 mL/I00g, respectively) and were not significantly different ($p < 0.01$). The use of liquid nitrogen in grinding had not only increased the content of volatile oils (about 36% more as compared to high temperature method) but also improved the fineness of the product. In Industrial scale of applications where the highest temperature of powder can reach as high as 93 C, the content of volatile oils may even be higher with the application of liquid nitrogen. The chilled water circulation would also retain same quantity of volatile oils, as it happened in the case of liquid nitrogen method. But, chilled water technique was not sufficient to significantly reduce the temperature rise of the product (Singh and Goswami, 1999a). Also the particle size is also high. The direct mixing of liquid nitrogen and spices could efficiently cool (due to enhanced heat transfer rate) the spice rather than indirect cooling using chilled water technique in large scale grinding operations. It was thus, inferred that liquid nitrogen was an efficient cooling system (and also to obtain fine particles) as compared to other existing methods of grinding mentioned in this study.

Table 4.3.4

GC analysis data of black pepper oil samples obtained under different grinding conditions (Values are expressed on relative percent basis) .

Component	Grinding methods			
	High temperature	Ambient	Chilled water	LN_2 frozen
1. α-pinene	5.05	5.60	6.65	7.00
2. β-pinene	13.52	14.36	15.12	15.68
3. Myrcene	21.20	19.5Q	20.45	23.20
4. Limonene	22.80	22.18	22.90	23.80
5. B-caryophyllene	21.20	20.20	19.75	17.65
Total	83.77	81.84	84.87	87.33
Monoterpenes (%) (1-4)	62.57	61. 64	65.12	69.70
Sesqueterpenes (%) (5)	21.20	20.20	19.75	17.65
Ratio of monoterpenes to Sesq ueterpenes	3.00	3.10	3.30	3.90

4.3.3.4 Analysis of Volatile oil by Gas Chromatography

Chemical composition of the black pepper oil has been reported (Lewis *et al.,* 1969 and Govindrajan, 1977). Pepper oil is mainly made up of monoterpenes (70-80%), and sesqueterpene (20-30%), and a small amount (less than 5%) of oxygenated compounds is also present. The major monoterpenes present in the oil are α- pinene, β-pinene, myrcene, limonene and sabinene while β-caryophyllene is the chief sesqueterpene (the presence of myrcene, a monoterpene component was also observed in this variety of black pepper). The gas chromatographic analysis of the four oil samples obtained under different grinding (high temperature, ambient, chilled water and liquid nitrogen frozen) conditions and the relative percentage of some the main constituents of oil are presented in Table 4.3.4. Better retention of monoterpenes (α-pinene, β-pinene, myrcene, limonene) was observed in the case of chilled water and LN_2 cooled grinding (10 and -120 C) as compared to ambient and high temperature (24 and 40 C) ground conditions of grinding. The ratio of monoterpenes to sequeterpenes varied from 3.0 to 3.9 which indicated that all the four samples yielded volatile oil with a strong peppery note (Hubert, 1991). Figure 4.3.1 shows the variation of constituent compounds of volatile oil (in absolute quantities in mLlI00g). The content of all the four compounds was higher for chilled water and liquid nitrogen frozen ground samples compared to other powders. Considering β-caryophyllene, the values were slightly low (19.8 and 17.7) in the case of chilled water and LN_2 frozen (10 and -120 C) ground samples than that for ambient and high temperature (24 and 40 C) ground samples. Figure 4.3.2 shows the variations of constituent compounds of volatile oil viz., total oil, monterpenes and sesqueterpenes in absolute quantities (mL/100g). The contents of sesqueterpenes in the volatile oil was marginally different (0.6 to 0.75 mLlI00g), while these of monoterpenes were in the range from 1.6 to 2.5 mLlI00g. This was because the sesqueterpenes compounds were less sensitive to temperature unlike the monoterpene compounds. It is thus, concluded that LN2 samples possess highest quantity of monoterpenes compared to all other samples which gives the desirable feeling of flavour freshness.

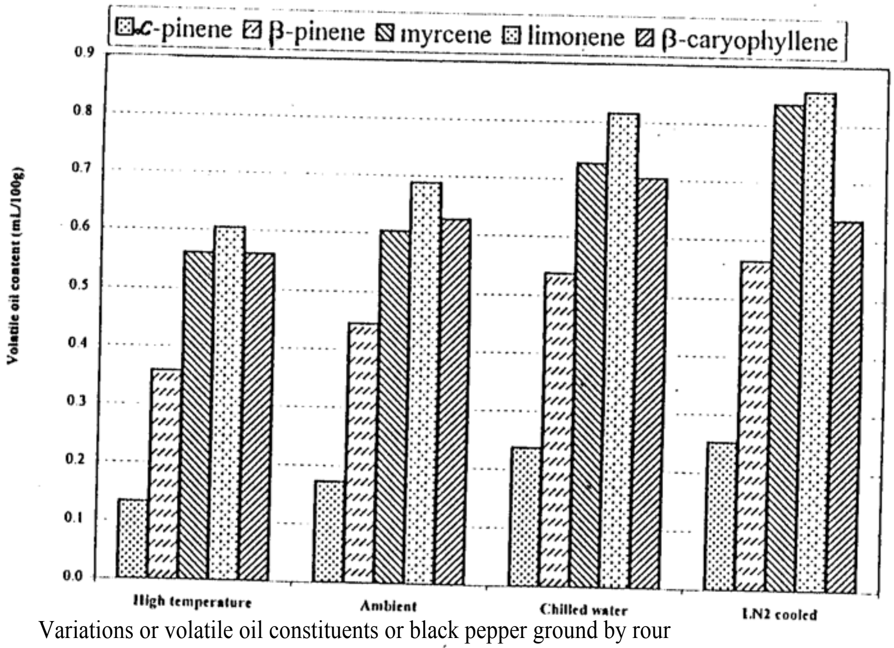


Fig. 4.3.1 Variations or volatile oil constituents or black pepper ground by rour diflerent grinding methods

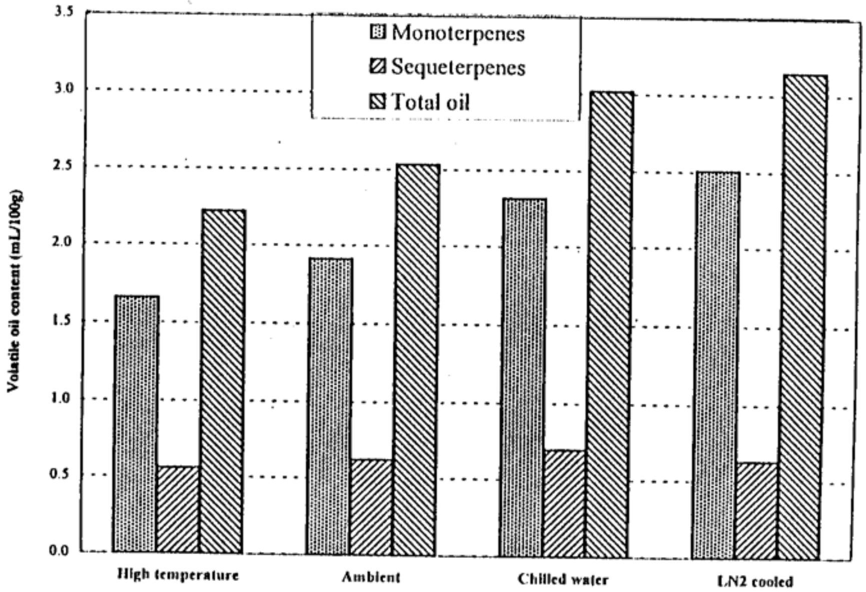


Fig. 4.3.2 Variations or total, monoterpene and sesqueterpenes content in volatile oil or black pepper ground by rour dirrerent grinding methods

4.3.3.5 Conclusions

It was concluded from the foregoing discussion that,

I) The particle size of black pepper powder ground by cryogenic method was the finest as compared to other three methods.

2) The cryogenic and chilled temperature methods .of grinding yielded similar quantities of volatile oil as compared to low quantities in ambient and high temperatures grinding methods. There was a gain of about 36% in the content of volatile oil by cryogenic grinding method as compared to high temperature grinding method. Chilled water technique was not adequate to markedly reduce the temperature rise during grinding of the product.

3) Gas chromatographic analysis showed that in cryogenic grinding technique, the contents of monoterpenes was higher compared"to those obtained by other methods. The content of sesqueterpenes was fairly similar in all four grinding methods employed in this study.

4.3.4 Cryogenic Grinding on a Pilot Scale

It was reported in the Section 4.3.3 that cryogenic grinding of black pepper in the laboratory scale grinding gave better grinding characteristics in terms of particle fineness, volatile oil content and quality of volatile oil. However, most of the studies have reported the results obtained on experiments conducted for a small batch size of spice (l00 to 200g). The reason being the high unit cost of spices and unavailability of high capacity LN_2 grinding facilities. Since experimental results are scanty in terms of pilot scale cryogenic grinding of spices, a study of cryogenic grinding of black pepper in a pilot scale (each sample run of 4 kg) grinder at various feed rates and temperature conditions was carried out to evaluate the grinding characteristics. This would not only simulate the industrial process but also generates data that would be useful for large scale trials, scaleup and process standardisation. A central composite rotatable design (CCRD) concept was used in this study to determine the effect of these variables and to find optimum grinding conditions in cryogenic grinding. The use *at'* experimental design was beneficial in reducing the number of experiments and thus reducing quantity of spices which are expensIve.

The raw material (black pepper) obtained from a local spice processing company (not from the local market) was used to simulate the real industrial situation to compare the cryogenic ground powder with that for ambient ground samples. This raw material was of a variety of low volatile oil content and had an average particle seed diameter of 4.1 mm.

The mill employed for both ambient and cryogenic grinding was the pin mill obtained from Hosakowa Alpine, Germany, 80 kg h(1 capacity having 3.7 kW motor (3 phase, 440 V and 50 Hz) and was made of stainless steel. It consisted of two rotors (one fixed and another rotating type) with a number of cylindrical stainless steel pins of 4 mm diameter affixed perpendicularly on them. The feed spice was fed axially, ground between the pins and powder exit was in the radial direction. The schematic diagram of the pilot scale cryogenic grinding set up is shown in Fig. 3.7.

4.3.4.1 Comparison of Cryogenic Grinding with Ambient Grinding

The following sections deal with the results obtained in cryogenic grinding technique compared with those of ambient grinding on pilot scale grinding operations in terms of quantity of volatile oil content, particle size of the powder, mill choking characteristics and quality of volatile oil. **In** this investigation, cryogenically ground samples (CI to C9) were compared with ambient ground samples (AI, A2) (Table 4.3.5).

Table 4.3.5

Results of volatile oil, moisture content and particle size of powder in cryogenic and ambient grinding in pilot scale

Codes for Sample *	Feed rate (kg hr-^{1})	Product temperature (C)	Moisture content (% wb)	Volatile oil content** (mL/100g)	Mean particle diameter (mm)
C1	35.00	-15.00	10.00	1.67± 0.05	0.22
C2	35.00	-40.00	10.80	1.91± 0.03	0.26
C3	60.00	-40.00	12.00	1.82± 0.06	0.25
C4	15.00	-54.00	12.00	1.87± 0.08	0.25
C5	15 .00	-40.00	11.00	1.35± 0.03	0.20
C6	52.00	-25.00	11.50	1.90± 0.04	0.27
C7	35.00	-60.00	10.00	1.78± 0.09	0.22
C8	7.00	-15.00	10.00	1.44±0.07	0.24
C9	52.00	-54.00	12.00	1.42±0.06	0.25
Al	35.00	53.00	10.00	0.98± 0.05	0.24
A2	15.00	86.00	8.40	0.78± 0.04	0.16

* C 1 to C9 were the cryogenic ground samples and Al & A2 were ambient ground samples
** Moisture free basis

4.3.4.1.1 Feed Rate and Product Temperature

The feed rate of grinding influenced the rise in product temperature during ambient grinding (Section 4.2.1) which in turn affected the quality attributes of the powder. The feed rate and product temperatures were found to be interrelated in ambient grinding. On the other hand, in case of low feed rate, the rise in product temperature (temperature gradient) was high (Table 4.2.2). Therefore, it was necessary to control the feed rate and the product temperature (independent variables) to study their effect on the grinding characteristics of black pepper.

In the pilot scale cryogenic grinding experimentation, the feed rate and the product temperatures during grinding were controlled by controlling both the feed rate of black pepper and flow of LN_2, according to the experiment design (Section 3.4.4.1). The feed rates, shown in Table 4.3.5, were varied from 7 to 60 kg h(1 using a vibratory (magnetic type) feeder. The product temperatures were maintained at a predetermined temperature using a temperature controller by suitably monitoring the flow of liquid nitrogen into the mill. The product temperature were in the range of -15 ± 3 to -60 ± 3 C (Table 4.3.5). The range of feed rate was chosen based on the equipment specification, particularly the capacity. However, the product temperature chosen was based on the following aspects of industrial situations, (1) the minimum temperature chosen should not be very low which would otherwise leads to difficulty in storage of powder for retail distribution, and (2) the maximum temperature chosen should be slightly away from the freezing point of water (0 to 5 C). Hence, the temperature range of about -IOta -65 Cwas chosen. The feed rates of two control (ambient grinding) samples (in addition to that of experimental design) were maintained at 15 and 35 kg h(1 and the product temperature reached were 86 and 53 C, respectively.

4.3.4.1.2 Particle Size of Powder

The average particle sizes of the powders were determined by adopting the sieve analysis technique using Eq.3.2 and the results are shown in the Table 4.3.5. The geometric mean particle diameters in the case of cryogenic grinding varied from 0.20 mm to 0.27 mm, with an average of 0.25 ± 0.02 mm and in case of ambient grinding, it was

0.20 ± 0.04 mm. The geometric mean particle diameter in the case of cryogenic grinding was higher (coarser) than the ambient ground black pepper powder. This apparently contradicted the data reported in the literature that cryogenic grinding improved the fineness of powder (Section 2.4.5 (b)). Higher (coarser) particle size in case cryogenic grinding may be attributed to the fact that the moisture content of cryogenic ground powder was higher as compared to samples ground in ambient conditions. Higher moisture content of powder improved the cohesiveness of particles and they stuck to each other, thereby increases apparent particle mean diameter. However, the mean diameters of the powder particles was more consistent across the batch of nine cryogenic ground samples (samples C1 to C9). These results indicate that particle size of product also depended upon moisture content of feed apart from varying with feed rate and temperature. Thus, the grinding trials were conducted with constant moisture feed.

4.3.4.1.3 Mill choking characteristics

Mill choking or sieve choking is a phenomenon in grinding of foods in which ground material which is sticky (not free flowing) in nature adheres to the grinding surfaces or blocks the sieve opening. It is a crucial characteristic in grinding of spices which usually have higher fat content. In large scale ambient grinding operations, the ground products accumulate on the walls of mills or. block the sieve opening (Anon, 1962) which may result in fire hazard or breakdown of the mill. It has been reported (Landwehr and Pahl, 1986) that almost all grinding experiments on pepper without chilling caused choking of sieve and ultimately led to breakdown of the mill. Watanabe *et at* (1978) reported that grinding of nutmeg was impossible above 20 C but it was possible to grind at temperature below -40 C. Sieve choking characteristics were photographed at various temperatures of powder in cryogenic grinding of cumin and clove (Singh and Goswami, 1999a and 2000), who observed that at high temperatures, the blockage of sieves was high.

In the present investigation, it was observed that there was higher accumulation of pepper powder on the different grinding surfaces viz., between the pins, and mill walls during ambient grinding. The reasons for powder accumulation may be due to the fact that during grinding at the temperature higher than the brittle point of black pepper and

4.2.1.2 Particle Size of Powder

The particle size of the ground material affect the consumer acceptability and, hence is an important quality attribute. The particle size' of powder was determined by 'sieve analysis technique (method cited in Section 3.2.1.1). Table 4.2.2 shows that the three feed rates viz., 3.6, 4.8 and 9.5 kg hr^{-1} yielded the powders (when the mill attained stabilized condition) having geometric mean particle sizes of 0.13, 0.20 and 0.61 mm, respectively. The feed rate of 9.5 kg hr^{-1} (highest feed rate) reached the equilibrium temperature at the earliest (15 min). Fine particle size could be achieved with low feed rate because of longer residence time of the sample inside the grinding system.

Table 4.2.2

Effect of feed rate on particle size and on rise in product temperature at the time of stabilisation of grinding mill

Sl No.	Feed rate (kg hr^{-1})	Temperature of feed* (C)	Rise in product temperature (C)	Time for stabilization of mill** (min)	Geometric mean particle size of powder after grinding ** (mm)
1	3.6	27	49	22	0.14
2	4.8	31	29	24	0.20
3	9.5	27	09	15	0.61

* Indicates ambient temperature
** Coefficient of variation (CY) < 15%

4.2.1.3 Volatile oil Content of Powder

Volatile oil content in the spice powder is a measure of its aroma and flavour, and hence its quality. Higher the volatile oil content in spice powder, the higher is its market value in financial terms since spices are valued for their aroma and flavour (Gopalkrishnan *et al.,* 1991). Therefore, in order to have a better quality of the ground spice, it is desirable that the volatile oil content should be as high as possible. It is thus desirable to determine the volatile oil content with a detailed analysis of the volatile oil.

Volatile oil content as determined by distillation (method cited in Section 3.2.1.3) has been reported as volatile oil content of black pepper powder throughout the present research. The moisture content of spice samples are reported in a similar way. The coefficient of variation (CY) was less than 10%.

The volatile oil contents (moisture free basis) of black pepper powder drawn at different temperatures and feed rates are shown in Table 4.2.3. The volatile oil content in the powder varied with both particle size and the temperature. The loss of volatile oil in comparison to the hand pounding (control sample) is reported in Table 4.2.3, which shows that as the temperature of the product increased, the volatile oil content decreased and hence the loss of volatile oil as compared to control sample increased markedly. These two indices also varied with feed rate, and a high feed rate (and hence, low grinding or residence time) reduced the loss of these important quality parameters. The closest value of 1.91 mL/100g, as compared to control sample (2.15 mL/100g), was obtained only with highest feed rate of 9.5 kg hr^{-1} because the rise in temperature during grinding was hardly 9 C. In other words, the loss of volatile oil was the lowest (11.2%) at a feed rate of 9.5 kg $hr-^{1}$ and highest (50.7%) at a feed rate of 3.6 kg hr^{-1}. The corresponding geometric mean particle sizes were 0.61 and 0.14 mm respectively (Table 4.2.2). It was observed in the present study (Section 4.2.1.2) that low feed rate gave a powder of fine particle size, and high powder temperatures (at equilibrium during grinding) but with highest loss of volatile oil. Similar results have been reported by Gopalkrishnan *et al.* (1991) for ambient grinding of cardamom, wherein the loss of volatile oil varied from 26% to 52% for particle size of 1.00 to 0.25 mm, respectively.

The volatile oil content in the black pepper samples followed a negative relation with product temperature analysis, according to the following empirical equations at different feed rates of 3.6 and 4.8 kg $hr-^{1}$ (regression equation was not possible for 9.5 kg hr^{-1} due to insufficient data points):

At 3.6 kg hr^{-1}:

$$V_o = - 0.011\ T + 1.898 \tag{4.2.4}$$

2) At 4.8 kg hr^{-1}: (4.2.5)

$$V_o = - 0.024\ T + 2.781$$

where V_o is the volatile oil content (mL/100g) and T is the corresponding product temperature (C). The coefficients of determinations were 0.99 and 0.96, respectively.

The predicted product temperatures at different feed rates by using Eqs. 4.2.4 and 4.2.5 are given in Table 4.2.3. The predicted values by regression compared well with the experimental ones.

Table 4.2.3

Effect of feed rate on temperature, moisture and volatile oil content of the ground black pepper powder samples

(Initial volatile oil content by hand pounding (control) sample = 2.15±0.04 mL/100g)

Feed rate (kg hr^{-1}	Ground material temperature (C)	Moisture content (%) wet basis	Volatile oil content (moisture free basis) (mL/100g) Experimental values	Predicted from the regression equation	Loss of oil due to grinding* (%)
3.6	43	8.0	1.43 ± 0.09	1.42	33.5
	50	7.4	1.32 ± 0.03	1.34	38.6
	67	7.3	1.15 ± 0.05	1.15	46.5
	75	6.0	1.06 ± 0.08	1.06	50.7
4.8	40	8.0	1.82 ± 0.09	1.83	15.3
	48	8.0	1.65 ± 0.07	1.64	23.3
	50	7.9	1.62 ± 0.05	1.59	24.6
	52	7.2	1.51±0.12	1.54	29.7
9.5	36	8.2	1.91 ± 0.10	-**	11.2

* Loss of oil was calculated in comparison to the control sample

** Could not fit an equation due to insufficient data points

Similar results have been reported by Singh and Goswami (1999b) during ambient grinding of cumin seed. In their study, the volatile oil content decreased from 2.86 to 2.26 mL/100g with grinding temperature increasing from 40 to 85 C. Further, the statistical analysis of the data obtained by these researchers revealed the decrease in volatile oil content was significant at all the grinding temperatures ($p \leq 0.01$) under ambient condition. This was because of the fact that during the ambient grinding process, the mass transfer rate increased due to an increase in vapour pressure at higher temperatures which resulted in a loss of volatile oil at corresponding temperatures (Wolf and Pahl, 1990). The empirical equation ($r^2=0.99$, $p \leq 0.01$) obtained by regression analysis using the experimental data of Singh and Goswami (1999b) for ambient grinding of cumin seeds is represented as:

$$V_o = - 0.014 T + 3.460 \qquad (4.2.6)$$

where V_o is the volatile oil content (mL/100g) and T is the corresponding product temperature. It is observed that the empirical Eq. 4.2.6 was similar to the empirical equations (Eqs. 4.2.4 and 4.2.5) obtained in the present study.

The moisture content of the ground samples varied from 6.0 to 8.2 %, and higher the powder temperature lesser was the moisture content of the samples. The highest moisture loss (moisture content was 6%) was observed at a product temperature of 76 C which was expected because of high rate of vaporisation of moisture from the powder sample at a high temperature.

4.2.1.4 Conclusions

From the foregoing results and discussion on performance study of swing type hammer mill at different feed rates, it was concluded that

1) The product (black pepper powder) temperature reached a temperature of as high as 76 C at the lowest feed rate of 3.6 kg h(l. The product temperature during grinding followed a polynomial of third order with grinding time. The rise in product

temperature was of the order of 49, 29 and 9 C at the feed rates of 3.6,4.8 and 9.5 kg hr^{-1} respectively.

2) The geometric mean particle sizes of the products were 0.14, 0.20 and 0.61 mm at the feed rates of 3.6, 4.8 and 9.5 kg hr-^{1}, respectively. The lower the feed rate the finer was spice powder and vice-versa.

3) The volatile oil contents of black pepper samples at the stabilisation temperatures of 75, 52 and 36 C were 1.06, 1.51 and 1.91 mL/lOOg, respectively. The volatile oil contents varied negetively with the product temperature at different feed rates. The loss of volatile oil due to grinding was calculated with respect to the control sample (hand pounding) and the values varied from 11.2 to 50.7% depending on feed rate and product temperature. Volatile oil content also varied with both powder temperature and average particle size. Lower feed rate gave a powder of finer particle size, higher powder temperatures but highest loss of volatile oil whereas the high feed rate gave a powder of coarse particle size, low powder temperature but lowest loss of volatile oil.

3)

4.2.2 Performance Study of Different Types of Mills of Various Capacities

Based on grinding trials (Section 4.2.1) in a particular size reduction unit at different feed rates, and determining the temperature rise during grinding and loss of volatile oils in ground samples, the second set of experiment was planned, to study the performance of different types of commonly used grinding mills. The objective of this investigation was not only to confirm the earlier results reported in Section 4.2.1, but also carry out further detailed studies on the characteristics of grinding vis-a-vis volatile oil components in five commonly used grinding mills.

Black pepper seeds were ground in five different grinding mills VIZ., Swing hammer mill, Hammer mill (APEX make), Plate (DIAF make) mill, Plate Mill, Roller Mill which are commonly used for grinding of spices in India. These mills were of different capacities (Table 4.2.4) as it was extremely difficult to obtain commercial mills of similar capacities. The results of the study are discussed in the subsequent sections.

4.2.2.1 Particle Size of Powder

The geometric mean particle sizes of the ground powders were determined from the sieve analysis technique using Eq. 3.1. Swing hammer mill and Hammer (APEX make) mill had the provisions to introduce sieves to roughly control the particle size, whereas other mills did not have the provisions to introduce any sieve. The geometric mean particle sizes obtained by grinding in Swing hammer mill, Hammer (APEX) mill, Plate (DIAF) mill, Plate type, Roller mill and hand pounding, were 0.20, 0.25, 0.38, 0.16, 0.50 and 0.63 mm, respectively (Table 4.2.4). The raw material (black pepper) had a geometric mean particle diameter of about 5 mm. Fine particle 《0.2 mm) was obtained when ground in Plate mill, whereas coarse particles (> 0.5 mm) resulted by to hand pounding (Table 4.2.4).

Table 4.2.4

Performance evaluation of commonly used grinding mills during ambient grinding of black pepper

(Ambient temperature = 30 C)

Parameters	Type of Mill					
	Swing hammer Mill	Hammer (APEX) Mill	Plate (DIAF) Mill	Plate Mill	Roller Mill	Hand pounding (control)
Capacity of mill (kg/hr)	10	25	10	60	100	-*
Quantity of material ground (kg)	5.0	5.0	5.0	10.0	5.0	0.1
Volatile oil content # (mL/100g)	1.61 t 0.08	2.58 to.09	2.65 to.07	1.24 to. 10	2. 15tO.08	2.15 t 0.04
Product Temperature$^{\#\#}$ (C)	52	43	47	68	30+	30+
Moisture content (%, wet basis)	11.0	10.6	11.2	8.6	11.6	10.0
Particle size (mm)**	0.20	0.25	0.38	0.16	0.50	0.63

* Not determined.

\# Moisture free basis ##

SD is less than 1 C

**Geometric mean particle diameter +

+Indicates ambient temperature

4.2.2.2 Volatile oil Content of Powder

The volatile oil contents (moisture free basis) from Swing hammer mill, Hammer (Apex) mill), Plate (DIAF) mill, Plate type and Roller mill from Swing hammer mill, Hammer (Apex) mill), Plate (DIAF) mill, Plate type and Roller mill were 1.61,2.58,2.65, 1.24 and 2.15 rnL/100g, respectively (Table 4.2.4). The results were comparable *with* those of the control sample obtained by conventional hand-pounding (2.15 rnL/I00g).

Seeds ground in swing type hammer mill and Plate mill yielded powders having less volatile oil content. This may be attributed to higher grinding temperature and finer particle size of powder. On other hand Plate (DIAF) type and Hammer (APEX) type yielded powders having higher oil contents than the control sample because of the low temperature attained during grinding in these mills. Seeds ground in both Roller mill and hand pounding (control sample) yielded similar quantities (2.15 mL/100g) of volatile oil. In these mills, despite having lower grinding temperature (30 C), the volatile oil content was less than that of volatile oil obtained from Plate (DIAF) mill and Hammer (APEX) mill. This may be due to coarser particle size of powder which resulted in incomplete distillation of volatile oil (Vide Section 4.2.3.4). The temperatures of the powders were 52, 43, 47, 68, 30 and 30 C, respectively in those selected six different systems at stabilised grinding condition, while the ambient temperature was around 30 C. These results indicated that the quality of ground powder in terms of volatile oil content depended on the type of the mill employed for grinding. This indicates to the fact that appropriate mill is needed to have a good quality spice powder.

4.2.2.3 Analysis of Volatile **oil** by Gas Chromatography

The gas chromatographic (GC) analysis of volatile oils is a method of separation and identification of volatile compounds based on their retention time within gas chromatographic column. Clevenger's method of distillation of volatile oil gives the total volatile oil content in the powder sample, whereas the gas chromatography is a tool to identify the various constituents of volatile oil for measuring the quality of the oil.

Hasselstrom *et al.* (1957), Uday Sankar (1989) and Pino *et al.* (1990) have reported the constituents of black pepper oils obtained, by steam distillation and by supercritical carbon dioxide extraction methods, respectively. Pepper oil constitutes mainly monoterpenes (70-80%), sesqueterpenes (20-30%) and a small amount (less than 5%) of oxygenated compounds (Lewis *et al.,* 1969 and Govindarajan 1977). The compounds viz., α-thujene, α -pinene, sabinene, β-pinene, 1,8-cineole and limonene are the monoterpenes present in the volatile oils of black pepper, whereas the sesqueterpenes are α-copaene, β-caryophyllene, β-bisabolene and caryophyllene oxide (which is an oxygenated compound, and is also classified under sesqueterpenes). The chemical formula, molecular weights and boiling points of the above compounds are shown in Table 2.2 of Review of Literature. Monoterpenes are the lower molecular weight compounds (molecular weights being 136 to 154), having lower boiling points as compared to the sequeterpenes (molecular weights being 204 to 222).

Table 4.2.5

Gas chromatographic analysis of ground pepper samples using different mills (Relative concentrations are shown as percentages)

SI No	Compounds	Mill type					
		Swing hammer type mill	Hammer (APEX) type mill	Plate (OlAF) type mill	Plate mill	Roller mill	Hand pounding
I	Thujene+α-pinene	6.01	7.60	8.69	2.80	7.04	8.97
2	Sabinene+ β-pinene	18.84	22.53	24.31	11.79	21.34	22.19
3	1,8-cineole+ limonene	20.98	23.06	20.13	15.90	22.25	22.01
4	α-copaene	5.24	4.79	4.25	6.25	4.74	4.25
5	β- caryophyllene	8.93	5.33	3.39	10.65	4.58	8.74
6	β -bisabolene	9.61	7.63	5.23	11.14	6.90	8.81
7	Caryophyllene oxide	8.55	10.18	9.14	12.24	9.86	5.49
8	Total	78.16	81.12	75.14	70.77	76.71	80.46
9	Monoterpenes (1 to 3)	45.83	53.19	53.13	30.49	50.63	53.17
10	Sesquiterpenes (4 to 7)	32.33	27.93	22.01	40.28	26.08	27.29
11	Ratio of Monoterpenes to Sesquiterpenes	1.42	1.90	2.41	0.76	1.94	1.95
12	Monoterpenes (%)*	58.64	65.57	70.71	43.08	66.00	66.08
13	Sesquiterpenes (%)*	41.36	34.43	29.29	56.92	34.00	33.92

* Percent present in total oil

The ratio of monoterpenes to sesqueterpenes in the volatile oil is an important quality attribute. Hubert (1991) observed that the ratio of monoterpenes to sesquiterpenes of more than 1.74 would give strong peppery note in oil. According to Salzer (1977), the ratio of monoterpenes to sesquiterpenes represents the quality of the volatile oil and indicates aroma value. Monoterpenes provide the odour and body to the volatile oil whereas the sesquiterpenes provide the spicy note to the volatile oil. In other words, while the powder is fresh, it contains more of monoterpenes in the volatile oil. Hence, it is desirable to have more monoterpenes in the volatile oil.

The concentrations of black pepper volatile oil compounds obtained in the present study are shown in Table 4.2.5. Pino *et al.* (1990) identified a total of 46 compounds (Table 2.1) present in the volatile oil which included, trace elements. In present research, however, only nine major volatile oil compounds were chosen and used for analysis. The quantity of monoterpenes viz., α-thujene+α-pinene, sabinene+β-pinene, 1,8cineole+limonene, present in the volatile oil were analysed by gas chromatography technique. The quantity of sesqueterpenes viz., α-copaene, β-caryophyllene, β-bisabolene and caryophyllene oxide (an oxygenated compound), present in the oil were also analysed by gas chromatography technique. The total relative percentage concentrations of black pepper volatile compounds used in all the selected mills varied roughly between 70% and 80% in the present study. Among the mills, Hammer mill (APEX), Plate (DIAF) mill, Roller mill and hand pounding gave ratios of monoterpenes to sesqueterpenes as 1.90, 2.41, 1.94 and 1.95, respectively, which indicated that the volatile oils had a strong peppery note. The oils obtained from samples ground in these mills had more concentrations of monoterpenes. The oil obtained from Swing type hammer mill gave a ratio of monoterpenes to sesqueterpenes of the order of 1.42, whereas that from Plate mill gave a least value of 0.76, which indicated that oil obtained from these two mills had more concentration of sesqueterpenes. This might be due to high volatility of monoterpene compounds at higher temperature, as grinding temperatures in Swing type hammer mill and Plate mill were 52 C and 68 C, respectively. Table 4.2.6 shows the vapour pressure and temperature data available for a few monterpene compounds of volatile oil (Perry, 1950). It can be seen from Table 4.2.6 that if the vapour pressure of the compound was reduced below atmospheric pressure then the boiling point of that particular compound also reduced. During grinding, the high rotational speed of mill reduced the pressure in the grinding zone to less than the atmospheric pressure (760 mm Hg). At this point, the boiling point of the volatile oil compound came down depending on the pressure drop in the grinding zone (Table 4.2.6). If the temperature gradient (the difference between the grinding temperature and boiling point) was reduced considerably then there was an increase in mass transfer of that particular compound from powder to (the surrounding atmosphere. The temperature gradient was much high in case of Swing type hammer mill and Plate mill due to increased grinding temperature (52 and 68 C). Singh and Goswami (l999b) have also observed loss of highly volatile components with low boiling points during ambient grinding of cumin at a temperature of 85 C.

Figures 4.2.2 - 4.2.4 show the contents of, various compounds present in the distilled volatile oil (expressed as mL/100g) as determined by combining Table 4.2.4 and Table 4.2.5. For example, in case of Swing type hammer mill, the content of β-caryophyllene was calculated as (8.93*1.61/100) = 0.14 mL/I00g. The total volatile oil (all the nine compounds) content was calculated as (78.16*1.61/100) = 1.25 mL/100g; the content of monoterpenes as (45.83* 1.61/100)= 0.74 mL/100g; the content of sesqueterpenes as (32.33* 1.61/100)= 0.52 mL/ 100g. Though the total volatile oil content was 1.61 mL/I00g (Table 4.2.5) in case of grinding in Swing type hammer mill, the total of all nine major compounds of volatile oil was only 1.25 mL/100g. The rest of volatile oil of about 0.36 mL/100g accounted for unidentified and trace compounds. The above method of determining the volatile compounds in mL/100g was followed throughout the present work.

Figure 4.2.2 shows the plot of total oil content, quantities of monoterpenes and sesqueterpenes for different grinding mills. The content of monoterpenes was lowest in samples ground in Swing type hammer mill and Plate mill. This was basically due to the fact that the powder temperatures were high (52 and 68 C) and powder particles were too fine (0.20 and 0.16 mm) for these mills which had resulted in the loss of light and highly volatile components viz., the monoterpenes (Pesek *et al.,* 1985; Pesek and Wilson, 1986). On the other hand, the total content of monoterpenes was dependent upon the type of mill. The maximum content of monoterpenes was observed in the powder obtained by grinding in Hammer (APEX) mill and Plate (DIAF) mill where the powder temperatures were slightly low (43 and 47 C) with powder particle size of 0.25 and 0.38 mm, respectively. The samples of Roller mill and by hand pounding did not yield highest quantity of monoterpenes despite having a low powder temperatures (30C) as the powder particle sizes were coarser viz., 0.50 and 0.63 mm respectively (this phenomenon was

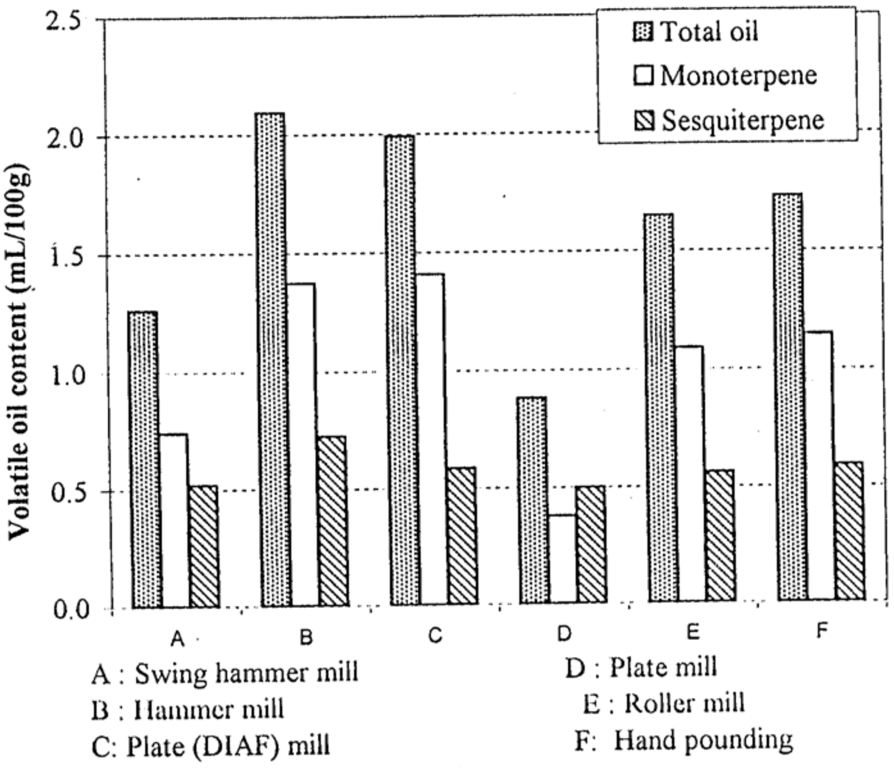


Fig. 4.2.2.. Variation of total, monoterpene and sesqueterpenes contents in black pepper volatile oil obtained by different grinding mills

also discussed in Section 4.2.3). However, the mean content of sesqueterpenes in the oil samples obtained from all mills was fairly constant (0.58 mL/100g). This content did not depend on the type of mill as compounds having higher molecular weight (sesqueterpenes) were not affected by grinding temperature (Pesek *et al.,* 1985; Pesek and Wilson, 1986) and particle size.

Table 4.2.6

Boiling points (C) of volatile oil compounds of black pepper at different vapour pressure (Perry 1950)

Compound	Pressure mm Hg										Melting Point (C)
		5	10	20	40	60	100	200	400	760	
	Temperatures (C)										
a-pinene	-1.0	24.6	37.3	51.4	66.8	76.8	90.1	110.2	132.3	155.0	-55.0
~~-pinene	4.2	30.0	42.3	58.1	71.5	81.2	94.0	114.1	136.1	158.3	
cymene	17.3	43.9	57.0	71.1	87.0	97.2	110.8	131.4	153.5	177.2	-68.2
limonene	14.0	40.4	53.8	68.2	84.3	94.6	108.3	128.5	151.4	.175.0	-96.9
myrcene	14.5	40.0	53.2	67.0	82.6	92.6	106.0	126.0	148.3	171.5	

- Indicates data not available

Figure 4.2.3 shows the distribution of three different sets of monoterpene compounds viz., α-thujene+ α-pinene, sabinene+β-pinene, 1,8-cineole+limonene. The distribution pattern of these compounds was similar in samples from all the mills except for Plate (DIAF) mill, where the quantity of (sabinene+ β-pinene) was the highest. Figure 4.2.4 shows the distribution of four sesqueterpenes compounds viz., α-copaene, β-caryophyllene, β-bisabolene and caryophyllene oxide. Though the total quantity of sesqueterpenes in the oil was nearly same, content of caryophyllene oxide was higher for samples ground in Plate mill (Table 4.2.5). It might be due to the oxidation of β-caryophyllene into caryophyllene oxide at higher temperature (62 C). Hand pounding (control) sample yielded low quantity of caryophyllene oxide as there was a little chance of oxidation of β-caryophyllene in the grinding process.

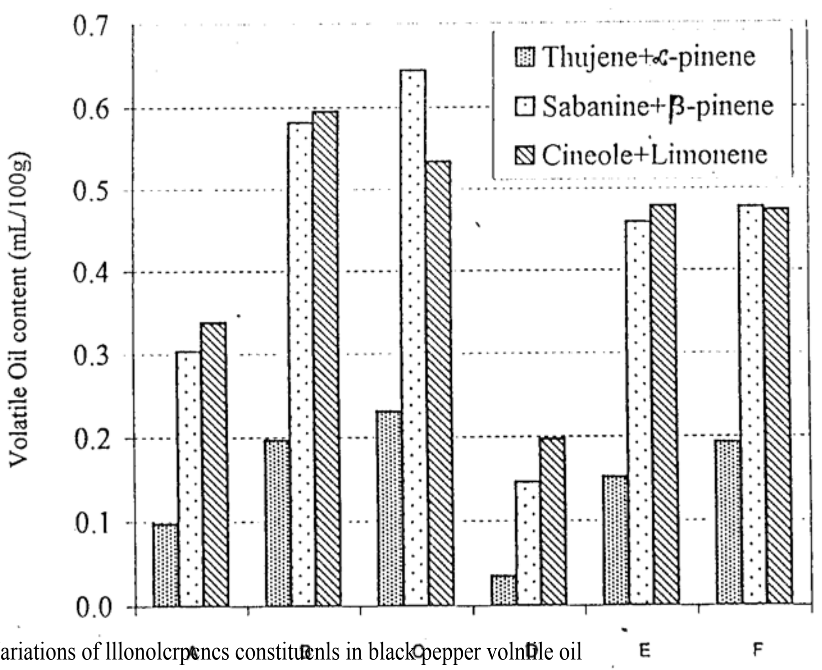


Fig. 4.2.3 Variations of monoterpenes constituents in black pepper volatile oil obtained by different grinding mills

A : Swing hammer mill D : Plate mill
B : Hammer mill E : Roller mill
C: Plate (DIAF) mill F: Hand pounding

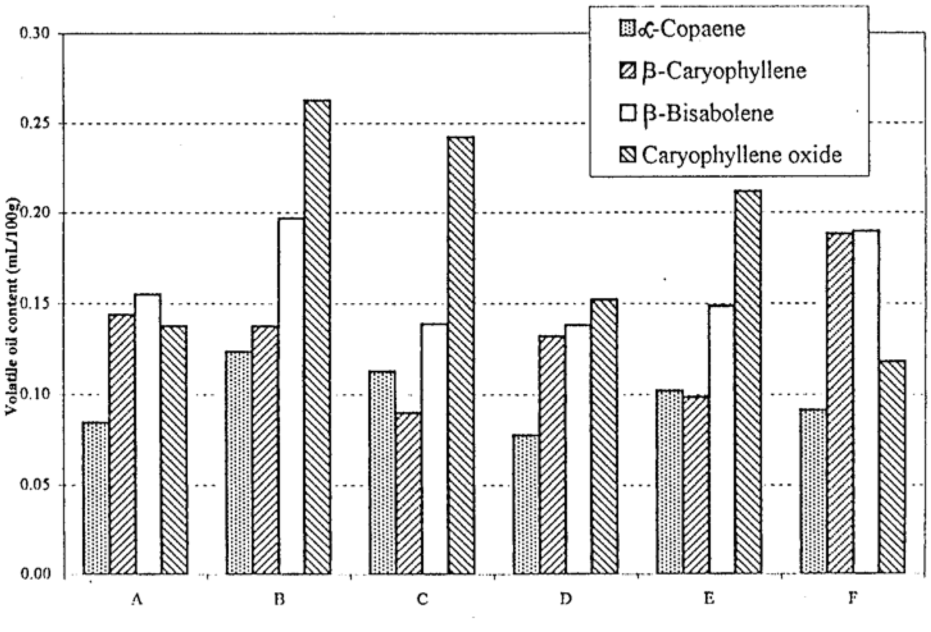


fig. 4.2.4 Variation of sesqueterpenes constitutcnts in black pepper volatile oil obtained by different grinding mills

4.2.2.4 Conclusions

The following conclusions can be drawn based on the results reported in the present section.

1) Among the mills employed for grinding, fine powder could be obtained using Plate mill, with a geometric mean particle diameter of 0.16 mm.

2) The volatile oil contents (moisture free basis)· of samples ground in Swing type hammer mill, Hammer (APEX) mill, Plate (D1AF) mill, Plate Mill, Roller mill and hand pounding were 1.61,2.58,2.65,1.24,2.15 and 2.15 mL/100g, respectively The corresponding product temperatures were 52, 43, 47, 68, 30 and 30 C. These results indicated that the quality of ground powder in terms of volatile oil content depended on a few factors such as the type of the mill employed for grinding, the product temperature, and the average particle size of the ground material.

3) The gas chromatographic (GC) analysis data of the volatile oil showed that grinding Hammer (APEX) mill, Plate (DIAF) mill, Roller mill and hand pounding gave oil with high quantity of monoterpenes. Monoterpenes were sensitive to grinding temperatures and their volatility increased with an increase in grinding temperature. The overall content of sesqueterpenes in the oil samples obtained from all the mills was fairly constant and it did not depend on the type of mill.

4.2.3 **Ambient Grinding** Characteristics **at Different Particle** Sizes

Generally, spices are ground either for direct consumption as powder or for making value-added products like essential or volatile oils or as oleoresins. Grinding facilitates the release of aroma and flavour principles from the spices for mixing with food materials (Gopalkrishnan, *et al.,* 1991). During grinding, most of the energy input to the grinder is converted into heat, whereas only a small portion is used for actual size reduction (Loncin and Merson, 1979). If the particle size of powdered product is low (fine powder), enormous quantity of heat is generated within the mill raising the temperature of the ground product to as high as 93 C (Wistreich and Schafer, 1962).

As observed in the previous sections, the grinding of black pepper at high temperatures and to low particle sizes (fine powder) resulted in the higher loss of volatile oil. At the same time, it was observed that even if the particle size obtained was high (coarse powder), the loss of volatile oil was also high though the powder temperature was low. Energy laws for grinding indicates that to obtain low particle size (fine powder), more grinding energy is required and grinding to' high particle size (coarse powder) consumed less grinding energy. However, the low particle size (fine powder) consumed less time in the distillation process for the extraction of volatile oil from the powdered samples, while high particle size (coarse powder) consumed more time for distillation. As volatile oils are critical components of spices, and spices are valued according to their volatile oil content, a detailed investigation was undertaken to find the optimum mean particle size (diameter) of powder at a point in which the loss of volatile oil would be minimum, and to study the corresponding conditions of grinding energy and distillation times.

The black pepper samples were coded as POI, P02, PD3, PD4, PD5 and P06 for easy identification and they were ground to different particle sizes as explained in Section 3.2.3 (Chapter 3, Materials and Methods). The powder obtained by grinding of sample PO 1 was the coarsest particle size and that of sample P06 was the finest particle size. The other samples (P02, P03, PD4 and PD5) were in the range from coarser to finer particle sizes; number increased with a decrease in particle size. (Table 4.2.7). Separate grinding trials resulted in powdered samples of different particle sizes viz., PD1 to PD6. For

Table 4.2.7

Grinding Characteristics of Black pepper by ambient grinding

Ambient Temperature = 30C

Codes for Samples	Mean particle size (mm)	Moisture content (%, wb)	Mill's discharge rate (g. min $^{-1}$)	Product temperature (C)	Maximum oil content (mL/100g)	Distillation on time (h)	Grinding energy (kJ.kg^{-1})	Fourier Number F_0	Diffusivity Dx10^{11} (m^2-s^{-1})
PD1	2.10	9.5	255	30	2.54±0.04	6.7	4.61	0.17	1.70
PD2	1.23	9.5	210	30	2.72±0.06	6.0	8.62	0.20	1.50
PD3	0.70	9.5	165	31	2.92±0.03	6.0	14.19	0.29	1.10
PD4	0.61	9.5	158	31	2.65±0.05	4.0	15.81	0.31	1.23
PD5	0.20	9.0	80	45	2.02±0.09	3.5	33.94	0.28	0.14
PD6	0.14	7.0	60	65	1.48±0.03	3.0	42.22	0.29	0.03

obtaining the different particles sizes of PD1 and PD2, the gap between the plates in the Plate (DIAF) mill was varied, whereas in case of other samples viz., PD3 to PD6, the sieves of different sizes were employed in the Swing hammer mill. The subsequent sections discuss the results of this study.

4.2.3.1 Temperature Rise during Grinding

The product (powder) temperatures of the samples PD 1, PD2, PD3, PD4, PD5 and PD6 measured at the outlet of grinding mill, were 30, 30, 31, 31, 45 and 65 C, respectively, whereas the feed material temperature was 30 C (ambient temperature) (Table 4.2.7). The ground products obtained from samples PD5 and PD6 (fine samples) had temperature rise of 15 and 35 C, respectively, whereas for the other samples, the rise in temperature was marginal. This was expected as fine particles could be obtained only with enhanced level of energy input.

4.2.3.2 Particle Size of Powder

The average particle sizes of the powders were determined from the sieve analysis data using equations (3.2) and (3.3) and are shown in the Table 4.2.8. The geometric mean diameters were 2.10, 1.23,0.70,0.61,0.2 and 0.14 mm for ground samples PD1, PD2, PD3, PD4, PD5 and PD6, respectively. The corresponding surface mean diameters of the above samples were 3.12, 2.52, 1.81, 1.50, 0.50 and 0.21 mm, respectively. The surface mean diameters of the powders were- determined for the purpose of estimating the effective diffusion coefficient of the distillation process (discussed later in Section 4.2.3.9).

4.2.3.3 Estimated Energy for Grinding

The grinding of spices is an energy intensive process. The energy needed for grinding of solids is a function of surface area of particles produced. There are several energy laws for grinding (Section 2.3.3 of Review of Literature) of which three of them viz., Kick's law, Rittinger’s law and Bond's law are commonly used for estimation of energy for grinding. However, Kick's law is best suited for small initial particle sizes whereas Rittinger's law is best applicable for larger initial particle sizes. As the Bond's law is best suited for medium particle sizes (which is true here), Bond's equation was plied for the estimation of energy in the present study.

The estimated energy required for size reduction or grinding from an initial article size of *5* mm (initial average size or diameter of a black pepper seeds) to different article sizes (PD1, PD2, PD3, PD4, PD5 and PD6) using Bond's Eq. 3.4 is shown in Table 4.2.7. As expected, the highest estimated energy (42.22 kJ kg-I) was consumed for 'obtaining fine powder (PD6) of geometric mean particle size of 0.14 mm and lowest energy (4.61 kJ kg-I) was consumed for obtaining coarse powder (PD1) having geometric mean particle size of 2.10 mm

Table 4.2.8

Sieve analvsis data of ground black pepper powder to different particle sizes

S1 No.	Mesh size	Mean sieve Diameters		Weight fractions (Wi) of different samples					
		d_m	d_g	PD1	PD2	PD3	PD4	PD5	PD6
1	4/5	4.375	4.359	0.058	0.010	-	-	-	-
2	5/10	3.000	2.828	0.683	0.231	0.044	0.012	0.003	-
3	10/20	1.425	1.304	0.157	0.582	0.438	0.392	0.016	-
4	20/30	0.725	0.714	0.020	0.017	0.092	0.096	0.167	-
5	30/40	0.513	0.505	0.032	0.048	0.130	0.144	0.209	-
6	40/60	0.338	0.326	0.026	0.034	0.098	0.120	0.088	0.057
7	60/80	0.215	0.212	0.010	0.052	0.055	0.097	0.108	0.084
8	80/100	0.165	0.164	0.016	0.024	0.066	0.054	0.1 04	0.218
9	100/120	0.138	0.137	-	-	0.040	0.036	0.043	0.215
10	120/140	0.116	0.115	-	-	-	-	0.106	0.160
11	140/200	0.091	0.089	-	-	-	-	0.098	0.101
12	200/270	0.064	0.063	-	-	-	-	-	0.091
Geometric mean diameter (Eq.3.2)				2.10	1.23	0.70	0.61	0.20	0.14
Surface mean diameter (Eq.3.3)				3.12	2.52	1.81	1.50	0.50	0.21

dm arithmetic mean sieve diameter
dg – geometric mean sieve diameter

Table 4.2.9

Cumulative volatile oil content of powdered samples obtained by Clevenger's distillation at different time intervals

Distillation time (min)	Volatile oil content of different samples (mL/100g)						Volatile oil content to the total volatile oil different distillation time (%)					
	PDI *	PD2	PD3	PD4	PD5	PD6	PD1	PD2	PD3	PD4	PD5	PD6
0	0	0	0	0	0	0	0.0	0.0	0.0	0.0	0.0	0.0
30	1.08	1.10	1.13	0.97	1.01	0.88	42.5	40.6	38.7	36.6	50.0	59.5
60	1.41	1.49	1.57	1.55	1.45	1.03	55.5	54.8	53.8	58.5	71.8	69.6
90	1.61	1.71	1.81	2.12	1.63	1.27	63.4	62.9	62.0	80.0	80.7	85.8
120	1.71	1.92	2.14	2.34	1.80	1.38	67.3	70.8	73.3	88.3	89.1	93.2
150	1.83	2.06	2.30	2.52	1.89	1.41	72.0	75.9	78.8	95.1	93.6	95.3
180	1.97	2.28	2.59	2.56	1.98	1.48	77.6	83.8	88.7	96.6	98.0	100.0
210	2.10	2.39	2.70	2.61	2.02	1.48	81.9	87.9	92.5	98.5	100.0	-
240	2.17	2.45	2.72	2.65	2.02	-	85.4	89.9	93.2	100.0	-	-
270	2.23	2.49	2.76	2.65	-	-	87.8	91.7	94.5	-	-	-
300	2.41	2.62	2.83	-	-	-	94.9	96.3	96.9	-	-	-
330	2.48	2.67	2.87	-	-	-	97.6	98.3	98.3	-	-	-
360	2.52	2.72	2.92	-	-	-	99.2	100.0	100.0	-	-	-
390	2.54	-	-	-	-	-	100.0	-	-	-	-	-

4.2.3.4 Volatile oil Content of Powder

The content of volatile oil or the yield of volatile oil distilled using Clevenger's apparatus at an intervals 30 min was determined to know the quality of ground spice samples. The cumulative contents of volatile oils for different samples (PDl, PD2, PD3, PD4, PD5 and PD6) are given in Table 4.2.9. Figure. 4.2.5 (a and b) shows the plot of volatile oil contents versus the distillation times for the different particle sizes of samples (PDl, PD2, PD3, PD4, PD5 and PD6). Table 4.2.7 shows the maximum volatile oil contents of powders ground to different particle sizes. The volatile oil contents of samples PDl, PD2 and PD3 were 2.54, 2.72 and 2.92 mL/100g, respectively. The volatile oil contents of samples P04, PD5 and PD6 are 2.65, 2.02 and 1.48 mL/100g, respectively. Figure 4.2.5 (a) shows that quantity of volatile oil released increased asymptotically with

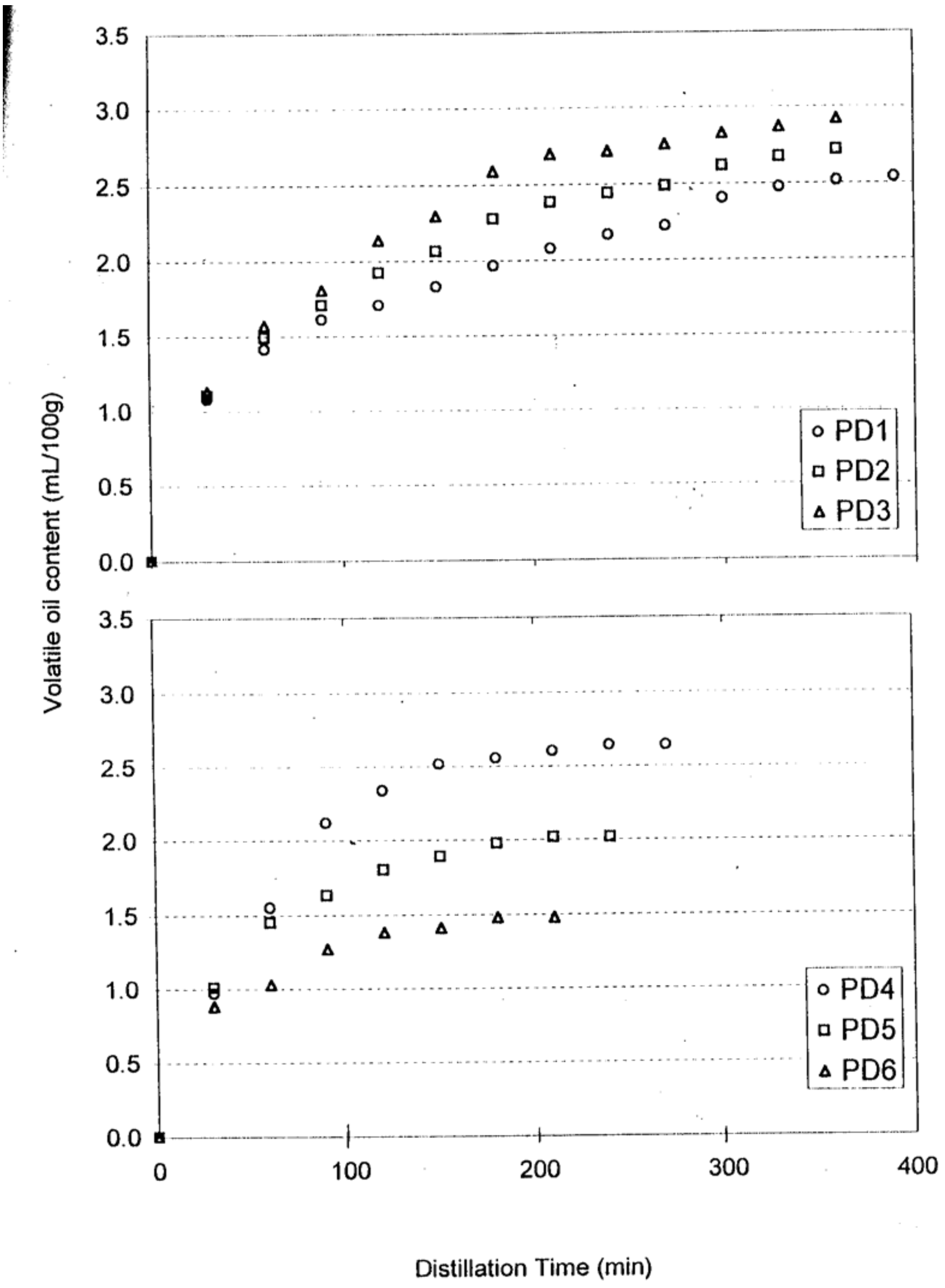


Fig. 4.2.5 Volatile oil yield versus distillation time at different particle sizes of black pepper powder (a) For samples of POI, P02 and P03 (b) For samples of PD4, PD5 and PD6 .

the distillation time for all the three samples of PD1, PD2 and PD3, indicating that the complete volatile oils present in these powdered samples were not removed in the distillation process as the curves were not flattened even at the end of 350 minutes. On the other hand, Fig. 4.2.5 (b) shows that as the entire quantity of oil present in the powdered samples (PD4, PD5 and PD6) was distilled, as the curves flattened at the end of distillation process. This meant that there was a definite loss in the volatile oil content due to grinding in case of samples PD4, PD5 and PD6 (finer powders) as these samples yielded less volatile oil when compared with the content of volatile oil of sample PD3. The lowest content of volatile oil was found to be in PD6, which had a very fine geometric mean particle diameter of only 0.14mm. There results indicate that particles with low average mean diameter possess low quantity of volatile oil.

4.2.3.5 Distillation Time

The distillation time for distillation of volatile oil from the samples changes due to the particle size of the powder (Table 4.2.9). The time for the complete distillation of volatile oil samples of PD1, PD2, PD3, PD4, PD5 and PD6 were 390,360,360,240,210 and 180 min, respectively. Table 4.2.9 shows that the content of volatile oil was about 40% of the total volatile oil in first 30 min of distillation for samples of PD1, PD2, PD3 and PD4, whereas the contents were 50 and 60% in case of P05 and PD6, respectively. The mean volatile oil content at the end of 90 min of distillation time was about 63% for samples of PD1, PD2, PD3, and about 80 to 86% in case of PD4, PD5 and P06. It indicated that if coarser were the particles slower was the rate of volatile oil distillation but finer the particles faster was the distillation of volatile oil. This might be because, if coarser were the particle size, the resistance offered by the particle for the movement of volatile oil from the core of the particle to the surface was higher and hence the mass transfer was slower. In the case of finer particle size, however, this resistance was relatively low, and hence, the mass transfer was faster, thereby reducing the distillation time. It was thus concluded that distillation time of the particles depended on the mean diameter of the powder particles.

4.2.3.6 **Optimization of Particle** Size

The foregoing discussions indicated that during ambient grinding of spices, very fine particle sizes had yielded less of volatile oil due to the volatile oil loss during grinding. On the other hand, if the powder was coarse, volatile content was also less as the complete volatile oil present in the powder was not released easily during distillation. Hence, there might exist a particle size between coarse and fine which could offer the highest content of volatile oil. The present section thus deals with finding of the best particle size of black pepper suitable for commercial purpose.

The optimal particle size of the powder is defined as the geometric mean particle diameter at which percentage recovery of volatile oil is maximum or the loss of volatile oil is minimum. Figure 4.2.6 shows the plot of volatile oil loss, distillation time and input energy for grinding versus geometric mean particle (d_{ga}) diameter. The loss of volatile oil was minimum at geometric mean particle diameter (size) of about 0.7 mm. If the particle size was less than 0.7 mm, the loss of oil was more (due to high temperature during grinding and due to enhanced surface area of the particles exposed to the atmosphere during grinding), the energy for size reduction was also high, though the distillation time was less. On the other hand, if the particle size was more than 0.7 mm, the content of oil was less as the oil present in the powder could not be completely distilled even after 6 hours of extraction, though the energy required for size reduction reduced. Hence, the particle size of about 0.7 mm (US 25 mesh) can be taken as optimum (Fig. 4.2.6) and the corresponding grinding energy and distillation time were 14.19 kJ $kg-^{1}$ and 6 hours, respectively. Gopalkrishnan *et al.* (1991) reported that the volatile oil content IS maximum for particles obtained with sieve size of 0.75 mm in case of grinding of cardamom.

This optimal particle size (about 0.7 mm) would be of commercial importance in the large scale industrial grinding operations where black pepper is ground for the production of volatile oil by distillation process.

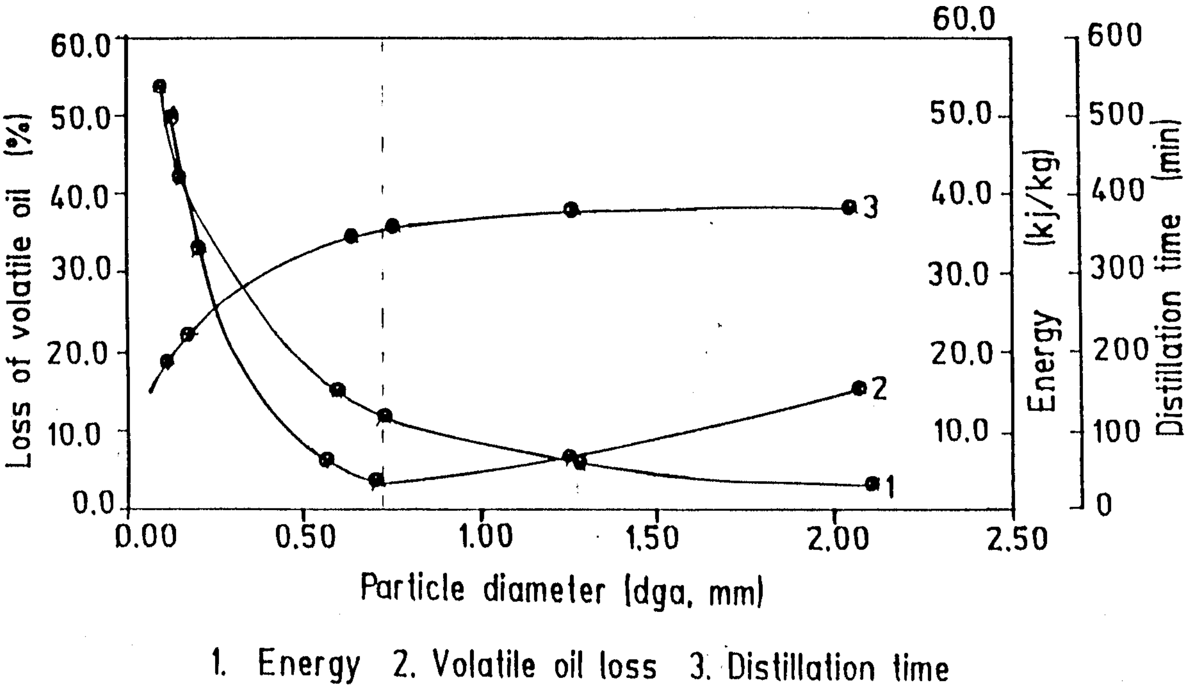


Fig. 4.2.6 Optimization of parameters in grinding of black pepper

4.2.3.7 Physical Properties of Volatile oil

The properties of volatile oil of black pepper samples were determined in order to determine the quality of ground samples (PD1, PD2, PD3, PD4, PD5 and PD6). The physical properties of volatile oil measured were specific gravity, refractive index and optical rotation (Table 4.2.10). No significant changes ($p \leq 0.05$) in the physical properties of oils at different particle sizes were observed. The average values of specific gravity, refractive index and optical rotation of oils were 0.94, 1.49 and -2.40°, respectively. The values indicated that these properties could not be used to differentiate the quality of ground black pepper. In other words, it indicates that in range of particle sizes studied, these selected physical properties of volatile oil remains unaltered.

Table 4.2.10

Physical properties of volatile oils of black pepper ground to different particle sizes in various mills.

	Plate Mill ⟶		Hammer mill ⟶			
Sample	POI	P02	P03	P04	P05	P06
Particle Diameter (mm)	2.08	1.23	0.70	0.61	0.20	0.14
Grinding temperature (C)	30	30	31	31	45	65
Volatile oil content *(mL/100*g)	2.54 ± 0.04	2.72 ± 0.06	2.92 ± 0.03	2.65 ± 0.05	2.02 ± 0.09	1.48 ± 0.03
Specific gravity	0.930	0.932	0.941	0.954	0.905	0.942
Refractive index	1.495	1.492	1.487	1.488	1.485	1.490
Optical rotation(degree)	-2.381	-2.340	-2.396.	-2.360	-2.495	-2.393

4.2.3.8 Analysis of Volatile oil by Gas Chromatography

The gas chromatographic analysis of volatile spice oils is a method of separation of volatile compounds based on their retention time within gas chromatographic column. Clevenger's method of volatile oil distillation gives the total volatile oil content in the powdered sample, whereas the gas chromatographic analysis is a tool to identify the various constituents of volatile oil for measuring the quality of the oil. As mentioned in earlier sections, volatile oil constitutes mainly of monoterpenes (70-80%), sesqueterpenes (20-30%) and small amount (less than 5%) of oxygenated compounds.

The Gas Chromatographic-Mass Spectra (GC-MS) analysis of one of the samples of volatile oil (Fig. 4.2.7) was done to identify these components. Based on the retention time, Kovats indices (Jennings and Shibamato, 1980; Davies, 1990) and also matching with the reference mass spectra (Adams, 1989) or by co-injection on GC, nine major compounds were identified (Table 4.2.11). These were taken as markers to study the flavour quality of the oil. These nine compounds constituted 79 to 90% of the total volatile oil (Table 4.2.12). The absolute recovery data with respect to each component in volatile oil are shown in Fig 4.2.8 and 4.2.9.

The quantities of monoterpenes (Fig. 4.2.8 and 4.2.10) viz., α-thujene, α -pinene, sabinene, β-pinene and limonene, present in the volatile oil was higher in large and medium sizes of particle. The quantity of monoterpene reached maximum when the particle size was 0.70 mm. At a higher particle size (2.10 mm), the release of monoterpenes was incomplete. At lower particle sizes (0.14 and 0.20 mm), less quantities of monoterpenes indicated that the loss was due to higher temperatures (45 to 65 C) during grinding.

Table 4.2.11

Identification of flavour compounds in volatile oil of black pepper by GC-MS analysis

Compounds	Peak No.**	Retention time (Min)	Refractive index	Method of identification * * *
α-Thujene*	-	-		Co-GC
α-Pinene	A	3.767	942	RI, GC, MS
Sabinene*	-	-	-	Co-GC
β-Pinene	B	4.867	982	RI, GC, MS
Limonene	C	6.633	1033	RI, GC, MS
α-Copaene	**O**	24.300	1368	RI,MS
β-Caryophyllene	E	26.700	1428	RI, MS, Co-GC
β-Bisabolene	F	32.567	1505	RI,MS
Caryophyllene oxide	G	35.383	1582	RI,MS

* Identified by co-injection in gas chromatography
** Please see Fig.4.2.7 for details of GC peaks
*** GC means Gas Chromatography, Co-GC means co-injection of GC,
RI means refractive index, MS means mass spectrography

The quantities of sesquiterpene (Fig. 4.2.9 and Fig. 4.2.10) viz., α-copaene, β-caryophyllene, β-bisabolene and caryophyllene oxide, present in the oil were maximum at the particle size of 0.14 mm. At higher particle sizes, the release of sesquiterpenes was incomplete (Table 4.2.12). The amount of oxygenated compound (major compound: caryophyllene oxide identified from its mass spectrum and Kovats index value) present in volatile oil at various particle sizes varied from 0.20 to 0.26 mL/100g. In the present study, no noticiable change was observed except its complete disappearance in. the volatile oil obtained from the powder of particle size 0.2 mm, probably due to its conversion to β-caryophyllene during processing as observed by a rise in its quantity.

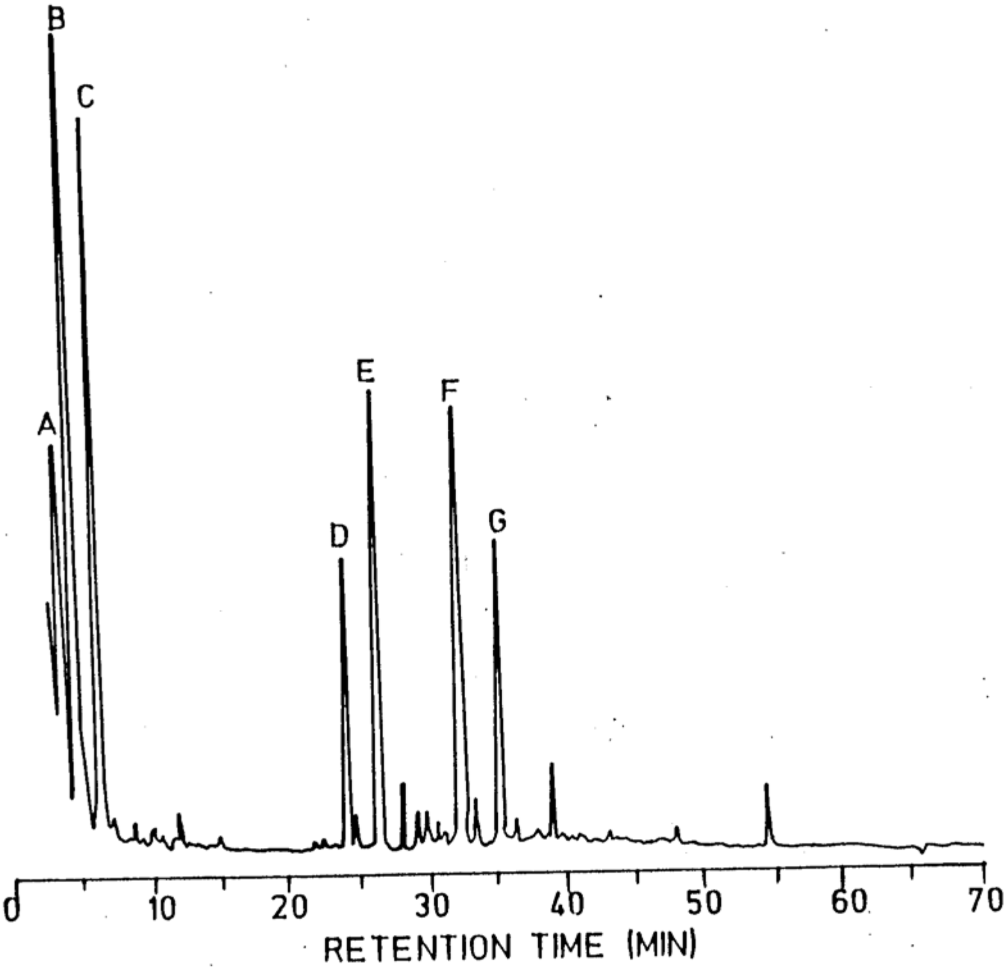


Fig. 4.2.7 GC-MS analysis of volatile oil for identifying constituents

Table 4.2.12

Gas chromatographic analysis data of volatile oil samples of black pepper ground to different particle sizes (% concentrations)

Compounds	Samples of black					
	PD1	PD2	PD3	PD4	PD5	PD6
1. α-Thujene	0.72	1.72	2.00	1.12	1.44	0.41
2. α-Pinene	3.38	5.57	8.58	4.59	4.87	1.65
3. Sabinene	16.68	19.52	24.47	17.23	15.19	7.80
4. β-Pinene	10.53	11.53	14.42	10.63	12.45	5.53
5. Limonene	26.17	24.20	23.31	22.70	23.82	15.62
6. α-Copaene	4.19	3.50	3.55	4.46	5.96	9.30
7. β-Caryophyllene	1.82	1.64	1.58	2.09	15.94	9.44
8. β-Bisabolene	6'(19	5.67	4.35	7.21	10.13	14.20
9.Caryophyllene	9.58	8.73	6.82	9.88	0.00	17.22
Total	79.16	82.10	89.08	79.91	89.80	81.17
Monoterpenes (%)	57.48	62.54	72.78	56.27	57.77	31.01
Sesqui terpenes (%)	21.68	19.54	16.30	23.64	32.03	50.16
Ratio of To Sesquiterpenes	2.65	3.20	4.47	2.38	1.80	0.62

* Particle sizes of, PD1, PD2, PD3, PD4, PD5 and PD6 are 2.10, 1.23, 0.70, 0.61, 0.20 and 0.14 mm, respectively

Hubert (1991) observed that the ratio of monoterpenes to sesquiterpenes more than 1.74 would give strong peppery note to oil. Table 4.2.12, shows that the ratio was greater than 1.74 for oils obtained from particles sizes greater than 0.2 mm, for maximum amount of volatile oil with overall flavour quality. According to Salzer (1977), good amounts of monoterpenes for odour and the body, moderate amounts of sesquiterpenes for spicy note and reasonable amounts of oxygenated compounds should be present in the oil. Accordingly, the particle sizes of 0.6 to 0.7 mm were preferred. If large amounts of sesquiterpenes in the volatile oil are required, the particle sizes of 0.20 and 0.14 mm may be preferred which gives sweet and flowery notes (Lewis *et al.,* 1969). The variation in the content of sesqueterpenes was not significant (in the range of 0.48 to 0.74 mL/100g) as compared to the contents of monoterpenes which varied from 0.46 to 2.13 mL/ 100g.

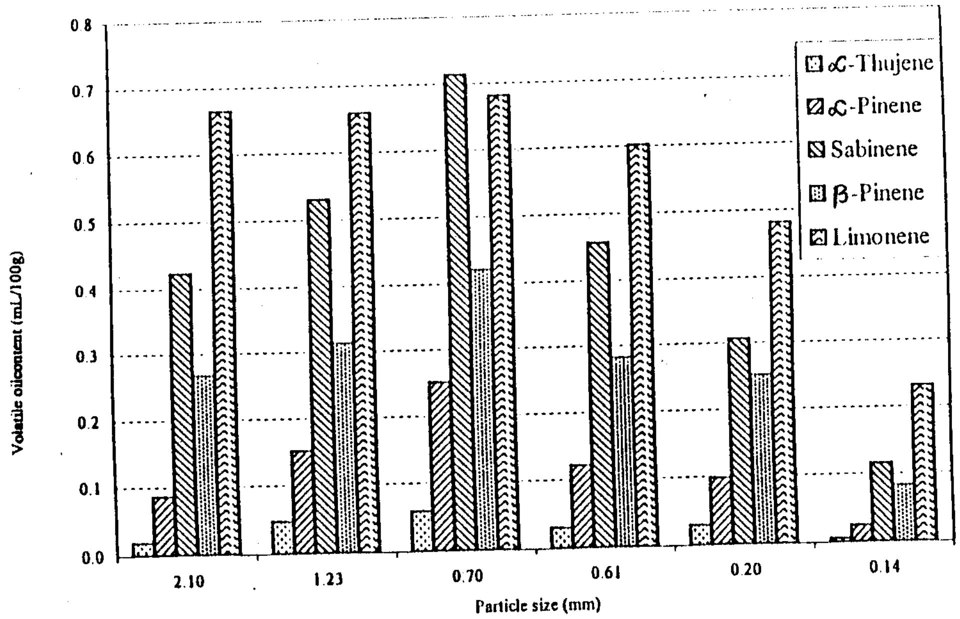
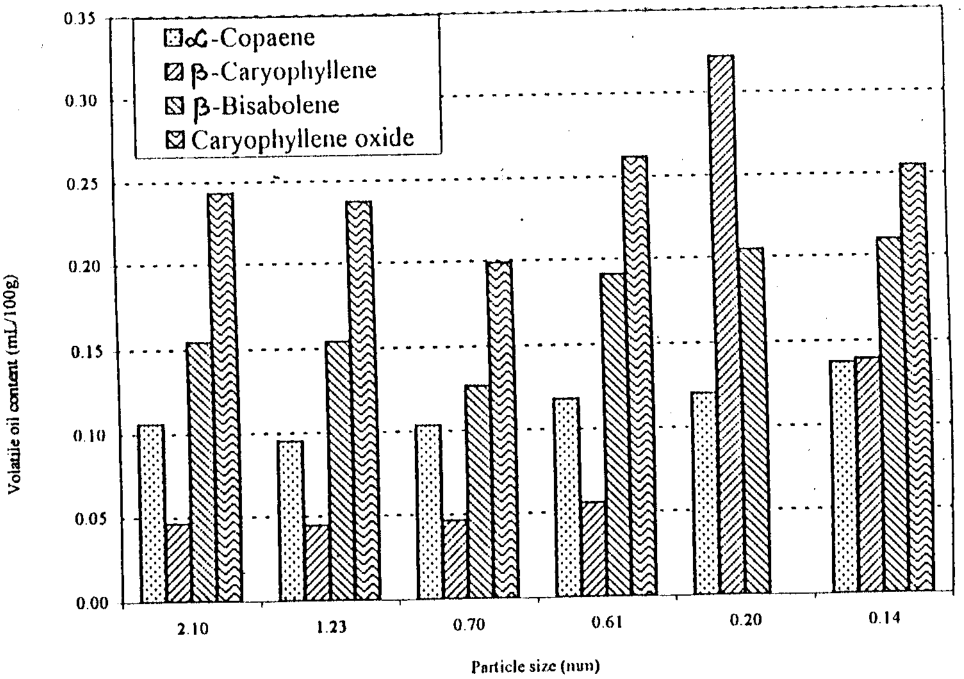


Fig. 4.2.8 Variations of monoterpenes constituents in black pepper volatile oil ground to different particle sizes



rig. 4.2.9 Variations of sesqueterpenes constituents in black pepper volatile oil ground to different particle sizes

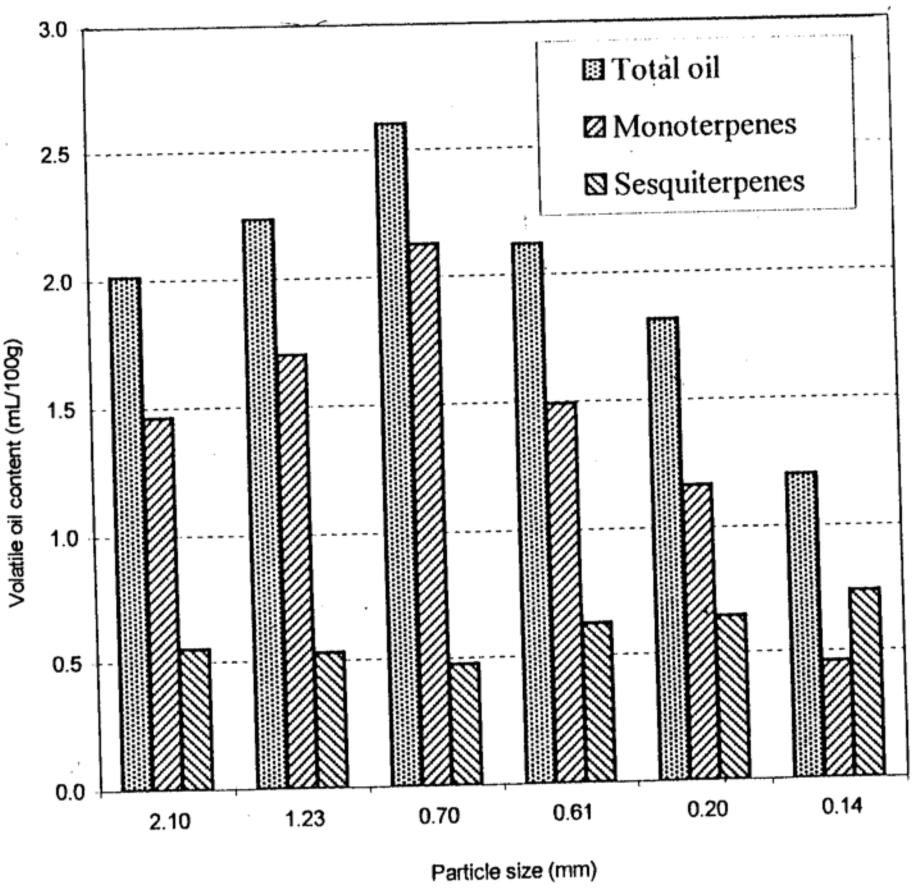


Fig. 4.2.10 Variations of total, monoterpene and sesqueterpenes content in pepper volatile oil ground to different particle sizes

Typical gas chromatographs of PD1 (2.1 0 mm) and PD6 (0.14 mm) are indicated in Fig. 4.2.11 (a) and (b), respectively for comparison of distribution pattern of gas chromatographic peaks in both particle sizes. These graphs indicated that at higher particle sizes (2.10 mm) the contents of monoterpenes (viz., peak numbers 1 to 5) in the volatile oil were higher whereas the contents of sesqueterpenes (viz., peak numbers 6 to 9) were lower. In the case of lower or finer particle sizes (0.14 mm) the contents of sesqueterpenes were relatively higher. This meant that at finer particle sizes, the loss of monoterpenes could be higher due to higher product temperatures.

4.2.3.9 Effective Diffusion Coefficient

Distillation of volatile oil involves removal of volatile oil present in the powdered black pepper samples using Clevenger's apparatus (Section 3.2.3.2 of Materials and Methods). The quantity of volatile oil content per unit distillation time is a function of particle size, as has been mentioned in the earlier sections. If the particle size is very fine then the content of volatile oil is less due to the volatile oil loss during grinding. On the hand, if the particle size of the powder is coarse then volatile oil content is also less as the complete volatile oil present in the powder is not released during distillation. In this section, this phenomenon was analysed employing the diffusion theory (mentioned in Section 3.2.3.5) by determining the effective diffusion coefficients for different particle sizes of samples namely PDI, PD2, PD3, PD4, PD5 and PD6.

The volatile oil from the black pepper powder was distilled using Clevenger's apparatus. When the mixture of black pepper powder and water system was heated, the volatile oil constituents of the powder were be diffusing into water at 100 C during the distillation process. As there was sufficient agitation of powder-water mixture system due to buoyant forces while boiling in the apparatus, the surface resistance became small. Therefore, it was assumed that the total resistance was due to only internal resistance, and the phenomenon was analysed using diffusion theory employing Pick's second law (Eq.3.8). The powdered particles were assumed to be spherical in shape and surface mean particle diameters were used in determining the effective diffusion coefficients.

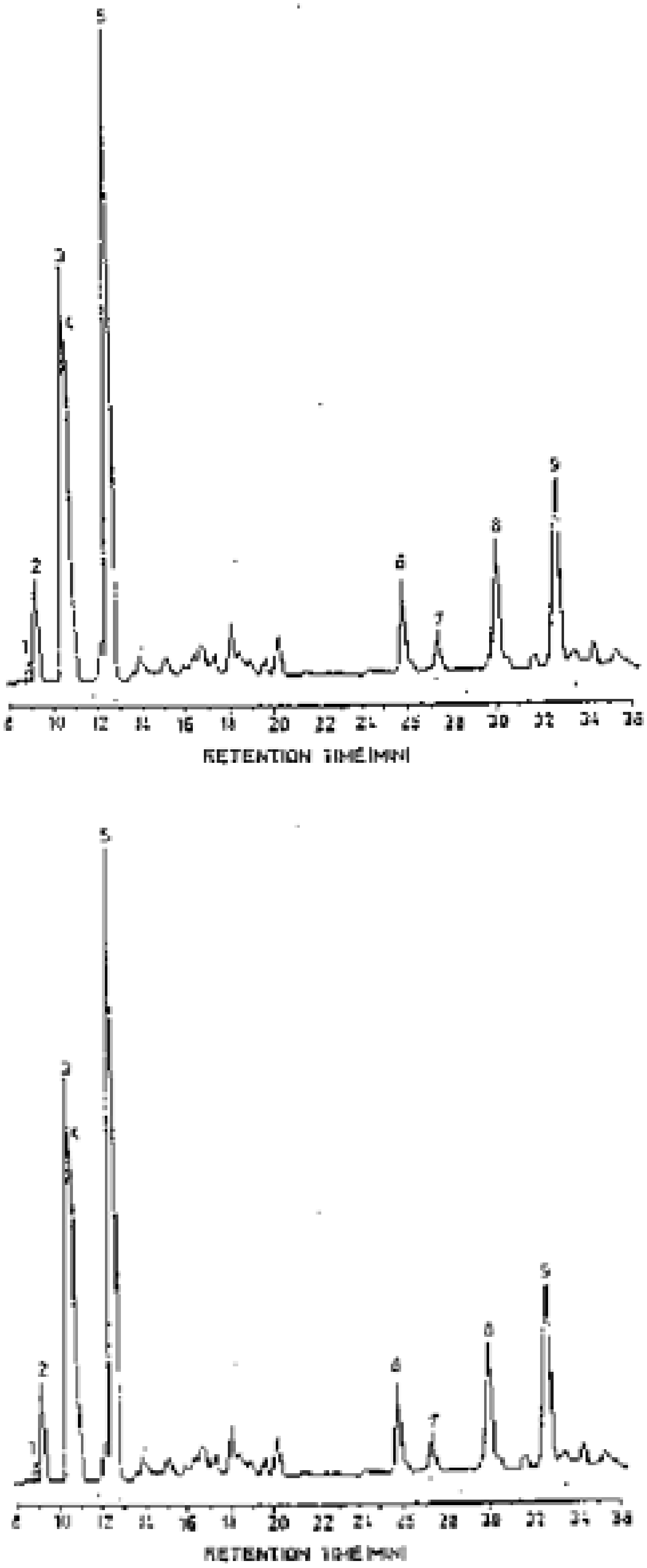


Fig. 4.2.11GC Profiles of black pepper volatile oil (a) at particle size of 2.10 mm and (b) at particle size of 0.14mm

The effective diffusion coefficient of the samples was calculated using Eq. 3.10, from the plots of In M^1 versus distillation time t, employing linear regression technique. However, the significance of the intercepts was overlooked (Spiro and Hunter, 1985). The initial oil content M$_r$ in case of PD1, PD2 and PD3 was taken as 3.07 ml/100g (assuming 95% distillation efficiency of sample PD3). In the case of PD4, PD5 and P06 the initial oil contents were 2.80, 2.13 and 1.56 ml/100g, assuming 95% distillation to give their maximum yield. The weighed surface mean particle radius was determined using Eq. (3.3) for the calculation of effective diffusion coefficient.

The experimental data fitted well with the Eq. 3.6, as evidenced by high correlation coefficients (0.96 to 0.99) and the plots are shown in Figs 4.2. 12(a & b). The values of effective diffusion coefficients are shown in Table 4.2.7. The values of diffusion coefficients for coarser particle samples PD1, PD2, PD3 and PD4 were of the same magnitude (1.7 x 10,11, 1.5 x 10,11, 1.1 x 10,11 and 1.2 x 10,11 m^2 s^{-1}, respectively) with an average of 1.38 x 10'11 m^2 s^{-1}. Gekas (1992) reported a value of diffusion coefficient to be 1.08 x l0^{-11} m^2 s^{-1} for the extraction of oil from soybean flakes (0.43 mm thick) using hexane as solvent. Thus, the values of diffusion coefficients obtained in the present study compared well with literature values for coarser particles of higher oil concentrations. For finer powders (PD5 and PD6), the values were very low, 0.14 x 10,11 and 0.03 x 10,11 m^2 s^{-1}, respectively, which might be attributed to low initial oil concentrations in these samples. The latter was in accordance with the observations made by Aguerre *et al.,* (1985) that the diffusion coefficients were not constant for drying and leaching operations at low concentrations.

4.2.3.10 Fourier Number

The Fourier number (F$_o$) was determined employing Eq. 3.9 which contains a range of values for n that can vary from unity to infinity. The values of effective diffusion coefficients were determined assuming n value as unity for simplification. To check whether this assumption was correct, the Fourier number (Fo= De tl^{r}s2) was determined using effective diffusion coefficients (De), obtained from the experimental data using distillation time (t) and surface mean radius of the powder. The values of Fourier numbers for powdered samples of PD1, PD2, PD3, PD4, PD5 and PD6 thus determined were 0.17,

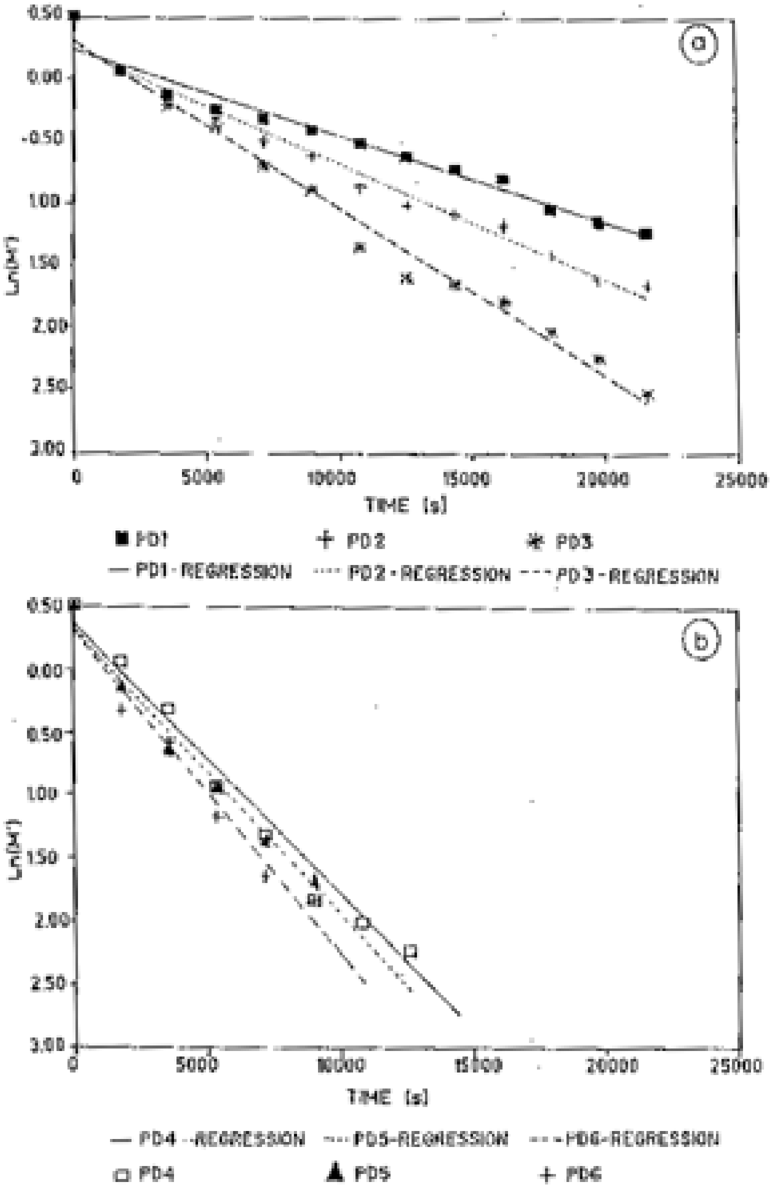


Fig. 4.2.12 Ln (M^l) versus distillation time at different particle sizes of black pepper powder (a) For samples of PD1, PD2 and PD3 (b) For samples of PD4, PD5 and PD6

0.20, 0.29, 0.31, 0.28, and 0.29, respectively. It has been reported (McCabe and Smith, 1976; Aguerre *et al.,* 1985) that if the Fourier number thus obtained is greater than 0.1 then the assumption of n=l in Eq. 3.9 is justified. It was observed in the present study that the Fourier numbers (Table 4.2.7) for all the particle sizes were greater than 0.1, which justified for considering only the first term (n=l) in Eq. 3.9, ignoring the higher order terms.

4.2.3.11 Conclusions

The study on ambient grinding characteristics has led to the following conclusions:

1) The particle size of powdered sample determined using sieve analysis varied from coarse to fine. The powdered sample of PD1, PD2, PD3, PD4, PD5 and PD6 had geometric mean particle diameters of 2.10, 1.23, 0.70, 0.61, 0.20 and 0.14 mm, respectively. The finer the particle size of powder the higher was the temperature of ground powder measured at the mill's outlet at steady condition, and obviously the finer the particle size the higher was the energy expenditure.

2) The time for volatile oil distillation of coarse to fine powdered samples varied from 390 to 180 min, respectively indicating that the finer were the powder particles the faster was the distillation.

3) The volatile oil content of samples of PD1, PD2, PD3, PD4, PD5 and PD6 at the end of distillation were 2.54,2.72,2.92, 2.65,2.02 and 1.48 mL/100g, respectively. The lowest volatile oil content was observed with fine particles. The particle mean diameter of 0.7 mm was found to be the optimum particle size which gave the desirable highest volatile oil content.

4) The physical properties of volatile oil viz., specific gravity, refractive index and optical rotation did not change in the range of experimental particle sizes.

5) The study on quality of oil using gas chromatographic analysis showed that higher ratio of monoterpenes to sesqueterpenes was present in coarse particles (> 0.2 mm),

and gave a very strong peppery note. Powdered particle sizes lesser than 0.2 mm contained more quantity of volatile oil that gave spicy, sweet and flowery notes. The content of sesqueterpenes varied marginally (0.5 to 0.7 mL/100g) as compared to the content of monoterpenes, which varied between 0.5 and 2.1 mL/100g for the range of particle sizes studied.

6. The effective diffusion coefficients (determined using Fick's second law) were fairly constant (1.38 x 10-^{11} m^2 S-I) for powdered samples of POI, P02, P03 and P04 having higher initial oil concentrations. These were low for powdered samples of P05 and PD6 having lower initial oil concentration. The Fourier numbers determined for all the powered samples were greater than 0.1.

4.3 Cryogenic Size-Reduction or Cryogenic Grinding of Black Pepper

The aim of spice grinding was to obtain powder of smaller particle sizes with good quality in terms of aroma and flavour. In the ambient grinding process, heat is generated when energy is used to fracture a particle into smaller sizes. This generated heat is detrimental to the finished product, as it rises the temperature to as high as 93 C (Wistreich and Schafer 1962), and it may result in considerable loss of aroma and flavour components, resulting in deterioration of quality.

The loss of volatile oil (aroma and flavour) can be significantly reduced by a cryogenic grinding technique (Pruthi, 1980). Liquid nitrogen at -195.6 C provides the refrigeration needed to pre-cool the spices and maintain the desired low temperature by not allowing the heat (generated during grinding operation) to increase the temperature of product. In addition to maintaining the low temperature, vapourisation of liquid nitrogen to the gaseous state, in effect, creates an inert and dry atmosphere for additional protection of spice quality. Pre-cooling of raw spice and continuous low temperature maintained within the mill reduce the losses of volatile oils and moisture contents, thereby retaining most of the flavour strength per unit mass of spice (Singh and Goswami, 1999a). As quantitative data on cryogenic grinding of Indian spices are scarce, this experiment was planned to study the grinding characteristics of black pepper employing the system of cryogenic grinding and to compare it with the conventionally followed ambient grinding method, both in laboratory scale (150 to 200 g) and at pilot scale (4 kg) grinding operations.

4.3.1 Evaluation of Cooling, Chilling and Cryogenic Freezing Methods for Grinding

A comparison of different cooling systems including cryogenic freezing is a prerequisite to know the advantages or limitations of these systems. Low temperature of the spice before grinding can be attained by different methods. The present section deals with four such methods for obtaining low temperature of feed spice prior and after grinding employing domestic mixer grinder (Fig. 3.4), using identical grinding conditions.

Table 4.3.1

Temperature of feed and products obtained by different methods of cooling

Sample Code	Method of cooling*	Temperature of black pepper (C)	
		Before grinding	After grinding
CAI	Cold room	13 ± 1	49 ± I
CA2	Plate Freezer	-11 ± 1	40±4
CA3	LN_2 indirect mixing	-38 ± 3	41 ± 2
CA4	LN_2 direct mixing	-195.6	-32 ± 3
CA5	Ambient	30± 0	61 ± 1

* Details of grinding systems employed are shown in Fig. 3.5 of chapd.er 3.

The following four cooling or chilling or freezing methods were employed. They were: (1) cooling black pepper in a cold room, (2) chilling black pepper using a plate freezer, (3) freezing by dipping black pepper enclosed in a polyethylene pouch in liquid nitrogen and (4) freezing black pepper by directly injecting liquid nitrogen into a known quantity of the spice. These methods of cooling or chilling or freezing are represented by schematic diagrams as shown in Fig. 3.5. The product temperatures were measured immediately after grinding. As expected, the lowest temperature of the product was obtained by directly mixing liquid nitrogen with black 'pepper sample (Table 4.3.1). This was because the heat transfer rate was higher in case of direct mixing of liquid nitrogen with black pepper as small droplets evaporated quickly by absorbing the latent heat of vapourisation from the sample. In other freezing methods, polyethylene cover acted as a barrier (insulating effect) for heat transfer between the spice and liquid nitrogen, and reduced the rate of heat transfer and hence, spice did not attain such a low temperature.

It was observed, from preliminary laboratory experimentation, that among the different methods of freezing (viz., cooling, chilling and cryogenic freezing) the cryogenic freezing method with liquid nitrogen, by direct injection into black pepper, was the most efficient method of freezing and reaching extremely low temperature of spice and spice powder. These results are used in subsequent sections and detailed grinding studies were conducted.

4.3.2 Evaluation of Cryogenic Grinding and Volatile oil Content of Black Pepper on a Laboratory Set-up

A comparison of cryogenic and ambient grinding was needed to judge the quality of the ground samples. Hence, the objective of this study was to compare the two grinding methods viz., cryogenic grinding and ambient grinding. Black pepper samples were ground using domestic mixer-cum-grinder under both cryogenic and ambient grinding conditions keeping other grinding parameters constant. Temperatures of the spice before and after grinding were recorded in both the cases (Table 4.3.2). These temperatures were -195.6 and -54.3 C, respectively for cryogenic conditions whereas for ambient grinding these temperatures were 28 and 36 C, respectively. The cryogenic condition yielded markedly higher volatile oil (3.18 mL/100g) as compared to ambient sample (2.85 mL/100g).

Table: 4.3.2

Cryogenic (LN_2) grinding and content of volatile 'oil of black pepper as compared to ambient grinding in laboratory scale

Samples	Temperature of black pepper (C)		Content of volatile oil (mL/100g)
	Before grinding	After grinding	
Cryogenic grinding	-195.6	-54.3 ± 8	3.18 ± 0.03
Ambient grinding	+28 ± 0	+36.0 ± 2	2.85 ± 0.07

It was concluded from this laboratory scale experiment that cryogenic grinding could yield about 12% higher quantity of volatile oil from black pepper as compared to that of ambient grinding.

4.3.3 Effect of Cryogenic, Chilled, Ambient and High Temperature Grinding Methods on Grinding Characteristics in Laboratory Scale

During the ambient grinding of black pepper, the mill and product temperature might rise to as high as 93 C, and at such high temperature, there will be considerable loss of volatile oil (Wistreich and Schafer, 1962). Section 4.2 also supported this finding that at a high grinding temperature, the loss of volatile oil was considerably high. Cryogenic grinding could overcomes this problem and help in retaining more volatile oils (Section 4.3.2 in the present study, Pruthi 1980 and 1991). It has been reported (Anon, 1993) by a grinding equipment manufacturer (Hosakawa Alpine, 'Germany) that cryogenic grinding increased total volatile oil by 40% (Table 2.9). Mckee *et al.* (1993) compared three grinding methods viz., ambient, chilled and liquid nitrogen with ground material temperatures of 40, 38 and 33 C, respectively and observed marginal variation in the volatile oil content.

The present section thus deals with studies on the effect of temperature on grinding characteristics of black pepper. The four grinding methods (as described in Section 3.3.3) were the powder samples of black pepper obtained by employing cryogenic, chilled, ambient and high temperature grinding methods. The temperatures of raw materials prior to grinding were maintained at -120, 10,24 and 40 C, respectively. The parameters determined for comparison were particle size, temperature rise, and quantity and quality of volatile oil. These parameters were selected considering the commercial importance of quality of ground spice.

4.3.3.1 Particle Size of Powder

Fineness of the powder is an index for quality of ground spice. It was measured in terms of quantity of powder by weight which passed through a 60 mesh sieve (US sieve) having aperture opening of 0.42 mm (Table 4.3.3). Fineness of powder was found to be greater (72.2 %) in case of LN_2 cooled samples. At cryogenic conditions, the material became brittle and crisp (Pruthi, 1991) making size reduction easy by shattering technique instead of tearing. At high temperature conditions, the fineness was the lowest (62.5%), and at chilled water and ambient grinding conditions, the values were 52.5 and

55.6%, respectively. These values indicate that LN2 ground samples possess the highest fineness which is highly desirable in commercial operations.

4.3.3.2 Temperature Rise During Grinding

The input and output temperatures of black pepper samples when subjected to grinding under different conditions are shown in Table 4.3.3. As expected, the product (powder) temperature was the lowest (-20 C) when liquid nitrogen was used for cooling the feed material, while, the product temperature was very high (62 C) when the feed material was stabilized at 40 C before grinding. At ambient conditions (24 C), the product temperature was 50 C while with chilled water circulation the product temperature was 30 C. The moisture content of the product varied from 11.8 to 13.5%. These results show that high temperature (prior or after grinding) is detrimental to quality of ground spice samples.

Table 4.3.3

Effect of grinding conditions on the volatile oil content and fineness of ground black pepper

Grinding Condition	Feed temperature (C)	Product temperature (C)	Moisture content (%)	Volatile oil content (mL/I00g)	Retention" of oil (%)	Fineness[b] (%)
High Temperature	40	62	11.8	2.65 ± 0.07		62.5
Ambient	24	50	13.5	3.10 ± 0.09	17.0	55.6
Chilled water	10	30	13.4	3.56 ± 0.05	34.3	52.5
LN_2 cooling	-120	-20	12.5	3.60 ± 0.04	35.9	72.2

a - Percentage increase in retention of volatile oil as compared to high temperature condition

b- Percentage of powder by weight passing through a 60 mesh US sieve

4.3.3.3 Volatile oil Content of Powder

The volatile oil content of a ground spice is the primary index for quality of product. It was (Table 4.3.3) the highest (3.6 mL/100g) in the case of cryogenically (liquid nitrogen) frozen-ground sample and was least (2.65 mL/100g) at the high product temperature of 62 C. The volatile oil content in chilled pepper sample and in liquid nitrogen frozen samples were close (3.56 and 3.6 mL/100g, respectively) and were not significantly different ($p < 0.01$). The use of liquid nitrogen in grinding had not only increased the content of volatile oils (about 36% more as compared to high temperature method) but also improved the fineness of the product. In Industrial scale of applications where the highest temperature of powder can reach as high as 93 C, the content of volatile oils may even be higher with the application of liquid nitrogen. The chilled water circulation would also retain same quantity of volatile oils, as it happened in the case of liquid nitrogen method. But, chilled water technique was not sufficient to significantly reduce the temperature rise of the product (Singh and Goswami, 1999a). Also the particle size is also high. The direct mixing of liquid nitrogen and spices could efficiently cool (due to enhanced heat transfer rate) the spice rather than indirect cooling using chilled water technique in large scale grinding operations. It was thus, inferred that liquid nitrogen was an efficient cooling system (and also to obtain fine particles) as compared to other existing methods of grinding mentioned in this study.

Table 4.3.4

GC analysis data of black pepper oil samples obtained under different grinding conditions (Values are expressed on relative percent basis) .

Component	Grinding methods			
	High temperature	Ambient	Chilled water	LN_2 frozen
1. α-pinene	5.05	5.60	6.65	7.00
2. β-pinene	13.52	14.36	15.12	15.68
3. Myrcene	21.20	19.5Q	20.45	23.20
4. Limonene	22.80	22.18	22.90	23.80
5. β-caryophyllene	21.20	20.20	19.75	17.65
Total	83.77	81.84	84.87	87.33
Monoterpenes (%) (1-4)	62.57	61. 64	65.12	69.70
Sesqueterpenes (%) (5)	21.20	20.20	19.75	17.65
Ratio of monoterpenes to Sesqueterpenes	3.00	3.10	3.30	3.90

4.3.3.4 Analysis of Volatile oil by Gas Chromatography

Chemical composition of the black pepper oil has been reported (Lewis *et al.,* 1969 and Govindrajan, 1977). Pepper oil is mainly made up of monoterpenes (70-80%), and sesqueterpene (20-30%), and a small amount (less than 5%) of oxygenated compounds is also present. The major monoterpenes present in the oil are α- pinene, β-pinene, myrcene, limonene and sabinene while β-caryophyllene is the chief sesqueterpene (the presence of myrcene, a monoterpene component was also observed in this variety of black pepper). The gas chromatographic analysis of the four oil samples obtained under different grinding (high temperature, ambient, chilled water and liquid nitrogen frozen) conditions and the relative percentage of some the main constituents of oil are presented in Table 4.3.4. Better retention of monoterpenes (α-pinene, β-pinene, myrcene, limonene) was observed in the case of chilled water and LN_2 cooled grinding (10 and -120 C) as compared to ambient and high temperature (24 and 40 C) ground conditions of grinding. The ratio of monoterpenes to sequeterpenes varied from 3.0 to 3.9 which indicated that all the four samples yielded volatile oil with a strong peppery note (Hubert, 1991). Figure 4.3.1 shows the variation of constituent compounds of volatile oil (in absolute quantities in mLlI00g). The content of all the four compounds was higher for chilled water and liquid nitrogen frozen ground samples compared to other powders. Considering β-caryophyllene, the values were slightly low (19.8 and 17.7) in the case of chilled water and LN_2 frozen (10 and -120 C) ground samples than that for ambient and high temperature (24 and 40 C) ground samples. Figure 4.3.2 shows the variations of constituent compounds of volatile oil viz., total oil, monterpenes and sesqueterpenes in absolute quantities (mL/100g). The contents of sesqueterpenes in the volatile oil was marginally different (0.6 to 0.75 mLlI00g), while these of monoterpenes were in the range from 1.6 to 2.5 mL/100g. This was because the sesqueterpenes compounds were less sensitive to temperature unlike the monoterpene compounds. It is thus, concluded that LN2 samples possess highest quantity of monoterpenes compared to all other samples which gives the desirable feeling of flavour freshness.

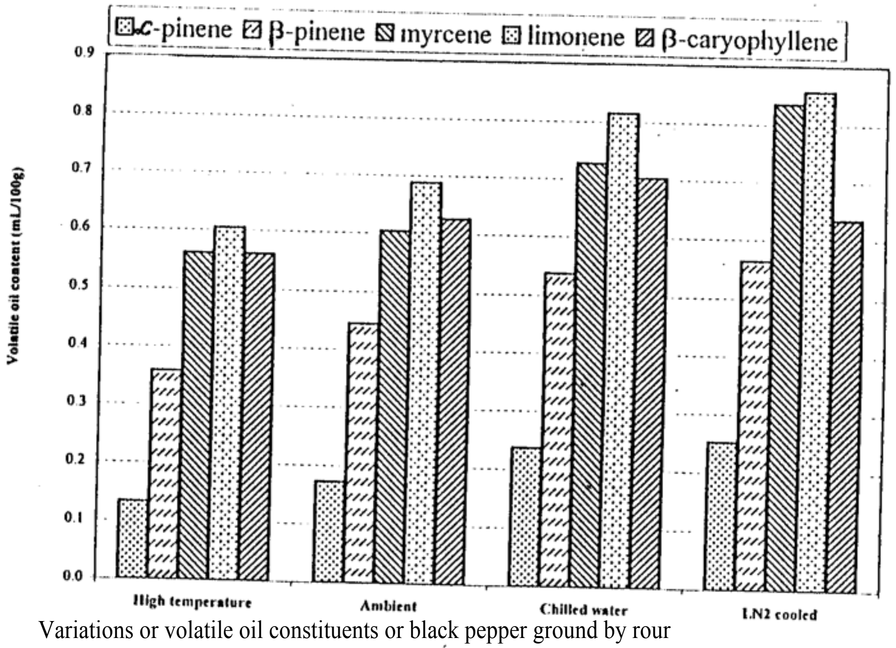


Fig. 4.3.1 Variations or volatile oil constituents or black pepper ground by rour diflerent grinding methods

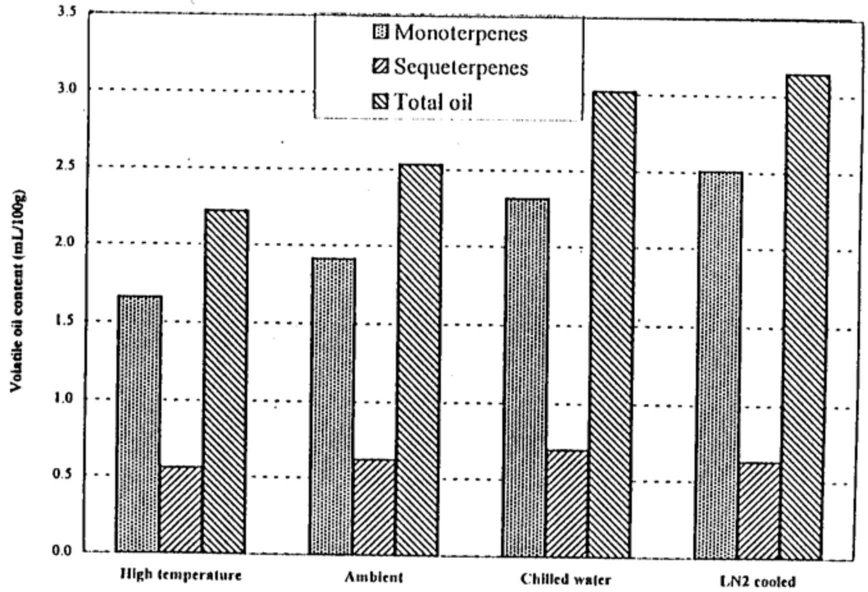


Fig. 4.3.2 Variations or total, monoterpene and sesqueterpenes content in volatile oil or black pepper ground by rour dirrerent grinding methods

4.3.3.5 Conclusions

It was concluded from the foregoing discussion that,

I) The particle size of black pepper powder ground by cryogenic method was the finest as compared to other three methods.

2) The cryogenic and chilled temperature methods .of grinding yielded similar quantities of volatile oil as compared to low quantities in ambient and high temperatures grinding methods. There was a gain of about 36% in the content of volatile oil by cryogenic grinding method as compared to high temperature grinding method. Chilled water technique was not adequate to markedly reduce the temperature rise during grinding of the product.

3) Gas chromatographic analysis showed that in cryogenic grinding technique, the contents of monoterpenes was higher compared to those obtained by other methods. The content of sesqueterpenes was fairly similar in all four grinding methods employed in this study.

4.3.4 Cryogenic Grinding on a Pilot Scale

It was reported in the Section 4.3.3 that cryogenic grinding of black pepper in the laboratory scale grinding gave better grinding characteristics in terms of particle fineness, volatile oil content and quality of volatile oil. However, most of the studies have reported the results obtained on experiments conducted for a small batch size of spice (l00 to 200g). The reason being the high unit cost of spices and unavailability of high capacity LN_2 grinding facilities. Since experimental results are scanty in terms of pilot scale cryogenic grinding of spices, a study of cryogenic grinding of black pepper in a pilot scale (each sample run of 4 kg) grinder at various feed rates and temperature conditions was carried out to evaluate the grinding characteristics. This would not only simulate the industrial process but also generates data that would be useful for large scale trials, scaleup and process standardisation. A central composite rotatable design (CCRD) concept was used in this study to determine the effect of these variables and to find optimum grinding conditions in cryogenic grinding. The use of experimental design was beneficial in reducing the number of experiments and thus reducing quantity of spices which are expensive.

The raw material (black pepper) obtained from a local spice processing company (not from the local market) was used to simulate the real industrial situation to compare the cryogenic ground powder with that for ambient ground samples. This raw material was of a variety of low volatile oil content and had an average particle seed diameter of 4.1 mm.

The mill employed for both ambient and cryogenic grinding was the pin mill obtained from Hosakowa Alpine, Germany, 80 kg hr^{-1} capacity having 3.7 kW motor (3 phase, 440 V and 50 Hz) and was made of stainless steel. It consisted of two rotors (one fixed and another rotating type) with a number of cylindrical stainless steel pins of 4 mm diameter affixed perpendicularly on them. The feed spice was fed axially, ground between the pins and powder exit was in the radial direction. The schematic diagram of the pilot scale cryogenic grinding set up is shown in Fig. 3.7.

4.3.4.1 Comparison of Cryogenic Grinding with AIl)bicnt Grinding

The following sections deal with the result obtained in cryogenic grinding technique compared with those of ambient grinding on pilot scale grinding operations in terms of quantity of volatile oil content, particle size of the powder, mill choking characteristics and quality of volatile oil. In this investigation, cryogenically ground samples (CI to C9) were compared with ambient ground samples (AI, A2) (Table 4.3.5).

Table 4.3.5

Results of volatile oil, moisture content and particle size of powder in cryogenic and ambient grinding in pilot scale

Codes for Sample *	Feed rate (kg hr-^{1})	Product temperature (C)	Moisture content (% wb)	Volatile oil content** (mL/100g)	Mean particle diameter (mm)
C1	35.00	-15.00	10.00	1.67± 0.05	0.22
C2	35.00	-40.00	10.80	1.91± 0.03	0.26
C3	60.00	-40.00	12.00	1.82± 0.06	0.25
C4	15.00	-54.00	12.00	1.87± 0.08	0.25
C5	15 .00	-40.00	11.00	1.35± 0.03	0.20
C6	52.00	-25.00	11.50	1.90± 0.04	0.27
C7	35.00	-60.00	10.00	1.78± 0.09	0.22
C8	7.00	-15.00	10.00	1.44±0.07	0.24
C9	52.00	-54.00	12.00	1.42±0.06	0.25
Al	35.00	53.00	10.00	0.98± 0.05	0.24
A2	15.00	86.00	8.40	0.78± 0.04	0.16

* C 1 to C9 were the cryogenic ground samples and Al & A2 were ambient ground samples
** Moisture free basis

4.3.4.1.1 Feed Rate and Product Temperature

The feed rate of grinding influenced the rise in product temperature during ambient grinding (Section 4.2.1) which in turn affected the quality attributes of the powder. The feed rate and product temperatures were found to be interrelated in ambient grinding. On the other hand, in case of low feed rate, the rise in product temperature (temperature gradient) was high (Table 4.2.2). Therefore, it was necessary to control the feed rate and the product temperature (independent variables) to study their effect on the grinding characteristics of black pepper.

In the pilot scale cryogenic grinding experimentation, the feed rate and the product temperatures during grinding were controlled by controlling both the feed rate of black pepper and flow of LN_2, according to the experiment design (Section 3.4.4.1). The feed rates, shown in Table 4.3.5, were varied from 7 to 60 kg h(1 using a vibratory (magnetic type) feeder. The product temperatures were maintained at a predetermined temperature using a temperature controller by suitably monitoring the flow of liquid nitrogen into the mill. The product temperature were in the range of -15 ± 3 to -60 ± 3 C (Table 4.3.5). The range of feed rate was chosen based on the equipment specification, particularly the capacity. However, the product temperature chosen was based on the following aspects of industrial situations, (1) the minimum temperature chosen should not be very low which would otherwise leads to difficulty in storage of powder for retail distribution, and (2) the maximum temperature chosen should be slightly away from the freezing point of water (0 to 5 C). Hence, the temperature range of about –10 to -65 C was chosen. The feed rates of two control (ambient grinding) samples (in addition to that of experimental design) were maintained at 15 and 35 kg hr^{-1} and the product temperature reached were 86 and 53 C, respectively.

4.3.4.1.2 Particle Size of Powder

The average particle sizes of the powders were determined by adopting the sieve analysis technique using Eq.3.2 and the results are shown in the Table 4.3.5. The geometric mean particle diameters in the case of cryogenic grinding varied from 0.20 mm to 0.27 mm, with an average of 0.25 ± 0.02 mm and in case of ambient grinding, it was

0.20 ± 0.04 mm. The geometric mean particle diameter in the case of cryogenic grinding was higher (coarser) than the ambient ground black pepper powder. This apparently contradicted the data reported in the literature that cryogenic grinding improved the fineness of powder (Section 2.4.5 (b)). Higher (coarser) particle size in case cryogenic grinding may be attributed to the fact that the moisture content of cryogenic ground powder was higher as compared to samples ground in ambient conditions. Higher moisture content of powder improved the cohesiveness of particles and they stuck to each other, thereby increases apparent particle mean diameter. However, the mean diameters of the powder particles was more consistent across the batch of nine cryogenic ground samples (samples C1 to C9). These results indicate that particle size of product also depended upon moisture content of feed apart from varying with feed rate and temperature. Thus, the grinding trials were conducted with constant moisture feed.

4.3.4.1.3 Mill choking characteristics

Mill choking or sieve choking is a phenomenon in grinding of foods in which ground material which is sticky (not free flowing) in nature adheres to the grinding surfaces or blocks the sieve opening. It is a crucial characteristic in grinding of spices which usually have higher fat content. In large scale ambient grinding operations, the ground products accumulate on the walls of mills or. block the sieve opening (Anon, 1962) which may result in fire hazard or breakdown of the mill. It has been reported (Landwehr and Pahl, 1986) that almost all grinding experiments on pepper without chilling caused choking of sieve and ultimately led to breakdown of the mill. Watanabe *et at* (1978) reported that grinding of nutmeg was impossible above 20 C but it was possible to grind at temperature below -40 C. Sieve choking characteristics were photographed at various temperatures of powder in cryogenic grinding of cumin and clove (Singh and Goswami, 1999a and 2000), who observed that at high temperatures, the blockage of sieves was high.

In the present investigation, it was observed that there was higher accumulation of pepper powder on the different grinding surfaces viz., between the pins, and mill walls during ambient grinding. The reasons for powder accumulation may be due to the fact that during grinding at the temperature higher than the brittle point of black pepper and freezing point of its oil, the powder adhered to the grinding surfaces. Also, during grinding, the spice oil might come out of the ruptured cells and formed a layer over the grinding surfaces (Li *et ai.,* 1991). The powder was deposited above this layer and formed a thick layer on the grinding surface, which caused hindrance in grinding. At the same time, the incoming raw material might overload the grinding surface and the mill and would finally stop the mill. At cryogenic temperatures, no blockage of pins or mill walls was observed. This was because at temperatures lower than the brittle point of black pepper and freezing point of spice oil, the oil got solidified and the grinding operation continued unhindered. Hence, there was a possibility to increase the grinding rate. In other words, the production capacity of the mill could be enhanced, thereby bringing better return to the spice processors. It was, thus inferred that cryogenic grinding operations could eliminate the problem of choking and thereby increasing the production capacity for grinding mills.

4.3.4.1.4 Volatile oil content of Powder

The content of volatile oil, in both cryogenic and ambient conditions are shown in Table 4.3.5. The volatile oil contents in case of cryogenic grinding were in the range of 1.42 to 1.91 mL/ l00g whereas in case of ambient grinding, they were poor (0.78 and 0.98 mL/100g). This was expected because grinding of black pepper at cryogenic temperature improved the volatile oil content in the powder. The average volatile oil content in case of cryogenic grinding was 1.7 mL/100g whereas in ambient grinding it was only 0.9 mL/100g. The loss of volatile oil in the case of ambient grinding was 50% more as compared to cryogenic grinding. This loss may be attributed to higher grinding temperature.

It was observed during ambient grinding that the loss of volatile oils from the powder took place in the atmosphere due to vapourisation of these oils which were sensitive to high product temperatures. This vapourisation also took place, if the powder was fine. These vapourised oils caused eye, nose and throat irritations if inhaled, thereby leading to fatigue of workers. The dust produced during ambient grinding could create respiratory problems.

During cryogenic grinding, the vapourisation of oils was minimum as most of the volatile oil compounds were retained within the powder itself because at cryogenic temperatures the oils got solidified. The dust formation was also marginal. These specific advantages of cryogenic grinding show the practical usefulness of this technology.

4.3.4.1.5 Analysis of Volatile oil by Gas Chromatography

The gas chromatographic analysis of the volatile oil samples obtained under different conditions and their relative percentage of some main constituents of volatile oil are presented in Table 4.3.6. The main monoterpene compounds of black pepper volatile oil were a-thujene, α-pinene, sabinene β-pinene, limonene, and the sesqueterpenes compounds were α-copaene, β-caryophyllene, β-bisabolene, caryophyllene oxide. These compounds accounted for 70 to 88% of the total volatile oil in both cryogenic and ambient grinding samples.

Table 4.3.6

Gas chromatographic analysis of cryogenic and ambient ground volatile oil

Compound	Al	A2	CI	C2	C3	C4	C5	C6	C7	C8	C9
1. Thujene+α-pinene	0.78	0.89	7.82	5.60	7.45	6.81	5.09	3.06	7.23	1.77	6.79
2. Sabinene+β-pinene	4.98	3.96	22.87	19.64	22.15	20.58	18.76	15.67	21.39	9.32	21.10
3. 1,8 Cineole	3.75	3.41	7.60	7.32	7.61	7.46	7.27	6.80	7.57	4.71	8.81
4. Limonene	7.85	5.99	15.50	15.49	15.73	14.82	15.66	14.94	15.73	9.90	16.82
5. α-Copaene	5.61	5.31	3.54	3.77	3.45	3.75	3.97	4.48	3.59	5.37	3.57
6. β-Caryophyllene	21.46	25.50	9.79	8.98	10.72	13.12	9.20	3.78	13.14	13.20	17.23
7. β-Bisabolene	16.03	19.95	7.66	8.35	8.13	9.19	8.06	6.88	8.81	12.87	10.51
8. Caryophyllene oxide	13.13	12.67	8.13	9.94	7.74	7.53	10.41	14.74	6.02	15.99	3.58
Total (%)	73.59	77.68	82.91	79.09	82.98	83.26	78.42	70.35	83.48	73.13	88.41
Moneterpenes (SI. No.I-4)	17.36	14.25	53.79	48.05	52.94	49.67	46.78	40.47	51.92	25.70	53.52
Sesqueterpenes (SI No.5-8)	56.23	63.43	29.12	31.04	30,(J4	33.59	31.64	29.88	31.56	47.43	34.89
Ratio of monotepenes and	0.31	0.22	1.85	1.55	1.76	1.48	1.48	1.35	1.65	0.54	1.53

* C I to C9 were the cryogenic ground samples and A I & A2 were ambient ground samples

The ratios of monoterpenes to sequeterpenes varied from 1.35 to 1.85 in the case of cryogenic ground samples with exception of one cryogenic ground sample (C8) for which the ratio was 0.54, while both the ambient ground samples had a very low ratios of 0.31 and 0.22.

Figure 4.3.3 shows the variation of constituent compounds of volatile oil viz., total oil, monterpenes and sesqueterpenes in absolute quantities (mL/100g). The contents of sesqueterpenes in the volatile oil was between 0.43 and 0.63 mL/100g while the contents of monoterpenes in the volatile oil was in the range of 0.61 to 1.55 mL/100g.

Figure 4.3.4 shows the variations of constituent monoterpene compounds of volatile oil in absolute quantities (mL/100g). The loss of monoterpenes was significant in ambient grinding, as there was a loss of volatile oil in terms of every monoterpene compound, which might be attributed to high product temperature.

Figure 4.3.5 shows the variations of constituent sesqueterpene compounds of volatile oil in absolute quantities (mL/100g). There was marginal difference in the distribution pattern of sesqueterpene compounds in both ambient and cryogenic ground samples as sesqueterpene compounds were not sensitive to high temperature. Figure 4.3.6(a) shows the comparison of these two grinding methods with respect to total oil, monoterpenes and sesqueterpenes in absolute quantities (mL/100g). The average content of monotepenes content in cryogenic grinding was 0.80 mL/l00g whereas that from ambient grinding was 0.15 mL/100g. However, the average sesqueterpenes content was fairly constant in both the grinding methods. This aspect is clearly brought out in the pie chart (Fig. 4.3.6 (b)), wherein it is indicated that· in the case of ambient grinding monoterpenes and sesqueterpens amount to 22 and 78%, respectively of the total oil, While the corresponding values in the cryogenic grinding are 60 and 40%, respectively, which shows that cryogenic grinding technique is superior to ambient grinding in terms of monoterpenes retention in the powder.

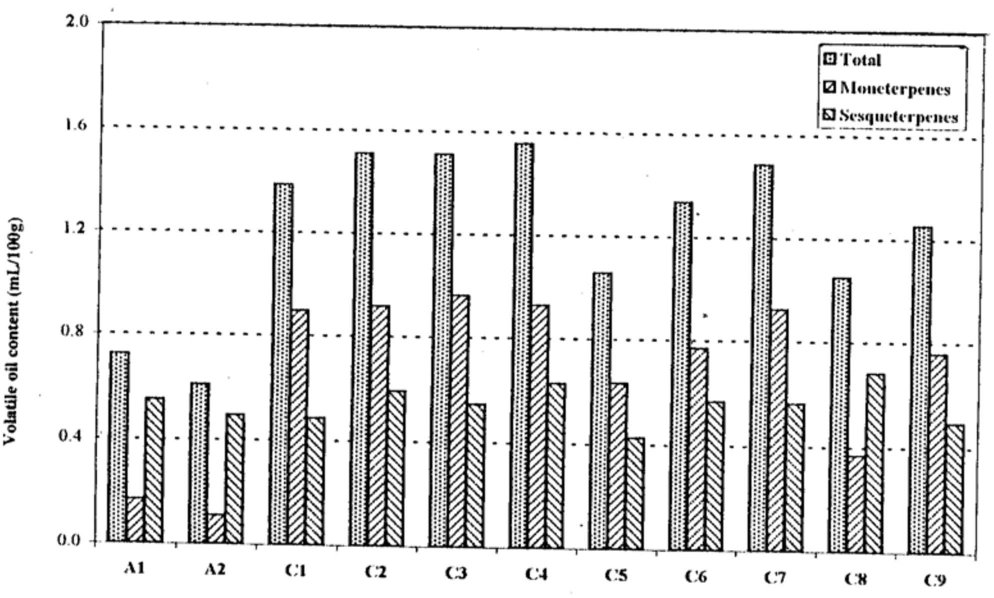


Fig. 4.3.3 Variations of total, monoterpene and sesqueterpenes content in black pepper volatile oil ground by cryogenic grinding (pilot scale)

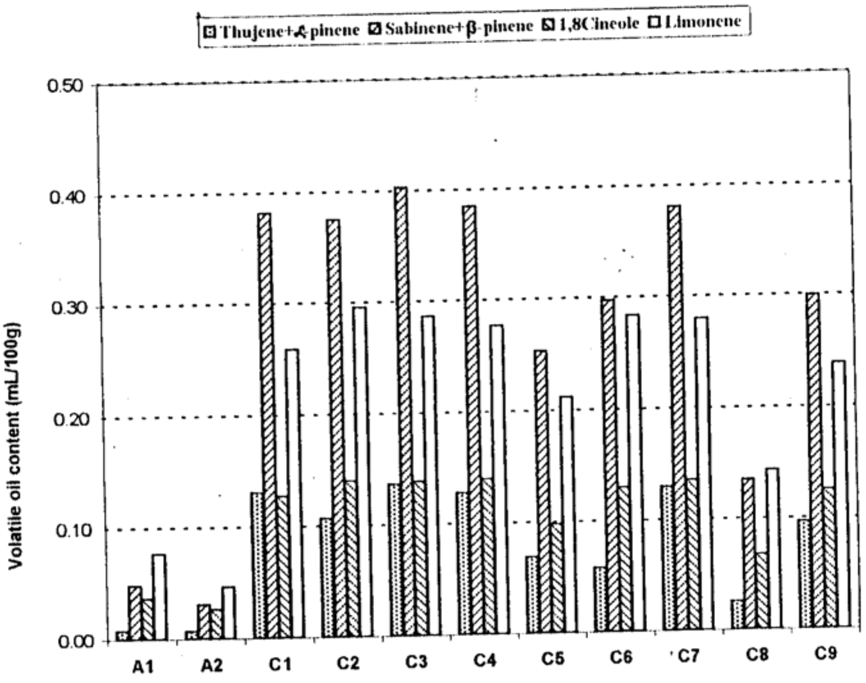


Fig. 4.3.4 Variations of monoterpenes constituents in black pepper volatile oil ground by cryogenic grinding (pilot scale)

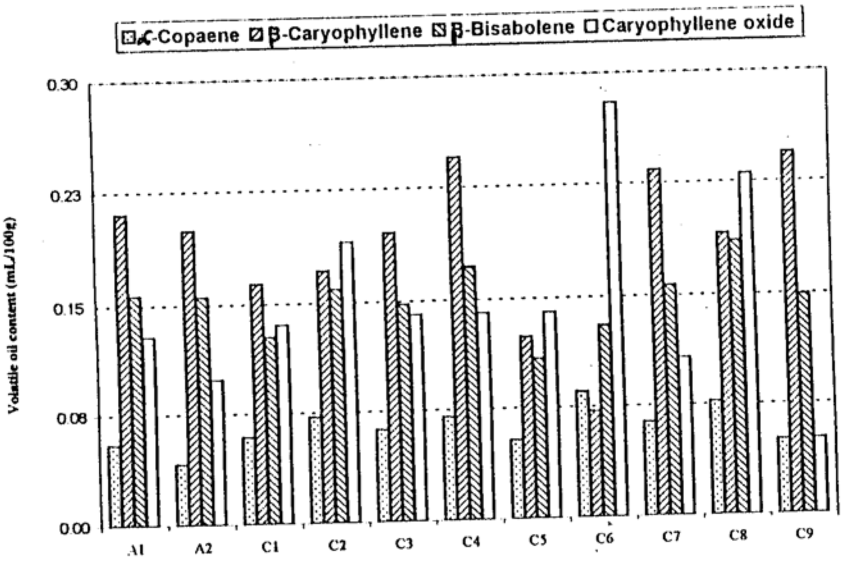


Fig. 4.3.5 Variations of sesqueterpenes constituents in black pepper volatile oil ground by cryogenic grinding (pilot scale)

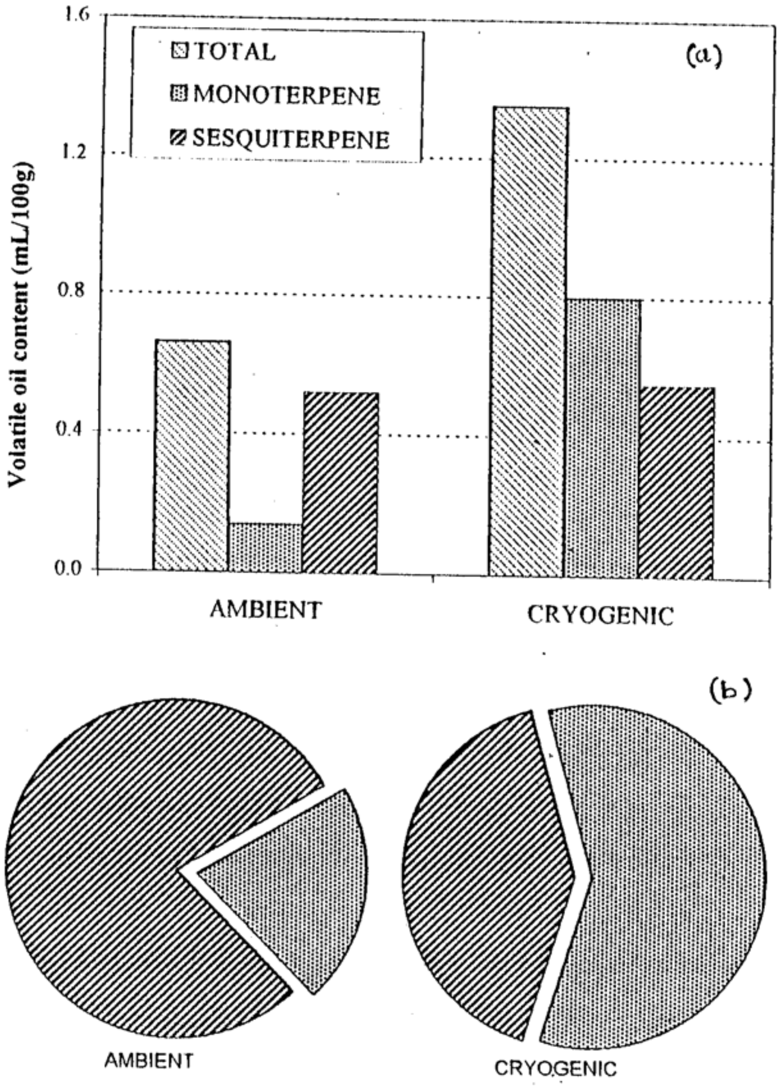


Fig. 4.3.6 Comparison of ambient and cryogenic grinding in terms of components volatile oil (Pilot scale) (a) In terms of total oil, monoterpenes and sesqueterpenes and (b) In terms of monoterpenes and sesqueterpenes

4.3.4.1.6 Sensory Studies of Powdered Samples

In the previous sections, the volatile oil obtained from the powdered black pepper samples was subjected to instrumental analysis by gas chromatography. However, instrumental analysis alone may not always be a correct measurement of quality of powdered sample. The consumers' acceptance of the powdered sample is a very important parameter in the studies on spice grinding. Therefore, powders of both cryogenically and ambient ground samples were subjected to' sensory studies. As odour is one of critical parameters in powered spice products (Narasimhan *et al,* 1990, 1992), the odour profiles were obtained with the help of a trained panel of 12 persons (please see Section 3.3.4.3 of Materials and Methods, chapter 3).

The odour profile of powdered black pepper was classified as top notes, basic notes, defective notes and the overall quality. The odour attributes such as floral, citrussy, fresh cut wood, camphory and green, were categorised as top notes. The odour attributes such as herbal, woody, irritant/sharp, earthy and rooty were catergorised as basic notes, and the stale and oxidised were catergorised as defective notes. It is desirable to have higher top notes and minimum defective notes, which means the freshness of the powder.

The panel training was found to be effective as their performance as compared by the coded duplicate sample was consistent. The understanding of the top and basic notes were in tandem. The results of the odour profile (the mean and SD) of both cryogenically and conventionally ground samples were plotted on a 10 point axis scale (Fig. 4.3.7). The top notes in case of cryogenically ground samples were in the zone of mean score between 5 and 7.5, whereas the conventionally ground samples was in the zone of mean score between 2.5 and 4.5. This means that cryogenically ground samples were better in odour quality and the powder was fresh. In the basic notes, the attributes such as earthy and rooty did not have any significant difference between the two grinding methods, whereas in other attributes cryogenically ground samples were better. The defective notes were higher in conventionally ground samples and were very low in cryogenically ground samples. The mean scores of overall quality was about 5 and 10 for conventional and cryogenically ground samples, respectively which indicated that powder obtained by the former was average and the latter was very good in overall quality.

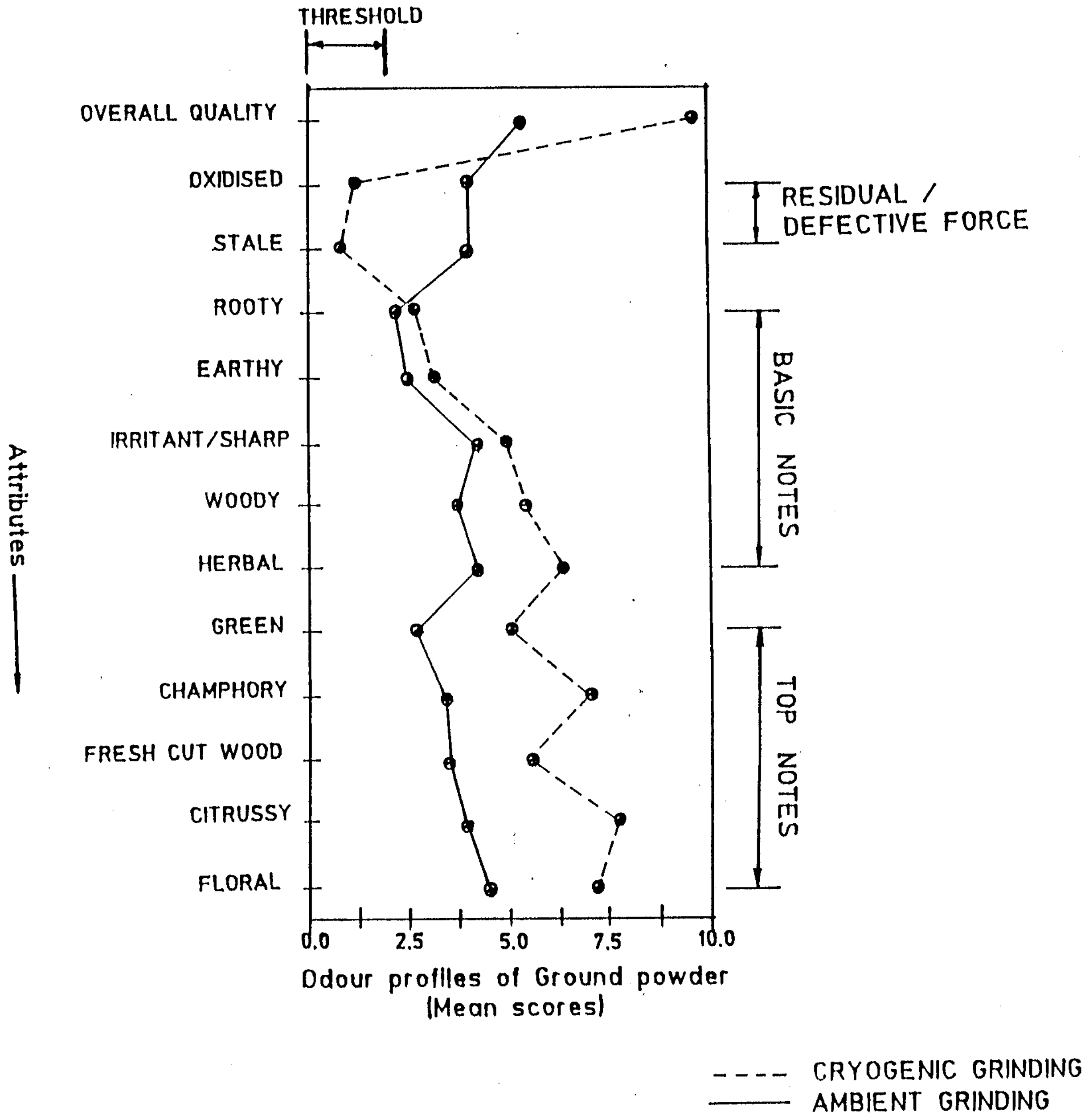


fig. 4.3.7 Sensory attributes of samples of cryogenic and conventional grinding

Further, among the nine cryogenically ground samples (Refer Table 4.3.5), the samples C4 (processed at 15 kg hr^{-1} and -54 C) and C6 (processed at 52 kg hr^{-1} and -25 C) were found to be ideal to give a good quality powder. This aspect was confirmed by repeated testing by the same sensory panel.

To conclude, the sensory studies data indicated that cryogenically ground samples were distinctly high in top notes which represented freshness, and marginally high in basic notes also. Hence, the quality of cryogenic ground samples were better than that of ambient ground samples.

4.3.4.2 Response Surface Methodology (RSM) for Cryogenic Grinding

In the previous Section 4.3.4.1 also, it was clearly mentioned that cryogenic grinding was superior to ambient grinding even in pilot scale grinding, in terms volatile oil content and quality of volatile oil. This section on response surface methodology for cryogenic grinding examines specifically the effect of independent variables such as feed rate and product temperature on dependent variables viz., volatile oil, particle diameter, energy expenditure, content of monoterpenes and sesqueterpenes in the volatile oil. Having concluded that cryogenic grinding is an alternative, this section deals with optimisation of experimental condition for volatile oil content and content of monoterpenes in the volatile oil. The objective of this section was to know the quantitative effect of these variables on quality parameters, and to find an optimised condition for practical application.

4.3.4.2.1 Effect of Variables on Cryogenic Grinding

Pilot scale cryogenic grinding of black pepper was conducted to quantify the effect of grinding variables such as feed rate (X_t) and temperature of product (X_2) at the mill's exit. The response functions or dependent variables were volatile oil (Y_1), geometric mean particle diameter of the powder (Y_2), energy expenditure for grinding (Y_3), and product characteristics such as content of monoterpenes (Y_4) and sesqueterpenes (Y_5) in the volatile oil. An experimental design (CCRD) in coded level of variables was employed (Section 3.3.4.1) to investigate the effect of the two variables on these five response functions. The experimental design in coded level (-1.414 to 1.414) of variables is shown in Table 4.3.7, while the experimental results concerning the response functions are shown in Table 4.3.8. To visualise the effect of the variables in a better manner, 3 dimensional response surfaces are shown in Figs. 4.3.8 to 4.3.12.

4.3.4.2.2 Volatile oil

The volatile oil contents in the powders varied between 1.35 and 1.94 mL/100g in the range of experimental variables. The analysis of variance (ANOVA) using a second order polynomial (Eq. 3.15) for volatile oil is represented by Table 4.3.9

Table 4.3.7

Experimental design in coded (x) and actual level (X) of variables
X_1 and x_1: Feed rate X_2 and x_2: Temperature

Expt No.	Variables			
	Coded level		Actual level	
	X_1	X_2	X_1	X_2
1	-1	-1	14.8	53.4
2	-1	1	14.8	-21.6
3	1	-1	52.2	-53.4
4	1	1	52.2	-21.6
5	-1.414	0	7.0	-37.5
6	1.414	0	60.0	-37.5
7	0	-1.414	33.5	-60.0
8	0	1.414	33.5	-15.0
9	0	0	33.5	-37.5
10	0	0	33.5	-37.5
11	0	0	33.5	-37.5

Table 4.3.8

Response functions ($Y1, Y_2, Y_3, Y_4$ and Y_5) obtained employing experimental design (corresponding to Table 4.3.7)

Expt. No.	Volatile oil Y_1 (mLl 100g)	Particle diameter Y_2 (mm)	Energy expenditure Y_3 (kJ/kg)	Monoterpenes Y_4 (%)	Sesqueterpenes Y_s (%)
1	1.87	0.25	278.0 I	49.67	33.59
2	1.35	0.20	208.51	46.78	31. 64
3	1.42	0.25	300.74	53.52	34.89
4	1.90	0.27	300.74	40.4 7	29.88
5	1.44	0.24	446.81	25.70	47.43
6	1.82	0.25	278.01	52.94	30.04
7	1.78	0.22	327 .66	51.92	31.56
8	1.67	0.22	327 .66	53.79	29.12
9	1.91	0.26	327.66	48.05	31.04
10	1.94	0.25	327 .66	48.05	31. 04
11	1.88	0.26	327.66	48.05	31.04

A high multiple correlation coefficient (r) of 0.967 (significant at $p \leq 0.0\ 1$) indicated the suitability of the second order polynomial to express the response function (volatile oil) in terms of the variables (feed rate and temperature). Among the variables, the effect of feed rate (linear and quadratic) was more prominent than that for temperature (Table 4.3.9). The quadratic effect of feed rate was negative but dominated over its positive linear effect. The quadratic effect of temperature was only significant ($p \leq 0.10$) and had a negative effect. On the contrary, the interaction effect of feed rate and temperature had the highest effect (significant at $p \leq 0.01$) compared to all the variables and its effect was positive. This indicated that the effect of feed rate depended on the level of temperature and *vice-versa.* The negative quadratic effect of feed rate tried to decrease volatile oil when feed rate was increased. Figure 4.3.8 shows this trend when the temperature was very low. On the other hand, the dominating effect of feed rate x temperature became prominent when one of them or both were high. The net result in such circumstances was an increase in volatile oil because this interaction term was positive in nature (Fig. 4.3.8) and possessed the highest effect. The inference that could

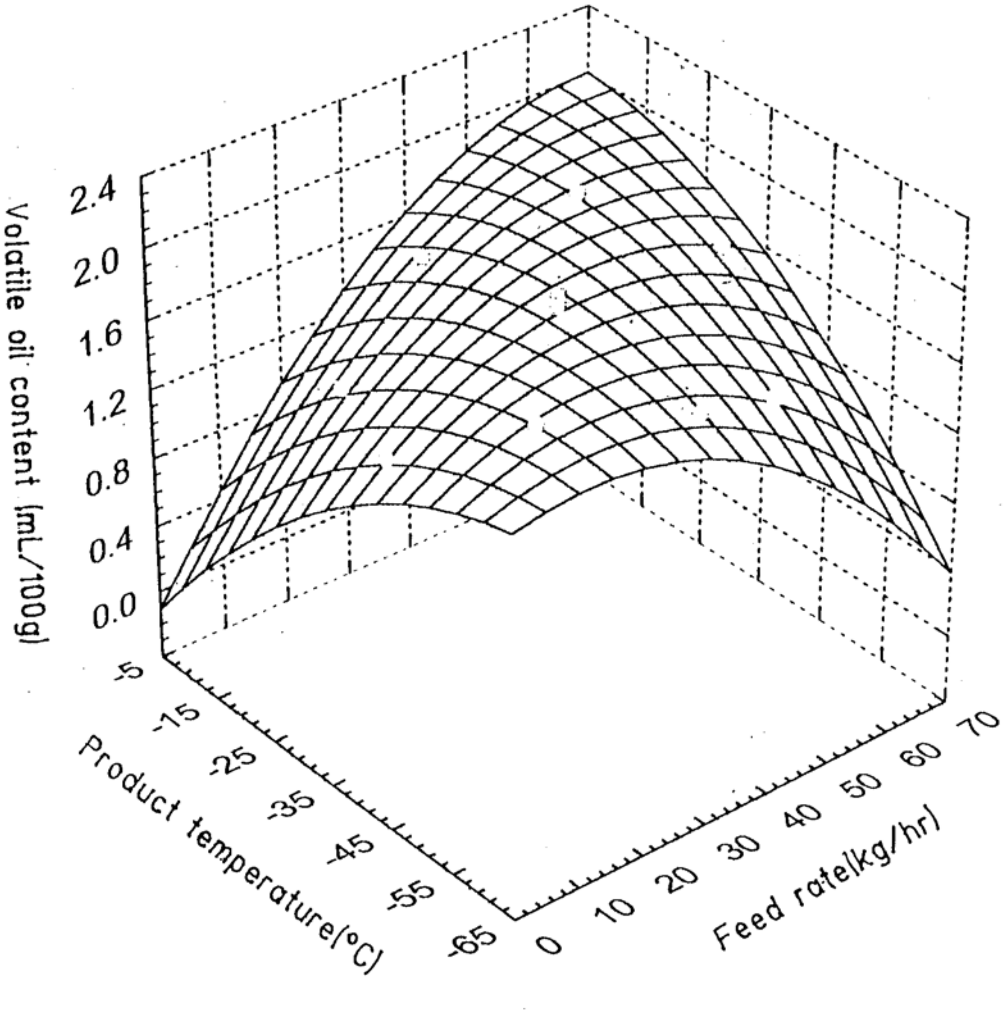


Fig. 4.3.8 Response surface plot of volatile oil, feed rate and product temperature **in** cryogenic grinding

be drawn from these results are that the effects of these two variables are inter-related, and a desirable condition is possibly low temperature in combination with a high feed rate.

4.3.4.2.3 Particle diameter

The change in geometric mean particle. diameter of the powder due to cryogenic grinding was between 0.20 and 0.27 mm (Table 4.3.8). The response surface relating particle diameter, and feed rate and temperature are shown in Fig. 4.3.9. The ANOVA table (Table 4.3.10) shows significant effects for linear feed rate (positive effect), quadratic negative effect of temperature, and the interaction effect of feed rate and temperature (positive effect). These meant that an increase in feed rate increased the particle size in a linear fashion, whereas an increase in temperature decreased the particle size in a quadratic manner. Among these three significant effects, the interaction term indicated that final particle size depended on the level of feed rate in conjunction with temperature. Thus, a low feed rate could produce particles with low average particle sizes.

Table 4.3.9

Analysis of variance (ANOV A) for response function volatile oil (Y_1) in coded level of variables

Source of variation	Coefficient of regression equation	Sum of Squares	Degrees of freedom	Mean sum of squares	F-value
Intercept	1. 91000	-	-	-	-
Feed rate	OJl7968	0.05078	1	0.05078	8.19 **
(Feed rate) $_2$	-0.15066	0.12812	1	0.12812	20.62 ***
Temperature	-0.02445	0.00478	1	0.00478	0.77 NS
(Temperature) $_2$	-0.10314	0.06005	1	0.06005	9.69 **
Feed rate x Temperature	0.25000	0.25000	1	0.25000	40.26 *** -
Error	-	0.03099	5	0.00620	-
r	0.967				

* Significant at $p < 0.25$
** Significant at $p < 0.10$
*** Significant at $p < 0.01$
NS Non-significant at $p = 0.25$

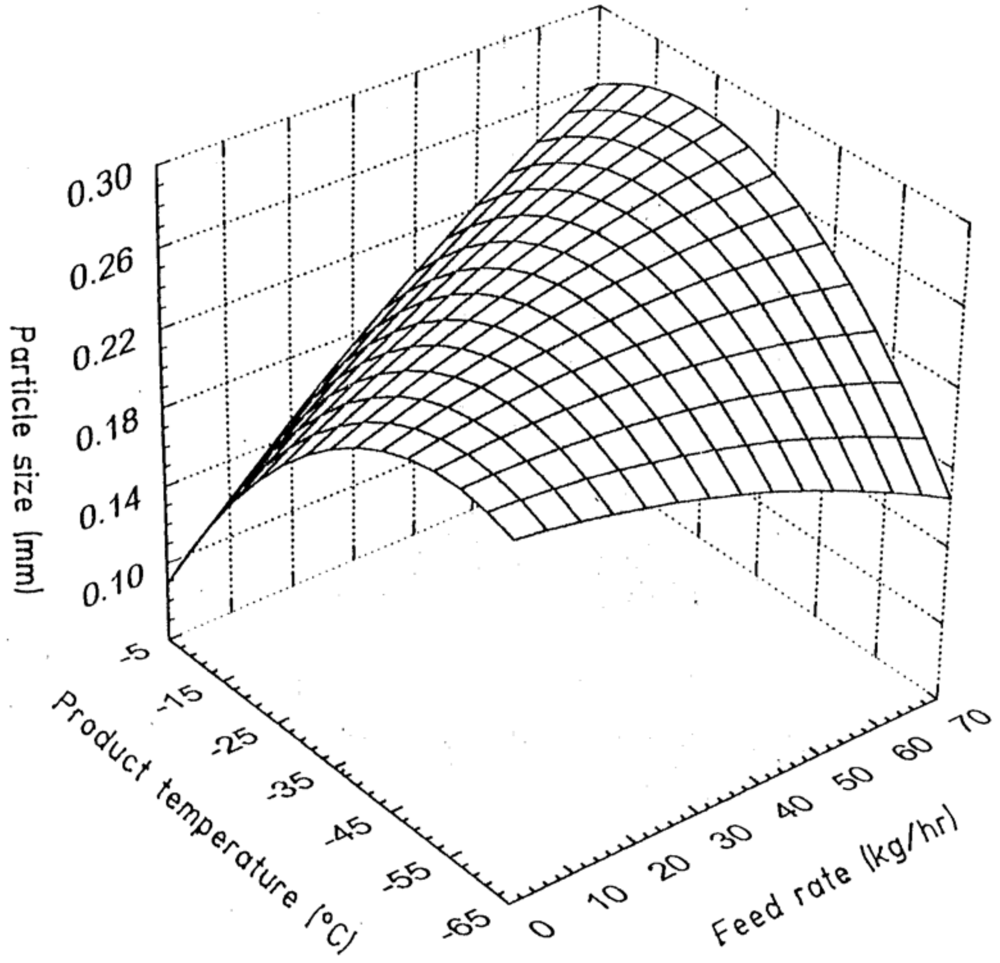


Fig. 4.3.9 Response surface plot of particle diameter, feed rate and product tcmperature in cryogcnic grinding

Table 4.3.10

Analysis of variance (ANOY A) for response function particle diameter (Y 2) in coded level of variables

Source of variation	Coefficient of regression equation	Sum of squares	Degrees of freedom	Mean sum of squares	F-value
Intercept	0.25666	-	-	-	-
Feed rate	0.01052	0.00089	l	0,()0089	5.75 **
(Feed rate) $_2$	-0.00333	0.00006	I	0.00006	0.41 NS
Temperature	-0.00375	0.00011	1	0.00011	0.73 NS
(Temperature) $_2$	-0.01584	0.00142	l	0.00142	9.21 **
Feed rate x Temperature	0.01750	0.00123	1	0.00123	7.96 **
Error	-	0.00077	5	0.00015	-
r	0.910***	-	-	-	-

* Significant at $p < 0.25$
** Significant at $p < 0.10$
*** Significant at $p < 0.01$
NS Non-significant at p =0.25

4.3.4.2.4 Energy Expenditure

The energy expenditure during cryogenic grinding of black pepper varied between 209 and 447 kJ kg^{-1} (Table 4.3.8) but gave very poor multiple correlation coefficient (r = 0.418, non-significant at p=0.25) while trying to fit to a second order polynomial. The response surface relating to energy expenditure, feed rate and product temperatures are shown in Fig. 4.3.10. The use of a higher order polynomial (such as third or fourth order) did not help to improve the r value. However, the ANOY A table (Table 4.3.11) showed all the F-values for the variables to be non-significant at p=0.25. This clearly indicated that energy expenditure could not be described or related with the variables like feed rate and temperature within the range of experimentation.

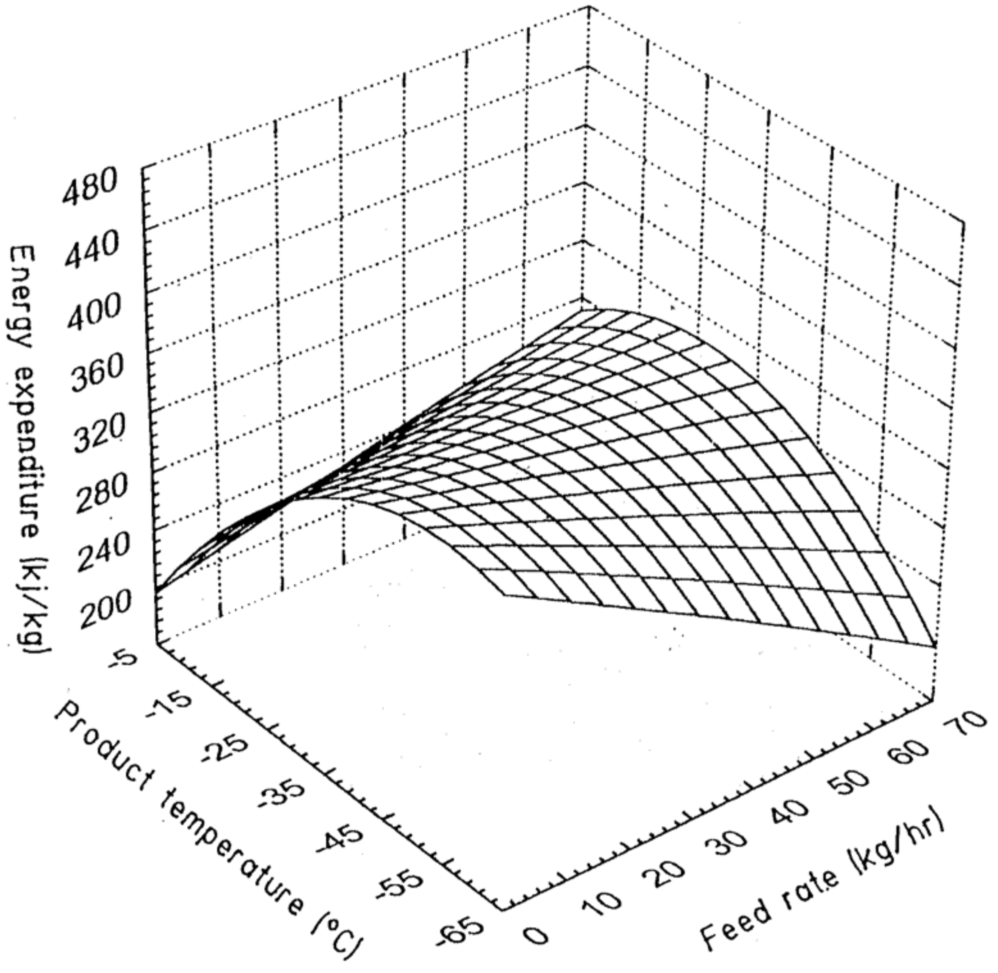


Fig.4.3.10 Response surface plot of energy expenditure, feed rate and product temperature **in** cryogenic grinding

Table 4.3.11

Analysis of variance (ANOVA) for response function energy expenditure (Y 3) in coded level of variables

Source of variation	Coefficient of regression equation	Sum of squares	Degrees of freedom	Mean sum of squares	F-value
Intercept	327.33471	-	-	-	-
Feed rate	-15.46774	1913.72	1	1913.72	0.36 NS
(Feed rate)^2	-0.72266	2.94	1	2.94	0.00 NS
Temperature	-8.68881	603.87	1	603.87	0.11 NS
(Temperature)^2	-18.10291	1849.87	1	1849.87	0.34 NS
Feed rate x	17.37500	1207.56	1	1207.56	0.22 NS
Temperature Error	-	26907.42	5	5381.48	-
R	0.418^{NS}	-	-	-	-

*Significant at $p < 0.25$
** Significant at $P < 0.10$
*** Significant at $p < 0.01$
NS Non-significant at $p = 0.25$

The possible explanation for this phenomenon could be that the mill used for the experimentation had the capacity of 80 kg hr^{-1} while the material ground was only of 4 kg batch sizes. Singh and Goswami (l999b) reported an increase in specific energy consumption with an increase in grinding temperature from -160 to -70 C during cryogenic grinding of cumin seed. Similar results have also been reported for cryogenic grinding of cloves by the same authors (Singh and Goswami, 2000). The latter studies have also found that a second order polynomial fitted well between specific energy consumption and the variables (feed rate, temperature, rotor speed and sieve opening sizes). But, the present research contradicted the above findings and indicated that energy expenditure values could not be related to such variables by using polynomials.

4.3.4.2.5 Monoterpenes

The quantity of monoterpenes in the cryogenically ground samples varied between 40.5 and 53.5% (with an exception of experiment No.5, where it was low and was only

25.7%). The analysis of variance (ANOVA) using a second order polynomial (Eq. 3.15) for monoterpenes is represented in Table 4.3.12. A multiple correlation coefficient (r) of 0.779 (significant at $p \leq 0.0I$) indicated the moderate suitability of a second order polynomial to express the response function (monoterpenes) in terms of the dependent variables (feed rate and temperature). In the experimental range of variables selected, the effect of feed rate (linear and quadratic) was prominent on the percentage of monoterpenes (significant at $p < 0.25$) whereas the effect of temperature (linear and quadratic) was non-significant ($p=0.25$). The linear effect of feed rate was positive whereas its quadratic effect was negative on the percentage of monoterpenes. This meant that an initial increase in feed rate increased monoterpenes but a very high level of feed rate marginally decreased the same, which was reflected in the response surface (Fig. 4.3.11). The highest value for monoterpenes appeared to be associated with a high value of feed rate (not at the highest level but close to about 50 kg hr^{-1}.

Table 4.3.12

Analysis of variance (ANOVA) for response function monoterpenes (Y4) in coded level of variables

Source of variation	Coefficient of regression equation	Sum of squares	Degrees of freedom	Mean sum of squares	F-value
Intercept	48.14969	-	-	-	-
Feed rate	4.50785	162.54	I	162.54	3.16 *
(Feed rate)$_2$	-4.03528	91.92	I	91.92	1.78 *
Temperature	- 1.66223	22.10	1	22.10	0.43 NS
(Temperature)$_2$	2.73426	42.20	1	42.20	0.82 NS
Feed rate x Temperature	-2.54000	25.81	I	25.81	0.50 NS
Error		257.84	5	51.48	-
r	0.779***	-	-	-	-

* Significant at $p < 0.25$
** Significant at $p < 0.10$
*** Significant at $p < 0.0\ 1$
NS Non-significant at $p = 0.25$

The phenomenon of increased feed rate (linear), increasing the percentage of monoterpenes might be due to the fact that the ground material spent less time within the

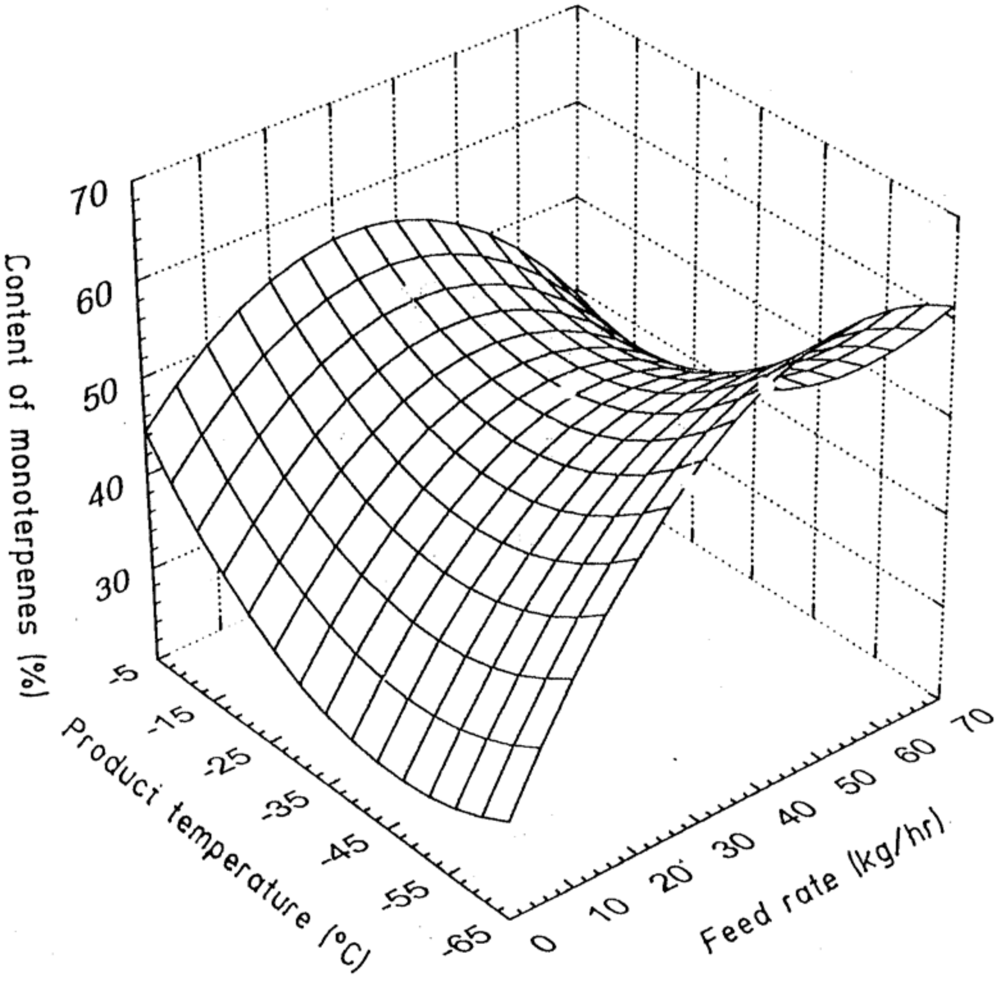


Fig. 4.3.11 Response surface plot of monoterpenes, feed rate and product temperature in cryogenic grinding

grinding zone as compared to the lower feed rate samples. Higher the time spent by the ground material within the grinding zone the higher was the loss of monotepernes, as these compounds were volatile in nature. The range of temperature (-15 to -60 C) did not appears not to affect the percentage of monoterpenes, indicating that selection of any temperature in this range was suitable. Hence, a temperature such as -15 C could be selected to have more monoterpenes in the product because selection of too low temperature was not a cost effective situation.

4.3.4.2.6 Sesqueterpenes

The percentages of sesqueterpenes (Table 4.3.8) in the samples were between 29.1 and 47.4%. The analysis of variance using the second order polynomial (Table 4.3.13) indicated a moderately good correlation coefficient of 0.882 (significant at $p \leq 0.01$). The effect of feed rate (linear) on the sesqueterpenes was negative ($p \leq 0.10$) which meant that the high feed rates gave low percentage of sesqueterpenes. The quadratic effect of the feed rate was positive (significant $p < 0.25$) indicating that at a very high level of feed rate, the response function would increase, which was visible in the response surface (Fig. 4.3.12).

Table 4.3.13

Analysis of variance (ANOV A) for response function sesqueterpenes (Y_5) in coded level of variables

Source of variation	Coefficient of regression	Sum of squares	Degrees of freedom	Mean sum of squares	F-value
Intercept	31.04376	-	-	-	-
Feed rate	-3.16916	80.33	1	80.33	4.77 **
(Feed rate)$_2$	3.31823	62.15	1	62.15	3.82 *
Temperature	-1.26396	12.77	1	12.77	0.82 NS
(Temperature)$_2$	-0.88053	4.38	1	4.38	0.25 NS
Feed rate x Temperature	-0.69000	1.90	1	1.90	0.14 NS
Error	-	81.23	5	16.24	-
r	0.827***	-	-	-	-

* Significant at $p < 0.25$
** Significant at $p < 0.10$
*** Significant at $p < 0.01$
NS Non-significant at $p = 0.25$

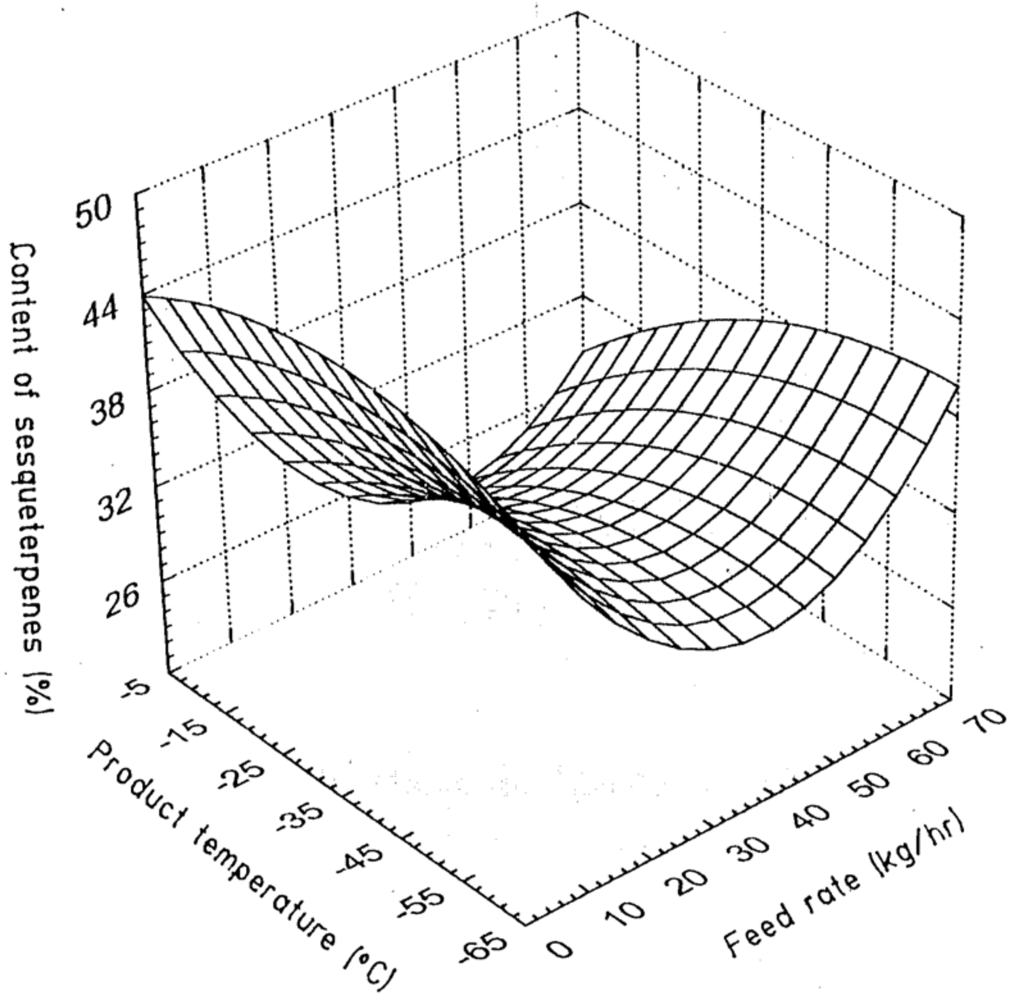


Fig. 4.3.12 Response surface plot of sesqueterpenes, feed rate and product temperature in cryogenic grinding

The coefficients of regression equation for the four dependent variables, viz., volatile oil, particle size, monoterpenes and sesqueterpenes in the actual level of variables are shown in Table 4.3.14. However, the correlation coefficients for energy expenditure have not been presented in the table due to inadequate suitability. These coefficients would be of practical use for large scale grinding operations of black pepper.

Table 4.3.14

Coefficients of the regression equation in actual level of variables*

	Volatile oil (Y_1)	Particle diameter (Y_2)	. Monoterpenes (Y_4)	Sesqueterpenes (Y_s)
Constant	-0.40224	0.05631	49.475	42.753
Feed rate	0.06455	0.00341	0.682	-0.902'
(Feed rate) 2	-0.00043	-0.00001	-0.011	0.010
Temperature	-0.06030	-0.00690	1.005	-0.249
(Temperature) 2	-0.00041	-0.00006	0.011	-0.003
Feed rate x Temperature	0.00084	0.00006	-0.009	-0.003

* The coefficients for energy expenditure (Y3) are not presented due to inadequate suitability.

4.3.4.2.7 Correlation among the Dependent Variables

It is interesting to know whether the response functions are inter-related, and if so, to what extent. Table 4.3.15, shows the correlation coefficients among the dependent variables. Volatile oil and particle size were having a moderate correlation of 0.62 (significant at $p \leq 0.05$). Similar correlation was reported in previous sections also (Section 4.2.3.4) for ambient grinding. Correlation of volatile oil with other dependent variables such as energy expenditure, monoterpenes and sesqueterpenes was nonsignificant ($p = 0.05$). The correlation of particle size with other dependent variables was non-significant ($p= 0.05$) for energy expenditure, monoterpenes and sesqueterpenes. The correlation of energy expenditure with monoterpenes and sesqueterpenes was negative and positive, respectively (significant at $p < 0.05$). This meant that, high energy consumption lowered the heat sensitive monoterpenes, while, increasing sesqueterpenes.

The correlation of monoterpenes with sesqueterpenes was negative (significant at $p < 0.05$) as expected because a decrease in one quantity would increase the other.

Table 4.3.15.

Correlation among the dependent variables

	Volatile oil (Y_1)	Particle diameter (Y_2)	Energy expenditure (Y_3)	Monoterpenes (Y_4)	Sesqueterpenes (Y_s)
Volatile oil (Y_1)	1.000	0.616*	0.019^{NS}	0.250 NS	-0.521 NS
Particle diameter (Y_2)		1.000	0.260 NS	-0.131 NS	-0.029 NS
Energy expenditure (Y_3)			1.000	-0.630*	0.690*
Monoterpenes (Y_4)				1.000	-0.800**
Sesqueterpenes (Y_s)					1.000

* Significant at $p < 0.05$
* * Significant at $p < 0.0$ I
NS Non-significant at $p = 0.05$

It could be inferred that high correlation between monoterpenes and sesqueterpenes and a moderate correlation existed between energy expenditure with monoterpenes and sesqueterpenes, and between volatile oil and particle size. These indicate that larger particle size has maximum volatile oil and an increased energy input reduced monoterpenes but simultaneously increased sesqueterpenes.

4.3.4.2.8 Optimization of Cryogenic Grinding Condition

The cryogenic grinding conditions could be optimised for obtaining maximum volatile oil, monoterpenes and combination of both from the point of commercial use as ground particles are priced mainly on these quality attributes. The optimisation process employed in these study was the canonical procedure (Section 3.3.4.1) along with overlapping of contour plots for obtaining the zone (s) of suitable opertating conditions.

4.3.4.2.8.1 Volatile oil

In cryogenic grinding volatile oil content in the powder varied between 1.94 and 1.35 mL/ 100g at various feed rates and. grinding temperatures as per the experimental design. The objective of this optimisation process was to obtain suitable conditions of feed rate and temperature which could yield the highest volatile oil from the powder by distillation. The contour plot (Fig. 4.3.13) indicated that volatile oil reached the maximum (1.94 mL/100g) at two zones. One zone being at low feed rates (7 to 15 kg hr^{-1} and low temperature (-53 to -60 C) and the other being at high feed rate (47 to 57 kg hr^{-1} and high temperature (-15 to -20 C).

However, in practical situation, it would be worthwhile to choose higher feed rate and higher temperature because higher grinding rates would be desirable in the industrial grinding applications to enhance production capacity and to save coolant requirement, respectively. Hence, the optimum cryogenic condition for maximum content of volatile oil could be selected as 47 to 57 kg hr^{-1} of feed rate and -20 to -15 C of product temperature. The values of optimum condition of cryogenic grinding agreed with the value of optimum product temperature (about -20 C) for obtaining the highest volatile oil (Anon, 1994).

4.3.4.2.8.2 Monoterpenes

The objective was to obtain optimum condition for cryogenic condition that would produce maximum quantity of monoterpenes, which in turn would give the freshness of the product. The response surface (FigA.3.14) showed that the optimum value of monoterpenes in the range of feed rate of 40 to 55 kg hr^{-1} and the product temperature of -56 to -50 C, gave the highest monoterpenes. These conditions yielded the product containing volatile oil having high aroma, high freshness and also strong peppery notes (Section 4.2.3.8).

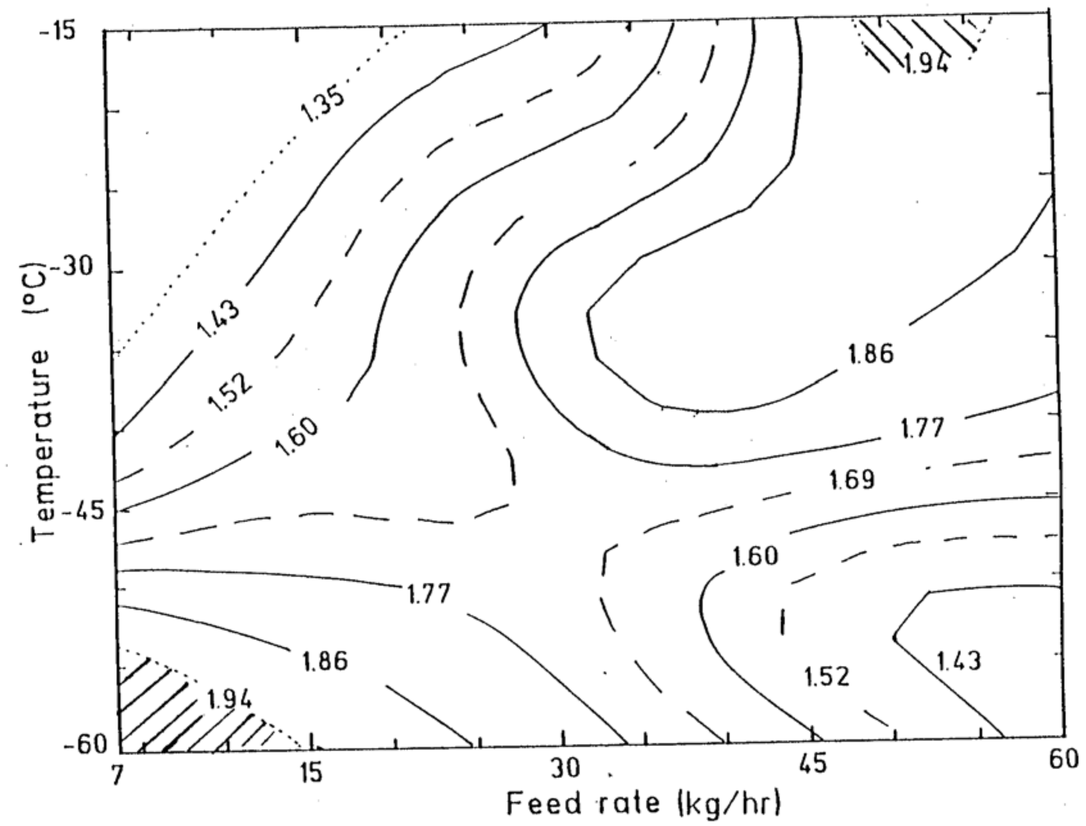


Fig. 4.3.13 Contour plot of volatile oil, feed rate and product temperature for optimizing cryogenic grinding condition

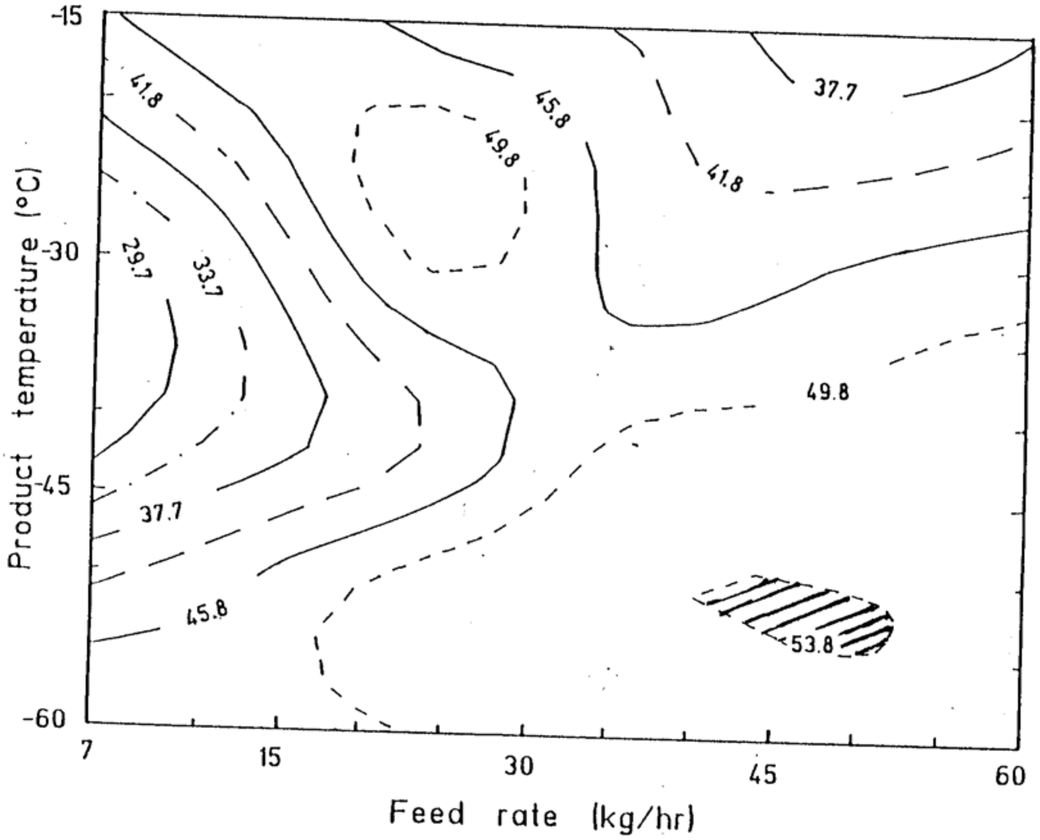


Fig. 4.3.14 Contour plot of monoterpenes, feed rate and product temperature for optimizing cryogenic grinding condition

4.3.4.2.8.3 Volatile oil and Monoterpenes

The optimisation of both volatile oil and monoterpenes is required, as for industrial applications, higher content of volatile oil is desirable with higher percentage of monoterpenes to have higher unit price of ground black pepper product. Accordingly, Fig. 4.3.13 and 4.3.14 were superimposed to have a combined graph of volatile oil and monoterpenes (Fig. 4.3.15) as functions of feed rate and product temperature. As indicated in the graph, .the combined optimum condition was 8 to 15 kg hr^{-1} of feed rate and -60 to -55 C of product temperature when the volatile oil content was 1.94 mL/I00g and monoterpenes content was about 47.8%. On the other hand a feed rate of 47 to 57 kg hr^{-1} and product temperature between -20 to -15 C also gave a high volatile oil content of 1.94 mL/100g but slightly lower monoterpene content of about 38%.

However, for the reasons mentioned in Section 4.3.4.2.7, a high feed rate and a high product temperature combination which would yield maximum volatile oil with a reasonable quantity of monoterpenes may be preferred. Hence, the feed rate of 47 to 57 kg hr^{-1} and product temperature of -20 to -15 C which gave volatile oil of 1.94 mL/100g and monoterpenes of about 38 % was the combined final optimum grinding condition.

4.3.4.3 Conclusions

The following inferences were drawn based on pilot scale grinding studies involving ambient and cryogenic grinding;

1) The control sample in ambient grinding reached a product temperature of 86 and 53C, at the feed rates of 15 and 35 kg hr^{-1}, respectively indicating that low feed rate would give higher temperature which would be undesirable.

2) The average volatile oil content in case of cryogenic grinding was 1.7 mL/100g whereas in ambient grinding it was 0.9 mL/100g. The loss of volatile oil in the case of ambient grinding was about 50% as compared to cryogenic grinding.

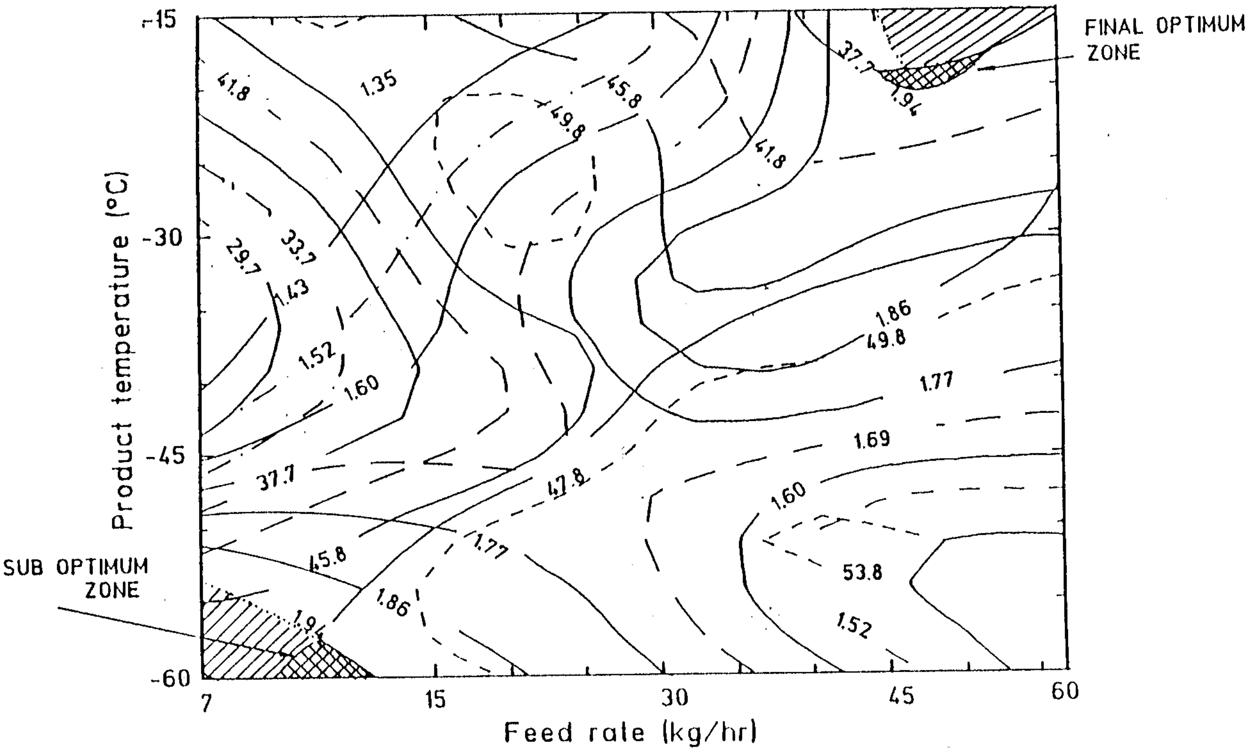


Fig. 4.3.15 Combined contour plot (Fig. 4.3.13 and Fig. 43.14) of volatile oil, monoterpenes, feed rate and product temperature for optimizing cryogenic grinding condition

3) The gas chromatographic analysis data of volatile oil indicated that the ratio of monoterpenes to sequeterpenes varied from 1.35 to 1.85 in the case of cryogenic grinding, whereas, the ambient ground samples had a very low ratio (0.22 to 0.31). The content of sesqueterpenes in the volatile oil was between 0.43 and 0.63 mL/100g while the content of monoterpenes in the volatile oil was in the range of 0.61 to 1.55 mL/100g, in both cryogenic and ambient conditions. The loss of monoterpenes was high in ambient grinding, as their was a loss of volatile oil in terms of every monoterpene compound. Cryogenic grinding technique was found to be superior to ambient grinding in terms of monoterpenes retention in the powder.

4) Mill choking characteristic or blockage of grinder pins in ambient grinding was severe which reduced the grinding rate. Such a phenomenon was absent in cryogenic grinding as oils got solidified and grinding operation was unhindered, resulting in enhanced grinding rate or production capacity.

5) Vapourisation of volatile oils to the atmosphere was high during ambient grinding which caused health hazards to workers whereas vapourisation was minimum during cryogenic grinding.

6) Sensory studies indicated that cryogenically ground samples were distinctly high in top notes which represented freshness, and marginally high in basic notes also. Hence, the quality of cryogenically ground sample was better than the ambient ground samples.

7) Feed rate and product temperature of the samples during cryogenic grinding had significant effects on dependent variables viz., volatile oil, particle diameter, monoterpenes content and sesqueterpenes content, but not with energy expenditure.

8) The optimum cryogenic conditions for maximum volatile oil content and reasonable quantity of monoterpenes were 47 to 57 kg hr^{-1} of feed rate and -20 to -15 C of product temperature.

CHAPTER 5: SUMMARY AND CONCLUSIONS

CHAPTER 5

SUMMARY AND CONCLUSIONS

Spices are important agricultural commodities throughout the world due to their high unit price. This is particularly true for India, which produces, processes, and markets spices in domestic sector. India also exports a number of spices to earn a good amount of foreign exchange, and black pepper *(Piper nigrum* L.) is one of the major spices being exported. Black pepper is a common spice produced in oriental countries but is used worldwide for its characteristic pungent flavour, aroma and taste. The demand for value added products viz., powders, volatile oils and oleoresins has been increasing every year. It is, therefore, necessary to give due attention to this commodity with particular reference to processing, quality aspects and value addition.

Spices are ground for obtaining value-added products like powders, pastes, oleoresins and volatile oils. Grinding facilitates the release of aroma and flavour components, and aids in improved and uniform mixing with food materials during preparation. Grinding or size reduction is an important step in spice processing as it leads to losses of volatile oil and aroma present in them. During grinding, the mill as well as the ground product get heated up due to dissipation of mechanical energy. The temperature of the ground spice may rise to as high as 95 C. Hence, such high temperature leads to considerable loss of aroma and flavour components in spice volatile oil for which they are valued. A spice with low flavour and aroma fetches poor return to the processor. Therefore, the challenge is to find an appropriate method to retain these components. Besides, spices with high fat and fibre contents are difficult to grind. **In** a large scale operation where grinding has to be conducted continuously, gumming of grinder walls and sieves results in frequent shut-off of the mill for cleaning purposes. This reduces the production capacity with simultaneous increase in the cost of processing.

It is thus desirable to practice grinding at a low temperature. Chilling and freezing are the possible ways to achieve a product with maximum possible retention of volatile oil components in the powder. With the increasing use of cryogens, particularly liquid nitrogen (LN_2), a few studies have been attempted on grinding of spices. The advantages of cryogenic grinding over ambient grinding system as per these reports include reduced loss of volatile oils and hence increased flavour strength, reduced oxidation of spice oils, increased grinding rate, and improved colour of the ground spices. Though a limited number of research investigations have been carried out on cryogenic size reduction of spices, literature on pilot or large scale grinding studies of spices is scanty. Spice processing industry is in need or an appropriate technology 1'01' the manufacture of improved quality products particularly for export purposes.

Keeping the status of the spice processing industries in mind, the present study was initiated on black pepper in view of its importance in world trade and in Indian context. The obj~ctives of the present research were (1) to determine the engineering properties of black pepper seeds related to size reduction operations, (2) to study the ambient grinding characteristics of black pepper, (3) to study the cryogenic grinding characteristics of black pepper at both laboratory and pilot scale, and to compare with ambient grinding technique. The results of these studies and the conclusions are mentioned briefly in the following sections.

Engineering properties

The engineering properties of black pepper such as size, shape, bulk density, angle of respose, flowability and uniaxial compression characteristics were determined at various moisture contents as these properties are important from the point of design of storage, processing and conveying systems. The study basically generated design data, relating to grinding and handling .of black pepper seeds.

The seeds of black pepper had a near spherical shape as reflected by roundness values (close to 1) and high sphericity values (close to 100%). Angle of respose of black pepper seeds was dependent on moisture content and was in the range of 35 to 48°. It was observed that an increase in the moisture content would increase the angle of repose but decrease the flowability, particularly when the moisture content was above 14%.

Compressive force is the most common force applied during grinding and hence uniaxial compression and failure characteristics were determined. Individual seeds of black pepper, subjected to uniaxial compression, showed two different zones (elastic and plastic behaviour) during compression. An increase in the linear strain limit but decrease in deformation modulus showed that black pepper seeds could be deformed to higher extent particularly at high moisture contents. The failure energy remained unaltered when the moisture content of black pepper was in the range of 11 and 17% (dry basis).

Ambient grinding

Ambient (or conventional) grinding is the commonly followed technique now in practice among the spice processing industries wherein material as well as the grinder gets heated up during operation which leads to significant loss in product quality. It is desirable that powder of black pepper shall have maximum volatile oil with higher percentage of monoterpenes after grinding which represent desirable freshness and strong peppery notes of powder.

Grinding characteristics at various feed rates using a commonly used grinding mill such as swing hammer mill were studied. The rise of product temperature, during grinding at different feed rates using a swing hammer mill, followed a polynomial of third order with grinding time. The product temperature reached a high temperature at lowest feed rate. The contents of volatile oil varied negatively with the product temperature at different feed rates. The loss of volatile oil due to grinding varied from 11.2 to 50.7% with respect to the control sample (hand pounding) in the range of selected feed rates. It also varied with both powder temperature and average particle size. Lower feed rate gave a powder of finer particle sizes and higher powder temperatures but highest loss of volatile oil. On the other hand, the high feed rate gave a powder with lower temperature and lower loss of volatile oil which is a desirable condition for grinding.

Grinding was also carried out employing different grinding mills viz., hammer (APEX) mill, plate (DIAF type) mill, plate mill and roller mill in addition to swing hammer mill. The grinding characteristics were compared with hand pounding technique. The results indicated that the quality of ground powder in terms of volatile oil content depended on the type of mill employed, the product temperature and the average particle size of the powder. Among these mills, hand pounding (control sample) and roller mill showed no increase in temperature during grinding. The rise in temperature was highest for plate mill though it could produce the finest particles with geometric mean particle diameter of 0.16 mm with very low content of volatile oil. The finer the particle size of powder the higher was the temperature of ground powder measured at the mill's outlet at steady condition, and obviously the finer the particle size the higher was the energy expenditure. Monoterpenes were sensitive to grinding temperatures and their volatility increased with an increase in grinding temperature. The overall content of sesqueterpenes in the oil samples obtained from all the mills was fairly constant and it did not depend on the type of mill. Plate (DIAF) mill was found to be better in terms of high content of both volatile oil and content of monoterpenes which were desirable product attributes.

Grinding was also carried out to different range of particle sizes (geometric average particle sizes of 0.14 to 2.10 mm) as volatile oil content of powder depended on the particle size. The results indicated that the contents of volatile oil of samples having various particle sizes at the end of distillation were 1.48 to 2.92 mL/I00g. The particle mean diameter of about 0.7 mm was optimum which gave the desirable highest volatile oil content. The time for volatile oil distillation of fine to coarse powdered samples varied from 180 to 390 min, respectively indicating that the finer were the powder particles the faster was the distillation. The gas chromatographic analysis of volatile oil showed that higher ratio of monoterpenes to sesqueterpenes was present in coarse particles, which gave a very strong peppery note. Finer particle sizes contained volatile oil that gave spicy, sweet and flowery notes. The content of sesqueterpenes varied marginally (0.5 to 0.7 mL/I00g) as compared to the content of monoterpenes, which varied between 0.5 and 2.1 mL/100g for the range of particle sizes studied. However, the physical properties viz., specific gravity, refractive index and optimal rotation of volatile oils of samples obtained for different particles sizes were constant.

In brief, during ambient grinding, the contents of volatile oil of the spice powder varied negatively with the product temperature at different feed rates. When different mills with varied grinding capacity were used, contents of volatile oil depended on product temperature, particle size and also on the type of mill. Grinding to a particle size of about 0.70 mm was optimum for highest content of volatile oil in the powder. As far as the quality of volatile oil was concerned, the monoterpenes were sensitive to high temperature but the sesqueterpenes were not much affected by high temperature.

Cryogenic grinding

Cryptogenic grinding of black pepper was carried out to study the grinding characteristics as well as to compare the quality of the ground powders with that of the samples obtained by ambient grinding. This study was divided into two aspects, viz., grinding at laboratory scale followed by pilot scale trials to generate data which is close to industrial situation.

The laboratory scale (200 g per batch) trials were conducted at four different feed material temperature conditions viz., high temperature, ambient, chilled and cryogenic (LN_2) temperatures. The results indicated that the particle size of black pepper powder ground by cryogenic method was the finest as compared to other three methods. The cryogenic and chilled temperature methods of grinding yielded similar quantities of volatile oil as compared to low quantities in ambient and high temperatures grinding methods. There was a gain of about 36% in the content of volatile oil by cryogenic grinding method as compared to high temperature grinding method; the latter had a product temperature of 62 C. Chilled water technique was not adequate to markedly reduce the temperature rise during grinding of the product. Gas chromatographic analysis also showed that in cryogenic grinding technique, the contents of monoterpenes was higher compared to those obtained by the other methods. The content of sesqueterpenes was fairly similar in all four grinding methods. Cryogenic grinding technique emerged as the most desirable technique during laboratory scale experimentation.

The trials on pilot scale grinding (4 kg/batch) indicated that the control sample in ambient grinding reached product temperatures of 86 and 53 C at the feed rates of 15 and 35 kg hr^{-1}, respectively indicating that low feed rate would give higher temperature which would be undesirable. The product temperature was controlled and maintained at a range of -15 to -60 C using liquid nitrogen, and the feed rate were in the range of 7 to 60 kg hr^{-1} as per the experimental design. The average volatile oil content in case of cryogenic grinding was 1.7 mL/100g whereas in ambient grinding it was only 0.9 mL/I00g. The loss of volatile oil in the case of ambient grinding was about 50% as compared to cryogenic grinding.

The gas chromatographic analysis of volatile oil indicated that the ratio of monoterpenes to sequeterpenes varied from 1.35 to 1.85 in the case of cryogenic grinding which is desirable, whereas, the ambient ground samples had a very low ratio (0.22 to 0.31). The loss of monoterpenes was high in ambient grinding, as there was a loss of volatile oil in terms of every monoterpene'compound. Cryogenic grinding technique was found to be superior to ambient grinding in terms of content of monoterpenes in the powder. It may be mentioned here that monoterpenes provided the freshness, aroma and body to the volatile oil with a strong peppery note whereas sesquiterpenes gave the spicy note. Hence, it is desirable to have more monoterpenes in the volatile oil to achieve a good quality product. This quality was established in both laboratory scale and pilot scale cryogenic grinding operations. In pilot scale grinding, the loss of volatile oil in ambient grinding was as high as 50% as compared to cryogenic grinding. Mill choking was severe in ambient grinding which reduced the grinding rate due to frequent stoppage of mill for maintenance. Such phenomenon was absent in case of cryogenic grinding as oils got solidified and grinding operation was unhindered which resulted in enhanced grinding rate which meant higher production capacity. Ambient grinding resulted in higher loss of volatile oils to atmosphere in the form of vapours, due to higher grinding temperature, which may cause health hazards (viz., ear, nose and throat diseases) to mill workers. This vapourisation was minimum during cryogenic grinding as the vapours of volatile oil were retained within the product. Sensory studies indicated that cryogenically ground samples were distinctly high in top notes which represented freshness, and marginally high 'in basic notes with very less undesirable defective notes. Hence, the quality of cryogenically ground sample was better than the ambient ground samples.

The effect of grinding variables (feed rate and product temperature of the samples during cryogenic grinding) on grinding and product characteristics had been determined employing response surface methodology. The experimental results were fitted to second order polynomials. These polynomials were able to relate the dependent variables viz., volatile oil, particle diameter, contents of monoterpenes and sesqueterpenes but failed to do so for energy expenditure. The optimum cryogenic grinding conditions considering maximum volatile oil content and reasonably high quantity of monoterpenes were 47 to 57 kg hr^{-1} of feed rate and -20 to -15 C of product temperature.

In brief, it can be mentioned that the present research generated data on engmeenng properties of black pepper related to size and shape, angle of respose, flowability, and compression characteristics at various moisture contents. These properties are important from the points of design of storage, processing and conveying systems, and for design of suitable grinding system for black pepper seeds. Data were also generated for grinding of black pepper employing ambient and cryogenic grinding systems. The superiority of the latter system was established and grinding conditions were optimised considering the important quality characteristics. This research clearly proved that cryogenic grinding improved the content of volatile oil in the powder by increasing the flavour strength to almost double. It has also increased the grinding rate by reducing choking of mills and grinding surfaces. It is hoped that cryogenic grinding technology would be widely used by the spice processing industries to enhance the quality of the ground product. It is also desirable that similar type of data would be generated for other heat sensitive spices in near future. A beginning has been made here.

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