CRYOGENIC PREPARATION OF *KULFI* USING DRY MIX AND ANALYSIS OF ITS HEAT TRANSFER AND MELTING CHARACTERISTICS

THESIS SUBMITTED TO THE

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IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR THE AWARD OF DEGREE OF

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IN

DAIRY ENGINEERING

BY

MUKHESHKUMAR G H

B. TECH. (DAIRY TECHNOLOGY)

DAIRY ENGINEERING SECTION
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APPROVED BY

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This is to certify that the thesis entitled, **"CRYOGENIC PREPARATION OF *KULFI* USING DRY MIX AND ANALYSIS OF ITS HEAT TRANSFER AND MELTING CHARACTERISTICS",** submitted by **MUKHESHKUMAR G. H.** towards the partial fulfillment for the award of the degree of **MASTER OF TECHNOLOGY** in **DAIRY ENGINEERING** of the **ICAR-NATIONAL DAIRY RESEARCH INSTITUTE (DEEMED UNIVERSITY)**, **KARNAL (HARYANA), INDIA**, is a bonafide research work carried out by him under my guidance, and no part of the thesis has been submitted for any other degree or diploma.

Dr. P. Heartwin Amaladhas
Major Advisor
(Guide)

DEDICATED
TO MY FAMILY
& FRIENDS

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ABSTRACT

Kulfi is a typical indigenous frozen dessert sold in many parts of the country. It is produced by freezing the mix of concentrated milk and sugar. It differs from ice cream in that it contains practically no air. Freezing of milk concentrate is one of the most important operations in the preparation of *kulfi*. Both quality and palatability of the final product depend upon the freezing technique. In traditional method, freezing is carried out by immersing the *kulfi* moulds in ice salt mixture or in deep freezers. In cryogenic freezing, liquid nitrogen (LN_2) is commonly used. In this study, *kulfi* was prepared from both concentrated milk and from spray-dried dry mix. The instant dry mix for *kulfi* was prepared by spray-drying of concentrated milk in a pilot-scale spray dryer at inlet drying air temperature of 185°C. From milk concentrated to 40% total solids (TS), *kulfi* was prepared by both conventional deep freeze and cryogenic methods. Similarly, the dry mix was reconstituted to the same TS content and the concentrate was frozen by cryogenic method. Deep freezing was done at -30°C and while cryogenic freezing was done using LN_2 at -173°C. The heat transfer coefficient during freezing was determined using one-dimensional transient heat conduction equation. The freezing times were determined using four established models, and their predictive performance was compared with experimental data. The physico-chemical, melting, textural and sensory properties were also analysed. The freezing curve of cryogenically frozen *kulfi* differed considerably from that of deep frozen product. Thermo-physical properties such as thermal conductivity, density, specific heat and thermal diffusivity varied widely above and below freezing due to phase change. Freezing was achieved in 267 min in deep freeze method while it reduced to just 185-190 s in cryogenic method. Cryogenic freezing was approximately 85 times faster than conventional deep freezing. The heat transfer coefficients for cryogenic freezing of *kulfi* prepared from condensed milk and dry mix concentrate were 210.57 and 216.84 W/m^2 K, respectively as compared to 8.33 W/m^2 K for deep freeze method. Amongst the freezing models evaluated, the Pham's model gave the best prediction of freezing time. The melting rate of *kulfi* frozen by deep freeze method was higher as compared to those frozen using LN_2. Melting rate of *kulfi* prepared from milk concentrate and frozen in deep freezer was 13.7 mL/15 min, while for cryogenic freezing of *kulfi* from milk concentrate, it was 12.1 mL/15 min. The similar value for cryogenic freezing of *kulfi* from dry mix was 12.3 mL/15 min. The melting curve of *kulfi* prepared by cryogenic and deep freezing methods differed considerably. The hardness of *kulfi* measured using Warner-Bratzler shear test was higher in deep frozen *kulfi* as compared to those frozen using LN_2. *Kulfi* prepared from dry mix and frozen using LN_2 had the least hardness. Similarly, *kulfi* prepared from dry mix and frozen using LN_2 ranked the highest in sensory evaluation using fuzzy-logic. The current work on cryogenic freezing of *kulfi* could be used in place of conventional freezing for both small-scale and large-scale operations. Using LN_2, *kulfi* could be frozen very rapidly, maintaining superior quality in terms of melting characteristics and hardness. *Kulfi* dry mix also could be used for production of *kulfi* with acceptable quality.

सारांश

कुल्फी भारत के कई भागों में बेंचा जाने वाला एक प्रचलित जमा हुआ मिठाई है। यह सान्द्रित दूध और शर्करा के मिश्रण के जमीकरण द्वारा बनाया जाता है। इसमें तथा आईसक्रीम में इतना ही अन्तर है कि इसमें वायु संमिश्रित नहीं किया जाता। कुल्फी बनाने के दौरान सान्द्रित दूध को जमाना अति महत्त्वपूर्ण क्रियाओं में से एक है। इसकी गुणवत्ता व स्वाद जमाने की विधि पर ही आश्रित होती है। पारम्परिक तरीके से कुल्फी को बर्फ–नमक के मिश्रण में या डीप फ्रिज में डुबाकर जमाया जाता है। क्रायोजेनिक जमीकरण विधि में सामान्यतः द्रवीभूत नाइट्रोजन (LN_2) प्रयोग किया जाता है। इस अध्ययन में, कुल्फी सान्द्रित दूध व स्प्रे–ड्राइड शुष्क मिश्रण दोनों से बनाया गया। कुल्फी का क्षणिक शुष्क मिश्रण प्रायोगिक स्तर के स्प्रे–ड्रायर में सान्द्रित दूध के स्प्रे–ड्रायिंग द्वारा बनाया गया, जिसमें प्रवेशित शुष्ककारी वायु का तापमान 185°C था। 40% कुल ठोस (TS) तक सान्द्रित दूध द्वारा कुल्फी का निर्माण डीप फ्रिज तथा क्रायोजेनिक जमीकरण दानों विधियों द्वारा किया गया। इसी प्रकार शुष्क मिश्रण को भी समान कुल ठोस की मात्रा तक जलीकृत कर क्रायोजेनिक जमीकरण विधि द्वारा जमाया गया। डीप फ्रिज का तापमान -30°C था, जबकि LN_2 के द्वारा क्रायोजेनिक जमीकरण -173°C पर किया गया। जमीकरण के दौरान ऊष्मा–स्थानांतरण गुणांक की गणना एक वीमीय क्षणिक ऊष्मा संवहन समीकरण द्वारा किया गया। जामन काल की गणना चार सुस्थापित मॉडलों के द्वारा किया गया तथा उनकी अनुमानित क्षमता की तुलना प्रायोगिक आंकड़ों के साथ की गयी। भौतिक–रासायनिक, गलन, आकृतिय व संवेदी गुणवत्ता संबंधी गुणों का भी अध्ययन किया गया। क्रायोजेनिक जमीकृत कुल्फी का हिमीय वक्र डीप फ्रिज में बने कुल्फी के हिमीय वक्र से सर्वथा भिन्न पाया गया। पदार्थ की अवस्था परिवर्तन के कारण हिमांक के नीचे व ऊपर ऊष्मा–भौतिकीय गुण जैसे ऊष्मीय चालकता, घनत्त्व, विशिष्ट ऊष्मा व ऊष्मीय विसरता में बहुत परिवर्तन पाया गया। डीप फ्रिज में जामन काल 267 मिनट था, जबकि क्रायोजेनिक जमीकरण विधि में यह घटकर 185–190 सेकेंड हो गया। क्रायोजेनिक जमीकरण विधि, डीप फ्रिज जमीकरण विधि की तुलना में लगभग 85 गुना तीव्र पायी गयी। क्रायोजेनिक जमीकरण के दौरान सान्द्रित दूध व सान्द्र शुष्क मिश्रण के ऊष्मा–स्थानांतरण गुणांक के मान क्रमशः 210.57 तथा 216.84 $W/m^2 K$ पाये गये, जो डीप फ्रिज जमीकरण विधि में 8.33 $W/m^2 K$ ही पाया गया। सभी फ्रिजिंग मॉडलों में से फाम मॉडल के द्वारा जामन काल का सर्वोत्तम निर्धारण हो सका। डीप फ्रिज जमीकरण विधि द्वारा बने हुये कुल्फी का गलन दर LN_2 द्वारा हिमीकृत कुल्फी के गलन दर से अधिक पाया गया। डीप फ्रिज जमीकरण विधि में सान्द्रित दूध द्वारा निर्मित कुल्फी का गलन दर 13.7 mL/15 min पाया गया, जबकि क्रायोजेनिक जमीकरण विधि में सान्द्रित दूध द्वारा निर्मित कुल्फी का गलन दर 12.1 mL/15 min पाया गया। यह मान क्रायोजेनिक जमीकरण विधि में सान्द्र शुष्क मिश्रण द्वारा निर्मित कुल्फी के लिये 12.3 mL/15 min पाया गया। वर्नर–ब्राट्ज्लर शियर जांच के द्वारा मापी गयी डीप फ्रिज जमीकृत कुल्फी की कठोरता LN_2 जमीकृत कुल्फी की तुलना में अधिक पायी गयी। सान्द्र शुष्क मिश्रण द्वारा निर्मित LN_2 जमीकृत कुल्फी की कठोरता न्यूनत्तम पायी गयी। इसी प्रकार फज्जी–तर्क–संवेदी–मूल्यांकन में भी सान्द्र शुष्क मिश्रण द्वारा निर्मित LN_2 जमीकृत कुल्फी को सर्वाधिक अंक प्राप्त हुये। कुल्फी के क्रायोजेनिक जमीकरण पर आधारित यह कार्य लघु व कुटीर दोनों तरह के उद्योगों में पारम्परिक जमीकरण के स्थान पर प्रयुक्त हो सकता है। LN_2 के प्रयोग द्वारा कुल्फी का हिमीयकरण अति शीघ्रता से किया जा सकता है, जिसकी गलन व कठोरता संबंधी गुण भी बेहतर होंगे। कुल्फी का शुष्क मिश्रण भी स्वीकार्य गुणवत्ता के कुल्फी के निर्माण में प्रयोग किया जा सकता है।

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS AND ABBREVIATIONS

Δ	Delta
α	Alpha
ρ	Rho
∞	Infinity
μ	Mu
ε	Epsilon
β	Beta
&	And
@	At
<	Lesser than
>	Greater than
%	Per cent
θ	Theta
°C	Degree centigrade
AOAC	Association of Official Analytical Chemists
ANOVA	Analysis of Variance
BIS	Bureau of Indian Standards
CIELAB	Commission Internationale de L'Eclairage
C_p	Specific heat
cP	Centi poise
Eq.	Equation
Fig.	Figure
FSSAI	Food Safety and Standards Authority of India

g	Gram
h	Heat transfer coefficient
K	Kelvin
k	Thermal conductivity
kg	Kilogram
kJ	Kilo Joule
kPa	Kilo Pascal
L	Litre
LN_2	Liquid nitrogen
min	Minute
mL	Milliliter
mm	Millimeter
MSNF	Milk-solids-not-fat
T	Temperature
t	Time
TS	Total solids
TPA	Texture profile analysis
TR	Temperature ratio
vs.	Versus
w/w	Weight by weight

I INTRODUCTION

In the past few decades, India has achieved tremendous progress in the field of dairy development (Joseph, 2000). The country ranks first with the milk production of 155.5 million tonnes in 2015-16, accounting for 18.5% of the world's output. This increase was from 146.3 million tonnes during 2014-15, registering a growth rate of 6.3%. The Indian dairy industry is thus witnessing a record growth, and is likely to sustain in the next few years. The per capita availability of milk has therefore increased from 176 g per day in 1990-91 to 322 g per day in 2014-15. It is more than the world's average of 294 g per day (NDDB, 2015-16). This is not a small achievement considering the factor that we were one of the largest importers of dairy products during the 1950s and 1960s, importing over 40% of milk solids of the total throughput. The Indian dairy sector contributes about 25% of the agricultural gross domestic product (GDP).

Incidentally, we are also the largest consumer of dairy products, utilizing more than 90% of our own milk production internally. Milk and milk products are major sources of nutrition to millions of people, and are the only acceptable source of animal protein for large vegetarian segment of Indian population. With the rising population and purchasing power, the demand for milk and milk products may even exceed the anticipated 200 million tonnes by the year 2020.

To minimize the seasonal impact on suppliers and buyers, conversion of milk to dairy powders and other products is growing at a faster rate. *Kulfi* is a typical indigenous frozen dessert sold in many parts of the country. It is mainly made by small milk vendors, *halwais*, sweet makers, etc., with the demand peaking in the summer season. Manufacturing of *kulfi* helps to develop small-scale industry and generate sizeable employment and income. Value addition of milk and milk products is necessary for export and to penetrate second-tier markets.

Kulfi differs from ice cream in that it practically contains no air. It is manufactured by mixing calculated amounts of ingredients such as whole milk, cream,

skim milk powder, sugar and stabilizers to give the desired total solids level. Thus, *kulfi* consists of ice crystals, some air bubbles and fat droplets in a viscous matrix of sugars, polysaccharides and milk proteins. The process of preparation of *kulfi* is tedious and requires considerable time for condensation of milk. If *kulfi* could be made from instant dry mix, the process time would reduce considerably. The instant dry mix could be produced by spray drying, which would then be reconstituted to get the required level of total solids (TS) before freezing of the mix. Milk and dairy powders are very often used for the preparation of many indigenous dairy products. These dry powders offer a lot of convenience during transportation and handling, processing and storage.

Freezing is one of the most important operations in the preparation of *kulfi*. Both quality and palatability of the final product depend upon the freezing technique. In traditional method, *kulfi* is frozen by immersing the cone in ice-salt mixtures in the ratio of 4:1. Freezing of foods involves three stages. In the first stage, the product is cooled from the initial temperature to the beginning of freezing temperature. In the next stage, phase change occurs, and the liquid water in the food is turned into ice. In the third stage, the product is cooled until the required freezing temperature is reached. Therefore, freezing is a complex process, and analysis of heat transfer during freezing becomes very important. The thermo-physical properties such as density, thermal conductivity, specific heat and thermal diffusivity influence the freezing process, and therefore, they need to be determined as a function of temperature in order to understand the freezing phenomenon of that specific food. The convectional heat transfer coefficient at the surface affects the freezing time and rate. It could be determined using two approaches namely lumped thermal capacity model and one-dimensional transient heat conduction model depending upon the prevailing conditions during freezing.

Traditionally, the milk concentrate for *kulfi* is filled in moulds, and the mix is hardened at -20ºC overnight. Alternatively, *kulfi* milk concentrate is frozen in deep freezer for a period of 4 to 6 h. Both these processes involved long freezing times, which could lead to large size unpalatable ice crystals in the frozen *kulfi*. The long freezing times make it difficult to serve order-to-make *kulfi* in fast food chains and ice cream parlours, meeting the customized taste and preference of consumers.

Cryogenic freezing offers freshly-prepared product to consumer and helps to provide customized options. The present study was conceptualized with a view to develop the technology for cryogenic freezing of *kulfi* both from milk concentrate and instant dry mix. The *kulfi* on preparation would have the characteristic flavour and texture comparable to that of traditionally frozen product. In cryogenic freezing, liquefied gases are used for freezing of foods in direct or indirect contact with the food. Normally, the food is exposed to an atmosphere below -60ºC using liquid nitrogen (LN_2) or its vapours. LN_2, with a boiling point of -196°C at atmospheric pressure, provides rapid freezing of *kulfi*.

Kulfi is an extremely complex, intricate and delicate food. The texture we perceive when *kulfi* is eaten is the sensory manifestation of its microstructure. Thus, the science of *kulfi* consists of understanding its ingredients, processing, texture, and more importantly, the intricacies between them.

LN_2 provides a great, dazzling, magical and special effect. The secret to the creamy *kulfi* is all in the rapid freezing of the mixture. The LN_2 causes the fat and the water particles to stay very small because the very cold temperature promotes nucleation-dominated freezing of the milk concentrate. Customer satisfaction is also the highest because each *kulfi* could be made specifically for the consumer, and the entire process happens right before his eyes. The customer can have his highly customized *kulfi* creation, which meet all his tastes, preferences and allergies. It gives the consumer the freedom to do anything with it.

The cryogenically frozen *kulfi* will be better in terms of microbiological quality. Some of the other perceived benefits of cryogenic freezing include rapid freezing times, reduction in dehydration and improved texture of products due to the growth of small ice crystals. The rapid formation of small ice crystal greatly reduces the damage caused by cell rupture, preserving colour, texture, flavour, and nutritional value. The principle is simple that the faster the *kulfi* is frozen, the creamier it will be. Smaller ice crystals make a smoother and luscious texture. The longer it takes to freeze, the larger the ice crystals

grow, the grainier the *kulfi* will be in texture. The quality of the dairy product equates survival and growth of the dairy business.

Properties that are important in *kulfi* are physico-chemical, melting, textural and sensory qualities. Physico-chemical qualities include TS, moisture, fat, protein, ash, and carbohydrates contents. Similarly, the melting properties are important in characterising *kulfi*, which includes melting rate and melting curve. Finally, the textural and sensory properties of the cryogenically frozen *kulfi* are very important for consumer acceptance of the product. In this study, the sensory qualities of *kulfi* were evaluated using fuzzy-logic approach.

Not much work has been done on cryogenic freezing of *kulfi*. Also, very limited information is available on preparation of *kulfi* from dry mix. Hence, this work has been proposed with the following objectives.

- Analyze the heat transfer characteristics of cryogenically-prepared *kulfi* using dry mix.
- Determine the physico-chemical, melting, textural and sensorial properties of cryogenically frozen *kulfi*.

II REVIEW OF LITERATURE

In this Chapter, the literature related to objectives of the current study is reviewed under the following heads:

- *Kulfi* and its significance
- Definition and standards of *kulfi*
- Methods of preparation of *kulfi*
- Chemical composition of *kulfi*
- Constituents of *kulfi*
- Processing conditions affecting quality of *kulfi*
- Physico-chemical properties of *kulfi*
- Freezing
- Cryogenic freezing of foods
- Prediction of freezing time
- Thermo-physical properties of foods influencing freezing
- Heat transfer coefficient during freezing

2.1 *Kulfi* and its Significance

Kulfi is a typical indigenous frozen dessert sold in many parts of the country. The word '*kulfi'* originated from the then Hindustani word '*kulaf*' which meant a 'lock' or a 'container' that has to be unlocked. *Kulfi* is prepared by boiling milk in a large vessel, followed by addition of sugar, and concentrating the contents to half its original volume (De, 1991). The partially-desiccated milk may be added with nuts and flavours, filled in metal or plastic containers and frozen by using ice salt mixtures. *Kulfi* is also known as *Malai kulfi* or Malai-*ka*-*burf*. It differs from ice cream in that it contains no air. Mostly *kulfi* is prepared by *halwais* and small scale manufacturers. Some organized dairies have also taken up production and marketing of *kulfi* in recent years (Aneja *et al.*, 2002). *Kulfi* is thus a highly palatable and nutritious frozen dairy product, and is widely consumed during summer seasons (Rao and Prakash, 2004).

2.2 Definition and Standards

2.2.1 Food Safety and Standards Act (2006) definition

"Ice cream", "*Kulfi*", "Chocolate ice cream" or "Softy ice cream" is the product obtained by freezing pasteurized mix prepared from milk and/ or other products derived from milk. *Kulfi* may be added with sweetening agents, fruit and fruit products, coffee, cocoa, chocolate, condiments, spices, ginger and nuts. It may also contain bakery products such as cake or cookies as a separate layer or coating. The milk concentrate with other ingredients may be frozen to hard or soft consistency and shall have pleasant taste and odour, free from off flavours and rancidity. The type of *kulfi* shall be clearly indicated on the label or otherwise the standard for ice cream shall apply. The standards for *kulfi* are given in Table 2.1.

Table 2.1. Food Safety and Standards Act (2006) (FSSAI) Standards for *kulfi*

Requirement	*Kulfi*	Medium-fat *kulfi*	Low-fat *kulfi*
Total solids	Not less than 36.0%	Not less than 30.0%	Not less than 26.0%
Milk fat	Not less than 10.0%	More than 2.5% but less than 10.0%	Not more than 2.5%
Milk protein (Nx6.38)	Not less than 3.5%	Not less than 3.5%	Not less than 3.0%

The standards given by Bureau of Indian Standards (BIS, 1983) for *kulfi* are given in Table 2.2, which include physico-chemical, microbial and indicator standards for normal and special kulfi containing fruits, nuts & chocolate.

Table 2.2. BIS Standards for *kulfi*

Characteristic	Requirement	
	Normal *kulfi*	Fruits, nuts and chocolate *kulfi*
Total solids, % by mass (min)	35.0	30.0
Milk fat, % by mass (min)	8.0	6.0
Protein, % by mass (min)	3.5	3.5
Acidity, % by mass (max) (as lactic acid)	0.3	0.3
Sucrose, % by mass (min)	13.0	13.0
Standard plate count (max) per gram	2,50,000	2,50,000
Coliform count per gram (max)	100	100
Phosphatase test of milk	Negative	Negative
Presence of starch	Negative	Negative

2.3 Methods of Preparation of *Kulfi*

2.3.1 Traditional method of preparation of *kulfi*

Milk is condensed without standardisation in an open pan. Sugar is added in the final stages of condensation of milk. Sometimes, the milk is added with nuts, colours and flavours. The concentrate is then filled into moulds of galvanised iron, plastic or aluminium, and the moulds are immersed in large earthen pots containing a mixture of ice and salt in the ratio of 1:1 (Warner, 1976).

2.3.2 Improved and standardised method of preparation of *kulfi*

Salooja and Balachandran (1982) used cow milk that was standardised to 3.5% fat and 8.5% SNF for preparation of *kulfi*. Ice and coarse salt in the ratio of 4:1 were used as freezing mixture. Slow heating of milk was followed to avoid burnt particles. The authors concluded that *kulfi* having 26% total milk solids yielded better body & texture and

overall quality. It was also reported that frozen *kulfi* had only 7.9% fat, which however, was below the standards of 10% fat.

Yerriswamy *et al.* (1983) used whole milk, cream and skim milk powder (SMP) for production of *kulfi*. The *kulfi* obtained had a composition of 13-14% milk fat, 10-12% milk solids-not-fat (MSNF) and 37-40% TS.

Ashokraju *et al.* (1989) used fresh milk and milk standardised to 5% fat and 9% SNF milk for the preparation of *kulfi*. The product was sweetened with 10% sucrose on weight basis of milk. After concentration to final TS level 35, 48 and 72% in an open pan, three samples were prepared namely, one without any stabilizer, the second one with addition of 3% starch and the third one with 0.15% sodium alginate. These samples were kept at 40°C for 6 h, filled in moulds of 80 mL volume and frozen using ice-salt mixtures. *Kulfi* with 48% TS and added with 3% starch scored the highest for body & texture and overall quality.

Ghosh (1991) developed a process to make *kulfi* with composition of 11% milk fat, 16% MSNF, 15% sugar and 0.2% Isabgol husk. The mix was homogenised at pressure of 6860/3430 kPa and heat-treated at 100°C for 10 min and cooled to 4°C in a tubular heat exchanger. The concentrated milk was filled into moulds and frozen in the brine tank at -20°C with continuous stirring until the product was frozen.

Nagajjanavar *et al.* (2017) used vacuum pan condensation for preparation of *kulfi* concentrate. A single effect evaporator with water evaporation capacity of 20 L/h was used for concentrating the milk. Standardised milk having 5% fat and 8.5% SNF was concentrated to 2:1 ratio of solids. Sugar was added at 13% by weight to the mix, and the mix was frozen by immersion freezing in liquid brine solution.

2.4 Chemical Composition of *Kulfi*

The chemical composition of *kulfi* varies from place to place. Several researchers have analysed the chemical composition, and the values obtained are summarized in Table 2.3.

Table 2.3. Chemical composition of *kulfi*

Method	Source of sample	Total solids (%)	Fat (%)	MSNF (%)	Protein (%)	Milk solids (%)	Sucrose (%)
Rao *et al.* (1979)	Market	30.1-49.3	3.4-6.5	-	2.1-3.4	-	13.0-20.0
Salooja (1979)	Experimental	39.0	10.7	15.2	-	26	13.0
Salooja and Balachandran (1982)	Experimental	39	7.9	18.3	-	26	13.0
Yerriswamy *et al.* (1983)	Market	36.0-41.4	3.5-11.0	10.5-10.7	2.5-4.9	-	-
Yerriswamy *et al.* (1983)	Experimental	38.2-40.2	13.0-14.0	9.9-12.1	4.6-5.0	-	-
Ghosh (1991)	Market	33.95-49.13	6.56-13.87	17-18	4.33-6.87	-	13.87-20.46
Ravindran (2003)	Experimental	39.84	9.98	17.04	-	-	12.82
Giri *et al.* (2014)	Experimental	40.2	10	-	6.4	-	-

2.5 Constituents of *Kulfi*

Kulfi is a complex mixture of dairy and non-dairy ingredients. The dairy ingredients include milk fat and MSNF as basic ingredients. Non-dairy ingredients include sweetener, stabilizers, colour and flavouring agents, fruits, nuts and other additives (Ghosh, 1991).

Milk fat is a source of fat soluble vitamins, improves body and texture of *kulfi*, provides desirable creamy rich flavour, mellowness, smooth texture and contributes to the melting resistance of the product. Sources of milk fat are fresh milk, fresh cream or khoa (Aneja, 1992). Various researchers came with different values regarding the optimum fat level in *kulfi.* Salooja and Balachandran (1982) reported 7.9% milk fat in *kulfi*, which contained 26% total milk solids, but it was well below the standards of 10%. Yerriswamy *et al.* (1983) reported that milk fat in the range of 13-14 % would produce superior product. Ghosh (1991) standardised the fat content to 11% to get good quality *kulfi*. Milk fat should be kept at optimum level from the economic point of view but the proportion should meet the legal standards (Nigam *et al*., 2016).

MSNF is the source of proteins, minerals and vitamins. It improves the texture, and gives better body to the product. MSNF, in right proportions, will help in producing desirable body, and prevents the product from being buttery in texture. The proteins in MSNF give compact and smooth body to *kulfi*, and prevent coarse texture and formation of weak structure (Ghosh, 1991). Salooja and Balachandran (1982) suggested that 18.3% MSNF was required to achieve good body and texture. Higher MSNF (20.5% or above) led to heavy and soggy body while lower MSNF (16.2% or below) resulted in a weak and crumbly body. In contrast, Yerriswamy *et al.* (1983) claimed that 9.9–12.2% MSNF gave superior body and texture in *kulfi*. Ghosh (1991) recommended the use of 16% MSNF to get good quality *kulfi.*

Sugar improves the palatability and adds total solids to *kulfi*. It is the most widely used sweetener in the food industry. A satisfactory level of sugar in *kulfi* was reported as 13% on the basis of condensed milk by Salooja and Balachandran (1982) while Yerriswamy *et al.* (1983) and Ghosh (1991) suggested as high as 15% sugar content. Giri

et al. (2014) prepared *kulfi* by replacing 50% of sugar by stevia, and the authors reported that more than 50% replacement of sugar with stevia led to bitterness and lack of brownish appearance. Giri *et al.* (2013) produced *kulfi* by replacing 50 % of sugar with stevia and the product was added with whey protein concentrate (WPC) to enhance the TS content.

The purpose of adding stabilizer in *kulfi* is to produce a rich and smooth body and texture, retard ice crystal formation during freezing, and provide resistance to melting. Body or consistency of *kulfi* is highly related to the mechanical strength of milk concentrate and its resistance to melting. Heat shock resistance is dependent on the nature and concentration of the stabilizer system used (Aneja, 1992). Sodium alginate is the most widely used stabilizer. Ashokraju *et al.* (1989) recommended the use of 0.15% of sodium alginate in *kulfi*. However, Rao and Prakash (2004) used 0.3% of food grade gelatin as a stabilizer in the preparation of *kulfi*.

2.6 Processing Conditions affecting the Quality of *Kulfi*

Processing conditions during manufacture will influence the quality of *kulfi* concentrate as well as the final product obtained. Major processing operations that affect the quality of *kulfi* include heat treatment, homogenization, freezing and hardening.

2.6.1 Heat treatment

Proper heat treatment of milk is necessary to destroy all pathogenic microorganisms, and to ensure product safety to the consumers. Heating of milk also improves the flavour and shelf life of the product (Ghosh, 1991). Yerriswamy *et al.* (1984) reported that *kulfi* concentrate containing 37-40% TS and heat-treated at 121°C for 15 min produced good quality *kulfi* in terms of organoleptic properties and keeping quality. The shelf life of *kulfi* concentrate in sealed bottles was more than 3 months at room temperature. However, heat treatment of concentrated milk at 100°C for more than 5 min in a tubular heat exchanger led to increase in acidity values and decreased pH (Ghosh, 1991).

2.6.2 Homogenization

The main purpose of homogenization is to make a stable, smooth and uniform suspension of fat by reducing the size of fat globules to less than 2 µm. When a mix is properly homogenized, the fat will not rise and form a cream layer (Goff and Hartel, 2013). Homogenization helps in imparting creamy flavour and greater digestibility of fat (Arbuckle, 1986).

2.7 Physico-chemical Properties of *Kulfi*

The constituents of milk exert influence on the physico-chemical properties of *kulfi*. These properties are altered because of the changes in the relative proportions of the constituents and the treatment given to the concentrate (Ghosh, 1991).

2.7.1 Acidity and pH

The normal titratable acidity of condensed milks and powders varies with the percentage of MSNF and its composition. Increase in MSNF increased acidity but decreased the pH (Goff and Hartel, 2013). Salooja (1979) reported the average values of acidity of *kulfi* concentrate prepared with 17, 20, 23, 26 and 29 % MSNF as 0.187, 0.217, 0.236, 0.286 and 0.383, respectively with corresponding pH values of 6.62, 6.52, 6.50, 6.41 and 6.32. Sterilization of *kulfi* mix at 121°C was found to increase the titratable acidity and reduce the pH (Yerriswamy *et al.*, 1983). The normal acidity of *kulfi* concentrate was due to milk proteins and minerals, and the mean acidity of *kulfi* was found to increase slightly with fat content beyond 11% (Ghosh, 1991). Rao and Prakash (2004) reported higher values of acidity in *kulfi* inoculated with *Lactobacillus acidophilus.* The authors reported the acidity of probiotic *kulfi* as 0.37, 0.41 and 0.45% lactic acid for addition of cultures at 3, 4 and 5%, respectively as compared to 0.24% for control. Thus, addition of probiotic cultures was found to increase the acidity of *kulfi*.

2.7.2 Specific gravity

The specific gravity of *kulfi* concentrate varies with its composition. Increased concentrations of MSNF, sugars and stabilizers increased the specific gravity whereas increased fat content decreased the specific gravity of the concentrate. The reduction in

specific gravity due to fat content could be attributed to variations in the ratio of solid to liquid fat (Webb *et al.,* 1974). The specific gravity of *kulfi* concentrate also increased with the extent of heat treatment to milk (Ghosh, 1991). Giri *et al.* (2014) measured the specific gravity of *kulfi* concentrate as 1.098 g/mL for *kulfi* without sugar replacement against 1.086, 1.080 and 1.076 for the concentrate containing 50, 40 and 30% sugar and blended with 0.05, 0.06 and 0.07 % stevia, respectively. The authors also reported that addition of whey protein concentrate (WPC) increased the specific gravity of *kulfi* concentrate.

2.7.3 Viscosity

Viscosity is the resistance of liquid to flow. It is the internal friction which tends to resist the sliding of one layer of liquid over another. The mean values of viscosity of *kulfi* concentrate expressed as s/100 revolutions increased from 34.62 to 58.08 with increase in TS from 17 to 29% due to partial clumping of fat globules and increased levels of MSNF (Salooja, 1979). Yerriswamy *et al.* (1983) reported the viscosity of *kulfi* concentrate as 28.1-36.6 cP, and after sterilisation of the mix, it increased to 66.53-128.53 cP. High fat content increased the number of fat globules, which in turn contributed to viscosity due to clustering of fat globules (Abu-lehia, 1989). The viscosity of *kulfi* concentrate was found to increase with increasing fat content. The rate of increase was more when fat content increased from 11-13% (Ghosh, 1991).

2.7.4 Textural properties of *kulfi*

Kulfi is desired to have slightly granular texture, free from large-sized ice crystals. The highest score for texture was obtained for *kulfi* containing 26% TS (Salooja and Balachandran, 1982). The body and texture score of control *kulfi* was 7.4 and for 2, 3 and 4% WPC added *kulfi*, the scores increased to 7.70, 7.84 and 7.48, respectively (Giri *et al.,* 2013). At higher level of sugar replacement (60 and 70%), the body and texture scores decreased. This might be due to formation of larger proportion of ice crystals (Giri *et al.,* 2014). The body and texture score of *chhana*-based *kulfi* varied from 6.0 to 7.0 (Nigam *et al.,* 2016). *Kulfi* blended with ash gourd pulp at 5, 10 and 15% was analysed for body and

texture against the control. The body and texture scores were higher for normal *kulfi* as compared to *kulfi* added with ash gourd pulp (Dodake *et al.,* 2015).

2.7.5 Melting characteristics of *kulfi*

The melting rate of *kulfi* depends upon the TS content, composition and processing conditions. Salooja (1979) reported that the average melt down rate of *kulfi* (expressed in mL) for 15 min of collection time were 12.8, 13.2, 14.4 and 14.8 for samples containing 17, 20, 26 and 29% milk solids, respectively. The addition of sodium alginate to the mix increased the melt down time (Ashokraju *et al.,* 1989). Ghosh (1991) reported that different levels of Isabgol husk in *kulfi* also affected the melt down properties. Giri *et al.* (2014) reported the melting rate (mL/15min) of control *kulfi* as 18.1 against the values of 14.8, 12.4 and 12.2 for *kulfi* containing 50, 40 and 30% sugar and 0.05, 0.06 and 0.07% stevia, respectively. Higher levels of sugar replacement with stevia increased the melting rate of *kulfi.*

Ghosh (1991) reported that *kulfi* prepared from *kulfi* mix powder and stored for 5 months melted at a faster rate with a slight curdy meltdown. This was attributed the destabilisation of protein in dry mix, caused by medium heat treatment of milk. Different freezing methods were also found to have considerable influence on the melting rate of *kulfi.* Ghosh (1991) reported that the melting rates were 24.3-24.6, 23.9-24.2, 20.8-21.5 and 26.8-27.3 mL/30 min for *kulfi* prepared by traditional method, brine tank, batch freezer and direct hardening methods, respectively. The lower melting rates in traditional, brine tank and batch freezer methods were due to rapid and complete freezing.

Stabilisers significantly reduce the melting rate of frozen desserts (Goff and Hartel, 2013). The melting resistance of *kulfi* also improved with the severity of heat treatment. Rao and Prakash (2004) reported that the melting rate of probiotic *kulfi* did not differ significantly from control. Giri *et al.* (2013) reported that as the level of WPC increased, there was significant decrease in melting rate, which might be due to the improved water-binding ability and stability of WPC.

2.7.6 Sensory properties of *kulfi*

A sensory property can be defined as the human physiological–psychological perception of a number of physical and other properties of food and their interactions. When food is tasted, the physiological apparatus (fingers, mouth, eyes, taste and aroma receptors and ears) examines the food and reacts to the properties of the food. Sensory properties can be subdivided into tactile properties, textural properties, colour and appearance, taste and odour (Rahman, 2008).

The parameters most commonly used in organoleptic evaluation of foods are colour & appearance, body & texture, flavour and overall acceptability. The most preferred sensory properties of *kulfi* include slightly cooked or caramelised flavour, creamy taste, fine grainy texture and slight brown colour. Presence of large-sized ice crystals and coagulated milk particles reduce the acceptability of *kulfi*. Also, different methods of freezing significantly affected the flavour score of *kulfi*. Brine tank method of freezing scored the highest amongst all methods of freezing (Ghosh, 1991).

2.7.6.1 *Sensory quality of kulfi from reconstituted kulfi mix powder*

Ghosh (1991) reported that flavour and body & texture scores of reconstituted *kulfi* decreased progressively with storage. *Kulfi* prepared from 5 month old mix resulted in a crumbly body and coarse texture. These defects were attributed to protein destabilization during storage. There was also reduction in colour and appearance score during storage. The light-brownish colour of freshly prepared *kulfi* mix powder turned into dark due to Maillard browning. Consequently, the smooth glossy appearance of *kulfi* prepared from that powder turned dull in appearance.

2.8 Freezing

Freezing is a process wherein temperature is decreased to a range which results in the formation of ice crystals within the product structure, besides extending the shelf life of the food (Heldman and Lund, 2007). It is a complex process. Prior to actual freezing, precooling is done to remove the sensible heat from the food so as to decrease the temperature to the freezing point. After the freezing point is reached, further cooling

occurs without phase change, and is called super-cooling. After super cooling, nucleation and phase change occur (Pham, 2014a). This initial freezing point in *kulfi* is lower than the freezing point of pure water due to the presence of solutes. At the initial freezing point, a portion of the water within the food crystallizes and the remaining solution becomes more concentrated, which consequently reduces further the freezing point of unfrozen portion of the solution (Fricke and Becker, 2002). This unfrozen solution can be assumed to obey the freezing point depression equation given by Raoult's law (Pham, 1987). This phenomenon of reduction in freezing point with increasing concentration of solution continues until the eutectic point of the solute is reached. At temperatures lower than the eutectic point, both ice and solute crystallize (Khadatkar *et al.*, 2004). The third step is the sub-cooling process, wherein the temperature is further reduced to final storage temperature. Removal of sensible and latent heat results in a reduction in the product temperature as well as a conversion of water from liquid to ice. The ice crystal size influences the product quality. The nucleation process during freezing has a direct influence on the size of ice crystals. If the rate of heat removal is slow and the product temperature is close to 0°C, very few nuclei will form and they grow to large size. However, if the rate of heat removal is fast and the temperature of super cooling is relatively low, a large number of nuclei is formed and the ice crystal size will be small (Khadatkar *et al.*, 2004).

Factors that influence the freezing time of food are initial freezing temperature, product size, thermal conductivity, density, effective specific heat or specific enthalpy, temperature of freezing medium, initial product temperature, amount or fraction of water in the product and convective heat transfer coefficient (Pham, 2008; Singh and Heldman, 2009; Gulati and Datta, 2013).

2.8.1 Freezing process

The freezing process can be accomplished by indirect or direct contact system (Singh and Heldman, 2009). A freezing system that brings a refrigeration medium into direct contact with the product surface is classified as a direct contact system. These systems are aimed at bringing the cold medium into contact with maximum product

surface area. Therefore, these systems are expected to be highly efficient as barriers to heat transfer are reduced to a minimum (Heldman and Lund, 2007). Examples are air-blast freezing, cryogenic freezing by pouring liquid nitrogen, etc. These systems are also referred to as individual-quick-freezing (IQF) systems, as each unit of the product is directly exposed to the refrigerant and freezing time is short. Fluidized-bed freezing is a modified version of IQF system. By maintaining the product in a fluidized state, the movement of low-temperature air at the product surface creates very high convective heat transfer coefficients.

In immersion freezing system, the common refrigerants used are nitrogen, carbon dioxide, etc. The product particles or pieces pass through a compartment where they are exposed to a spray of liquid refrigerant (Heldman and Lund, 2007).

In indirect freezing systems, the product and refrigerant are separated by a barrier throughout the freezing process. These systems include any system without direct contact (Singh and Heldman, 2009).

2.8.2 Freeing of *kulfi* mix

Freezing of condensed milk is as one of the important operations in the preparation of *kulfi*. Both palatability and quality of the final product depend upon the freezing technique. Ghosdekar and Rao (1982) mentioned that slow freezing of *kulfi* in the refrigerator led to formation of larger ice crystals, which in turn led to inferior product in terms of body and texture. The authors recommended cooling the *kulfi* mix to 5°C and then freezing quickly by immersing in ice-salt mixtures with intermittent shaking of the product. Salooja and Balachandran (1982) used ice salt mixture in the ratio of 4:1 as the freezing mixture. Earthen pots were used for freezing the moulds of *kulfi*. Similarly, Rajor and Vani (1991) filled the mix in *kulfi* moulds and froze them with agitation in butter churn filled with ice-salt mixture in the ratio of 4:1. Rao and Prakash (2004) another method was hardening the mix at -20^0C overnight. Similarly, Bhadakawad *et al* (2009) used a mixture of ice and salt in 4:1 ratio, placed the *kulfi* mould in a hand-operated butter churn and the churn was rotated to provide agitation for faster rate of

freezing in order to reduce ice crystal size in the product. Freezing was done for 17 min and then the moulds were transferred to deep freezer at -18°C (Nigam *et al.*, 2016).

Ghosh (1991) evaluated four freezing methods for *kulfi*:

1) Traditional method

In this method, metal *kulfi* moulds were immersed in ice salt mixture of 3:1 ratio inside an earthen pot, and continuous shaking of the contents was done in order to obtain uniform and quick freezing.

2) Brine tank method

The *kulfi* moulds containing condensed milk were immersed in brine tank at -20°C temperature and continuously shaken until the mix became frozen completely.

3) Batch freezer method

Kulfi concentrate was frozen partially and whipped in the batch type softy ice cream machine and this partially frozen mix was filled into moulds and hardened in a deep freezer maintained at -23°C.

4) Direct hardening method

In this method, the *kulfi* moulds were directly kept in a deep freezer maintained at -23°C, and no agitation or shaking was provided.

2.9 Cryogenic Freezing of Foods

Cryogens such as liquid forms of hydrogen (LH_2), helium (LHe), nitrogen (LN_2), oxygen (LO_2), methane (LCH_4), carbon dioxide (LCO_2), etc. boils at cryogenic temperatures at atmosphere pressure. Amongst these, the most commonly used cryogens for freezing are LN_2 and LCO_2. LN_2 and LCO_2 have boiling points of –196°C and –79°C, respectively giving large temperature differences and high rates of heat transfer. However, most are chemically inert and nontoxic in normal concentrations. Therefore, they are safe for direct contact with food. The product is either sprayed with, or immersed in the cryogen, at atmospheric pressure (Cleland and Valentas, 1997).

2.9.1 Liquid nitrogen

Liquid nitrogen (LN_2) is a colourless and odourless cryogenic liquid with a boiling point of -195.6°C and latent heat of 199.58 kJ/kg (ASHRAE Handbook, 1990). It is inert with a high expansion ratio of 646 between liquid and gaseous phases (ASHRAE Handbook, 1990). It is thus suitable for rapid freezing of foods. Although it is well established that rapid freezing is necessary to produce high quality frozen foods, large temperature gradients in the food may cause damage due to the induced thermal stresses.

LN_2 has a tremendous potential to be used as a total loss refrigerant for IQF at very rapid rates. Due to its rapidity, LN_2 freezing is capable of producing small ice crystals in size and reduces the drip loss substantially, thereby helping immensely to retain the quality (Goswami, 2010).

2.9.2 Cryogenic freezing process

Cryogenic freezing requires no mechanical refrigeration equipment. A simple cryogen tank and suitable spray equipment would be sufficient. However, there might be some distortion of shape of the food products during cryogenic freezing, which might have an impact on its commercial application (Zhou *et al.,* 2010).

Davidge (1981) reported that the early experiments in 1960's showed that foods (fish, meat and poultry) could be frozen by spraying them with LN_2 or LCO_2, by immersion or by tumbling the food. Efforts were concentrated on spray-freezing the food on a conveyor belt and the 'nitrogen tunnel' was invented.

Gutschmidt (1969) compared the freezing rate and sensory properties of green beans and strawberries frozen by spray and air blast freezer. The spray freezer consisted of a spray zone of LN_2 and counter-flow precooling by gaseous nitrogen. It was found that the effective freezing rate for one layer of beans was about 10–15 cm/h while for strawberries it was 1.5 m/h. In the case of air blast freezer, with an air temperature of -35 to -40°C and a speed of 3–4 m/s, the freezing rate was observed to be 7–10 times lower than that of the rate obtained in spray freezer. The frozen products leaving the spray freezer had a temperature of -25°C. It was also reported that the green beans and

strawberries that were frozen by spray freezer showed better colour, flavour and texture even after 12 months as compared to those frozen by air blast freezer.

Sills (1969) studied rapid chilling of smoked bacon with LN_2. It was found that quick chilling by LN_2 reduced the floor space required for the racks and also reduced the weight loss associated with conventional cooling. Hoeft *et al.* (1973) studied the cryogenic freezing of tomato slices. The tomato slices were first immersed in LN_2 for 20 s and then equilibrated in the evolving nitrogen gas for 30 s, and immediately transferred to -34°C.

Murthy (1995) studied the effect of exposure of food product to cryogens on its structure and the size of ice crystals formed. The authors reported that the cryogens could be applied to spice grinding, storage of fruits and vegetables.

Chen and Bonnie (1995) studied the freezing point and freezing rate of tilapia meat in LN_2 freezers at 186 and 145 K and in air blast freezers at 266, 253 and 237 K. The authors developed a relationship between meat thickness and freezing temperature with freezing rate. Freezing rates of tilapia meat in air blast and LN_2 were found to be 0.25 and 19.45 cm/h, respectively. It was found that the freezing rate in LN_2 was independent of thickness of the product to be frozen.

John and Narasimham (1998) studied the changes in quality of cryo-frozen ripe jackfruit bulbs at 255 K. Cryo-cans containing 25 L of LN_2 were used in the experiments. LN_2 was poured into a stainless steel vessel, which was well protected on all the sides by an insulated box made of polystyrene foam of 100 mm thickness. Cans were immersed into LN_2 and covered with an insulated lid. The authors observed that at the end of 6 months of storage, there was a reduction in toughness from the initial value of 139.25–158.86 kPa in the case of cryofrozen bulbs and to 126.5 kPa in the case of blast-frozen samples. Similarly, the colour retention was better in cryogenically frozen product. Cryofrozen bulbs were found to be superior to blast-frozen bulbs after 6 months.

Evans (2008) reported that the common method of cryogenic freezing was by spraying LN_2 directly over the product. Due to very low operating temperatures and high surface heat transfer coefficients between the product and the medium, the cooling rates

of cryogenic freezing systems were substantially higher than other freezing systems. Most of the cryogenic systems used total loss of refrigerants, wherein the refrigerant was released to the atmosphere and it was not recovered. Because of the shorter freezing times compared to conventional air freezing and because of the large temperature differences between the cryogen and the product surface, high rate of surface heat transfer was achieved from the cryogen that was boiling off (Zhou *et al.,* 2010).

Goswami (2010) reported that for IQF, LN_2 could be used as a refrigerant to get ultra-rapid freezing. Due to its rapidity, LN_2 freezing was capable of producing small ice crystals in size and thereby helped immensely in retaining the quality and substantially reducing the amount of drip loss.

Rodezno *et al.* (2013) studied the effects of cryogenic and air blast freezing on the quality of catfish fillets. The authors found that cryogenically frozen catfish fillets had better quality characteristics than blast frozen catfish fillets even beyond 6 months of storage. Seetapan *et al.* (2015) evaluated the effect of cryogenic freezing on textural properties and microstructure of rice flour/tapioca starch blend gel upon freezing and storage at -20°C for a period 3 months. The results suggested that the textural stability of such starch gels could be maintained for long periods with the use of cryogenic freezing due to delay of phase separation.

2.9.3 Advantages of cryogenic freezing

Advantages of LN_2 as refrigerant in freezing of foods over conventional and air blast freezing include reduced dehydration loss, exclusion of oxygen, minimization of oxidative rancidity, reduced drip loss, improved flavour, texture, colour, appearance, low investment cost, less handling losses, less man power requirement and rapid installation (Goswami, 2010).

Awonorin (1997) also proposed that cryogenic freezing was an attractive option for food processing industries because of the several benefits it offered over mechanical freezing namely, increased production capacity, better quality of food in terms of texture, taste and appearance and longer shelf life of the processed food.

2.9.4 Application of LN_2 in dairy industry

LN_2 provides rapid freezing and rapid hardening of ice cream in small-scale operations. It can also be used to rapidly freeze ice cream bars to very low temperatures in some novel manufacturing operations. Allowing ice cream concentrate to drop into LN_2 causes the drop to solidify almost immediately. Due to such rapid freezing, cryogenically frozen ice creams had very low air incorporation, making them fairly dense (Goff and Hartel, 2013).

The cryogenically-frozen ice cream will generally have very low air incorporation, making each drop fairly dense which will give premium feel and have better taste. Without the pockets of extra air whipped in, the ice cream also does not melt as quickly. Such a dense ice cream gives additional value to customers for their purchase and improves their satisfaction. Ice cream made with LN_2 will be better in on microbiologically quality. In today scenario, anything fresh, sells at a premium price. The LN_2 ice cream demands a premium because additives can be totally eliminated. In coming decades, the fresh product market will increase and will increase the popularity cryogenically-frozen ice cream in the first tier cities of India (Pushpadass *et al.,* 2016).

2.10 Freezing Time

Freezing time of a food is a function of product size, temperature difference between the coolant and the product, heat transfer coefficient of the freezing system and thermal diffusivity of the product (Muthukumarappan and Marella, 2007). Since the temperature distribution within a product varies considerably during freezing, freezing time must be defined with respect to a position. The thermal centre is generally taken as the reference, which is the location where the temperature changes are the slowest. Freezing time is defined as the time to reach a particular temperature at the slowest cooling point (the thermal centre) (Hossain *et al.,* 1992). Two definitions for freezing time are suggested (International Institute of Refrigeration, 1972). The nominal freezing time for a given product, with specified dimensions and uniform initial temperature of 0°C, is the time that takes the thermal centre to reach a temperature of -10°C below the initial freezing point. The other definition is the effective freezing time, also known as

standard freezing time (SFT) (Eek, 1991), which is the total time required to lower the product temperature from its initial value to a given final value at the thermal centre. The effective freezing time appears to be more acceptable, and thus most of the methods and techniques available in the literature are limited to predicting the effective freezing time (Ramaswamy and Tung, 1984; Hung, 1990).

2.10.1 Prediction of freezing time

Models available to predict the freezing process can be classified into two main groups: heat transfer models and coupled heat and mass transfer models. The approaches used to predict freezing times vary from simple analytical equations based on a series of approximations and suppositions to advanced numerical methods. The most realistic physical model for freezing is the non-linear unsteady heat conduction with variable thermal properties and surface convective cooling (Cleland *et al*., 1987).

Delgado and Sun (2001) reviewed the methods available to predict the freezing times of food materials. The complexities of the models were found to vary quite widely and the thermo-physical properties and heat and mass transfer coefficients greatly affected the accuracy of the prediction methods.

Sabliov *et al.* (2002) analysed the heat transfer during cooling of shell eggs using axisymmetric unsteady state finite element heat transfer model. Egg was assumed to be a composite system of elliptical shape. The simulated temperature profiles were compared with analytical and observed data, which showed good agreement.

Nahid *et al*. (2008) modelled freezing of butter and reported that the release of latent heat from the frozen water depended on the degree of supercooling, which in turn varied with the cooling medium temperature, the size and type of butter and the packaging used. The authors used four modelling approaches and validated the experimental data collected for 25 kg block of butter. The first approach was the ‘‘sensible heat only model’’ which accurately predicted the butter temperature until the point when freezing of water became significant. The second model was ‘‘equilibrium thermal properties model’’, which predicted the temperature plateau near the initial

freezing point of butter but it was inconsistent with the recorded data. The third model used was a "stochastic approach" to ice nucleation based on supercooling using classical homogeneous nucleation theory. The predicted temperatures showed that supercooling-driven nucleation alone was not sufficient to predict the freezing behaviour of butter. The fourth approach took account of time-dependent nucleation and ice crystal growth kinetics and was found to be the best model.

2.10.1.1 *Analytical and empirical approaches*

The general approach for predicting freezing time is to seek approximate or empirical relationships based on Plank's equation (Plank, 1913) (Eq. 2.1) or modifications of the Plank's equation. Plank's method assumes that foods freeze at a constant temperature and not over a range of temperatures as the case in actual food freezing processes. Therefore, the frozen food's thermal conductivity is assumed to be constant. However, in reality, thermal conductivity varies greatly during freezing. Another limitation of Plank's equation was that it neglected precooling and subcooling (ASHRAE Handbook, 2006).

$$\theta = \frac{L_f}{t_{f-}t_m}\left[\frac{PD}{h} + \frac{RD^2}{k_f}\right] \qquad (2.1)$$

where,

'θ' was the freezing time (s)

'L_f' was the volumetric latent heat (J/m^3)

't_f' was the initial freezing point (^oC)

't_m' was the temperature of freezing medium (^oC)

'P' was the constant (0.25 for cylinder)

'R' was the constant (0.0625 for cylinder)

'D' was diameter of mould used (m)

'h' was the heat transfer coefficient during freezing (W/m^2 K)

'k_f' was the thermal conductivity of frozen product (W/m K)

Pham (1986) proposed a model (Eq. 2.2) for predicting food freezing time. The advantage of this model was that it was easy to use and it provided solutions with reasonable accuracy.

$$\theta = \frac{V}{hA_s}\left(\frac{\Delta H_1}{\Delta T_1} + \frac{\Delta H_2}{\Delta T_2}\right)\left(1 + \frac{B_i}{4}\right) \tag{2.2}$$

where,

$$T_{fm} = 1.8 + 0.263T_c + 0.105T_m \tag{2.3}$$

$$\Delta H_1 = \rho_u \left(C_{pu}\left(T_i - T_{fm}\right)\right) \tag{2.4}$$

$$\Delta H_2 = \rho_f \left(L_f + C_{pf}\left(T_{fm} - T_c\right)\right) \tag{2.5}$$

$$\Delta T_1 = \frac{T_i + T_{fm}}{2} - T_m \tag{2.6}$$

$$\Delta T_2 = T_{fm} - T_m \tag{2.7}$$

'θ' was the freezing time (s)

'ρ_u' was the density of unfrozen product (kg/m^3)

'ρ_f' was the density of frozen product (kg/m^3)

'V' was the volume of product (m^3)

'h' was the heat transfer coefficient during freezing of product (W/m^2 K)

'A_s' was the surface area of mould (m^2)

'L_f' was the volumetric latent heat of the product (J/m^3)

'T_c' was the final centre temperature of the product (°C)

'T_i' was the initial temperature of the product (°C)

'T_f' was the initial freezing temperature of the product (°C)

'T_m' was the temperature of freezing medium (°C)

'C_{pu}' was the specific heat of unfrozen product (J/kg K)

'C_{pf}' was the specific heat of frozen product (J/kg K)

Nagaoka *et al*. (1956) modified the Plank's equation as shown below and predicted the freezing time.

$$\theta = \left[C_{pu}(T_i - T_f) + \lambda X_w + C_{pf}\left(T_f - T\right)\right]\left[1 + 0.008\left(T_i - T_f\right)\right] \mathrm{X} \left[\frac{\rho}{T_f - T_m}\left(\frac{P \times L}{h} + \frac{R \times L^2}{k_f}\right)\right] \quad (2.8)$$

where,

'θ' was the freezing time of the product (s)

'T_i' was the initial temperature of the product (°C)

'T_{if}' was the initial freezing temperature (°C) of the sample

'T_m' was the temperature of freezing medium (°C)

'C_{pu}' was the specific heat of unfrozen product (J/kg K)

'C_{pf}' was the specific heat of frozen product (J/kg K)

'λ' was the latent heat of fusion of ice (J/kg)

'X_w' was the water fraction in *kulfi*

'P' was the constant (0.25 for cylinder)

'R' was the constant (0.0625 for cylinder)

'D' was the diameter of mould (m)

'h' was the heat transfer coefficient during freezing of the product (W/m^2 K)

'k_f' was the thermal conductivity of frozen product (W/m K)

Cleland and Earle (1984) modified Plank's equation using the non-dimensional numbers as follows:

$$\theta = \frac{\rho \Delta H_{ref}}{E_f\left(T_{if} - T_m\right)}\left(\frac{2P_1 R}{h} + \frac{4P_2 R^2}{k_f}\right)\left[1 - \frac{1.65 Ste}{k_f}\left(\frac{T_c - T_m}{T_{ref} - T_m}\right)\right] \quad (2.9)$$

where,

$$P_1 = 0.5(1.026 + 0.5808 Np_k + N_{Ste}(0.2296 N_{Pk}) + 0.105) \quad (2.10)$$

$$P_2 = 0.125(1.202 + N_{Ste}(3.410 N_{Pk}) + 0.73360 \quad (2.11)$$

$$N_{Ste} = \frac{C_{pf}\left(T_{if} - T_m\right)}{\Delta H_{ref}} \quad (2.12)$$

$$N_{Pk} = \frac{C_{pu}\left(T_i - T_{if}\right)}{\Delta H_{ref}} \tag{2.13}$$

'θ' was the freezing time of the product (s)

'ρ' was the density of the product (kg/m^3)

N_{Ste} –Stefen's number

N_{Pk} – Plank's number

'ΔH_{ref}' was the enthalpy at reference temperature (-20°C)

'D' was the diameter of mould (m)

'E_f' was the shape factor (2 for cylinder)

'h' was the heat transfer coefficient during freezing of the product (W/m^2 K)

'k_f' was the thermal conductivity of frozen product (W/m K)

'T_c' was the final temperature of the product (°C)

'T_{if}' was the initial freezing temperature of the product (°C)

'T_m' was the temperature of freezing medium (°C)

'T_i' was the initial temperature of the product (°C)

'C_{pu}' was the specific heat of unfrozen product (J/kg K)

'C_{pf}' was the specific heat of frozen product (J/kg K)

The simplified analytical method especially suitable for practical industrial calculations and for products of simple regular geometries was developed by Salvadori and Mascheroni (1991).

$$t_f = \left(A\theta_e + B\right)\left(\frac{1}{Bi_u} + C\right)\left(1 - \frac{\theta_i}{\theta_f}\right)^n \left(\frac{\theta_a}{\theta_f} - 1\right)^{-m} \frac{R^2}{\alpha_u} \tag{2.14}$$

where,

$$\alpha_u = \frac{k_u}{\rho_u C_u} \text{ (thermal diffusivity of the unfrozen food)} \tag{2.15}$$

$$Bi_u = \frac{hR}{k_u} \text{ (Biot number based on unfrozen food thermal conductivity)} \tag{2.16}$$

and *A, B, C, m* and *n* were empirical parameters that depended on geometry of the product.

Salvadori (1994) further simplified the equation by assuming θ_f = -1°C, and obtained Eq. 2.17.

$$t_f = \left(A'\theta_e + B'\right)\left(\frac{1}{Bi_u} + C'\right)\left(1+\theta_f\right)^{n'}\left(-\theta_u - 1\right)^{-m'}\frac{R^2}{\alpha_u} \quad (2.17)$$

Unlike other models, the Salvadori and Mascheroni model did not require frozen food properties to be known or estimated. These properties were implicitly assumed to be uniquely related to the unfrozen food properties, and therefore, it was easier to apply than other prediction methods (Pham, 2014b).

2.10.1.2 *Numerical approaches*

Numerical methods are regularly used to model heat transfer during food freezing. The advantage of numerical models over simple equations is that the effects of phase change over a range of temperature, changing thermal properties and heterogeneity of food products can be analysed. If numerical methods are formulated and implemented correctly with minimum truncation and rounding errors, they are generally considered to be the most accurate, reliable and versatile freezing and thawing time prediction methods (Cleland *et al.,* 1987). Pham (1985) proposed a method that combined the positive characteristics of both enthalpy and temperature approaches. Similarly, Mannapperuma and Singh (1988) used an explicit numerical method involving enthalpy formulation to predict temperature distribution in foods during freezing. The method showed good agreement of calculated freezing times with experimental data for slab-shaped, cylindrical and spherical products.

Franke (2000) proposed a new calculation approach for freezing of foods based on the fictitious heat flow model. The author claimed that the model proposed for the simulation of freezing foods having a broader freezing range was able to describe the processes satisfactorily. Also, the freezing curve calculated implicitly by the model was similar to those measured for the same material.

2.11 Thermo-physical Properties of Frozen Foods

Thermal properties of foods must be known to perform various heat transfer calculations involved in freezing of foods because these properties mainly depend on temperature and chemical composition of the food (ASHRAE Handbook, 2006). The major constituents of foods are water, protein, carbohydrate, fat, ash and fibre.

Composition-based prediction models for determination of thermal properties of foods require detailed knowledge on the mass fractions of the various components that make up the food. Choi and Okos (1986) developed mathematical models for predicting the thermal properties of these constituents individually as a function of temperature.

Fricke and Becker (2001) reported that thermo-physical properties of foods that are required for heat transfer calculations were ice fraction, specific heat capacity, specific enthalpy and thermal conductivity. These properties were found to be well-behaved when the temperature was above the initial freezing point, but below the initial freezing point, these properties of foods varied greatly due to the thermodynamic changes involved during freezing. As the thermo-physical properties of ice and water are quite different, the thermo-physical properties of frozen foods vary dramatically with temperature.

2.11.1 Thermo-physical properties during freezing of foods

Renaud *et al.* (1992) measured the thermal conductivity and thermal diffusivity of model food gels using hot wire probe and pulse methods in the temperature range of -40°C to 20°C. The authors reported that there was strong correlation between the ice fraction and thermal properties of frozen gels.

Fikiin *et al.* (1999) established predictive equations for the equivalent thermo-physical properties during cooling of fruits in trays. The authors claimed that the results were appropriate to be used for mathematical modelling and engineering calculations in real industrial heat transfer scenarios.

Cogne *et al.* (2003) developed physical models that predicted the thermal properties of a standard overrun ice cream, based on the composition and intrinsic

thermal properties of each major constituent. These models were validated by measuring the thermal properties of ice cream experimentally. The predicted thermo-physical properties values were in close agreement with the experimental data.

Simpson and Cortes (2004) assumed a known function for apparent volumetric specific heat in the freezing temperature range and designed a simple heat transfer experiment to estimate the unknown parameters. The authors solved the partial differential equation with a finite difference scheme coupled with an optimisation technique and obtained the unknown parameters. This provided the best least square fit between the experimental and predicted time–temperatures curves.

2.11.1.1 *Initial freezing point*

The thermo-physical properties of foods include initial freezing point, ice fraction, density, specific heat capacity, enthalpy and thermal conductivity. Initial freezing point is the temperature at which the ice crystals appear first as temperature is lowered in a food. It is the highest temperature at which ice may exist in that food in thermal equilibrium (Miles, 1991). Initial freezing point of food systems is lower than that of pure water due to dissolved constituents in it. Majority of raw foods, due to their high moisture content, have their freezing point between 0 and -4°C (Rahman, 2009).

Ribero *et al*. (2007) measured the centre temperature profile and initial freezing point of unsalted Mozzarella cheese samples as -1.2 to -2.4°C. The authors reported that not only NaCl but also other soluble solids present in the aqueous phase significantly contributed to the freezing point depression of Mozzarella cheese.

Boonsupthip *et al.* (2009) developed a freezing point equation based on average molecular weights of food constituents for different categories of food products such as fruits, vegetables, meat products and dairy products (milk and cheese) as shown below.

$$\frac{1}{T_{fi}} = \frac{1}{T_{fo}} - \frac{R}{\lambda_{ice} M_w} \ln \left(\frac{\frac{\left(X_w - X_b\right)}{M_w}}{\left(\frac{X_u - X_b}{M_w} \right) + \sum_i \frac{X_i}{M_i}} \right) \qquad (2.18)$$

where,

'T_{fi}' was the initial freezing temperature of the product (K)

'T_{f0}' was the freezing temperature of pure water (273.15 K)

'X_w' was the mass fraction of total amount of water

'X_b' was the mass fraction of bound water

'X_i' was the mass fraction of major food constituents

'M_w' was the molecular weight of water, and

'M_i' was the molecular weight of major food constituents.

The mass of various constituents were calculated based on the total mass of food, excluding the amount of ice. This model predicted the initial freezing point of foods more accurately than other models.

2.11.1.2 ***Ice content***

Thermo-physical properties of frozen foods strongly depend on the fraction of ice in the food. For prediction of these properties, the mass fraction of water that has crystallized must be determined. The mass fraction of crystallised water in a food is a function of temperature below the initial freezing point (ASHRAE Handbook, 2006).

For estimating ice-fraction, the most widely used model (Eq. 2.19) was based on Raoults Law and Clausius–Clapeyron equation.

$$X_{ice} = \left(X_w - X_b\right)\left(1 - \frac{T_{if}}{T}\right) \tag{2.19}$$

where, X_w was the fraction of water, X_b was the fraction of bound water and T_{if} was the initial freezing point of food. The amount of bound water could be estimated using the following empirical equation (Schwartzberg, 1976).

$$X_b = cX_s \tag{2.20}$$

X_b was the bound water content in the food

C was a constant (0.4)

X_s was the concentration of protein and carbohydrates.

Tchigeov (1979) also proposed an empirical relationship to estimate the mass fraction of ice (X_{ice}).

$$\frac{X_{ice}}{X_w} = \frac{1.105}{1+\left(\frac{0.70138}{\ln\left(T_{if} - T + 1\right)}\right)} \tag{2.21}$$

where,

'X_{ice}' was the ice content

'X_w' was the water content

'T' was the temperature (°C)

T_{if} was initial freezing temperature of the product (°C)

Fikiin (1996) noted that the above Tchigeov model for determination of mass of ice provided satisfactory results.

2.11.1.3 *Density*

Modelling the density of foods requires knowledge of porosity, mass fractions and density of the individual constituents of food. The density 'ρ' of foods could be calculated by:

$$\rho = \frac{\left(1-\varepsilon\right)}{\sum \frac{x_i}{\rho_i}} \tag{2.22}$$

where,

'ε' was the porosity

'x_i' was the mass fraction of the food constituents and

'ρi' was the density of the food constituents.

2.11.1.4 *Specific heat capacity*

Specific heat capacity is the measure of energy required to change the temperature of unit mass of a substance by one degree. In unfrozen foods, specific heat is relatively constant with respect to temperature. However, in frozen foods, there is a large reduction

in specific heat capacity as temperature decreases. The specific heat capacity of a substance at temperature above its initial freezing point could be obtained from the mass average of the specific heat capacities of the constituents.

Reddy and Datta (1994) measured the thermo-physical properties of reconstituted milk during processing. Specific heat of milk was determined at concentrations between 40 and 70%, and at temperature of 35-65°C. It was observed that increasing temperature and moisture content resulted in increased specific heat. The maximum specific heat was 3.35 kJ/kg K and minimum was 2.0 kJ/kg K.

The specific heat of unfrozen food 'c_u' could be determined using Eq. 2.23.

$$c_u = \sum c_i x_i \tag{2.23}$$

where,

'c_i' was the specific heat of the individual food constituents and

'x_i' was the mass fraction of the various constituents of the food.

Below the freezing point, both sensible heat from temperature change and latent heat from fusion of water should be considered. Because latent heat is released over a range of temperature, an apparent specific heat must be used to account for both sensible and latent heat effects (Schwartzberg, 1976).

2.11.1.5 *Enthalpy*

Enthalpy of unfrozen foods could be obtained simply as a weighted mean of the enthalpies of pure constituents such as water, fat, carbohydrates, proteins, fibre, ash and salts (Mannapperuma and Singh, 1988). The change in a food's enthalpy could be used to estimate the energy that must be added or removed to effect a temperature change. Enthalpy consists of only sensible energy above the freezing point. However, below the freezing point, it consists of both sensible and latent energy. Enthalpy could be derived from the specific heat at constant pressure equation (Eq. 2.24).

$$c_p = \left(\frac{\partial H}{\partial T} \right)_P \tag{2.24}$$

where,

'c_p' was the specific heat,

'H' was the enthalpy and

'T' was the temperature.

By using Chen's (1985) method (Eq. 2.25), the enthalpy of an unfrozen food could be calculated as follows.

$$H = H_f + \left(T - T_{if}\right)\left(1.0 - 0.55x_s - 0.15x_s^3\right) \tag{2.25}$$

where,

'H' was the enthalpy of the product (kJ/kg)

'H_f' was the enthalpy of the product at initial freezing temperature (kJ/kg)

'T' was the temperature of the product

'T_{if}' was the initial freezing temperature of the product

'x_s' was the mass fraction of various solids of the product

In order to predict the enthalpy of a frozen food product, the thermal energy of the individual constituents are integrated over the desired temperature range, using a reference point at which enthalpy is set to zero. The total enthalpy could be calculated using Eq (2.26).

$$H(T) = \int_{-40}^{T} x_s C_{p,s} dT + \int_{-40}^{T_{fi}} x_u C_{p,w} dT + \int_{T_{fi}}^{T} x_u C_{p,w} dT + x_u \lambda_{ice} + \int_{-40}^{T_{fi}} x_{ice} C_{p,ice} dT \tag{2.26}$$

where, 'T' was temperature in °C. x_s, x_u and x_{ice} were the mass fractions of component solids, unfrozen water and ice, respectively. Similarly $C_{p,s}$, $C_{p,w}$ and $C_{p,ice}$ were the specific heats of solid constituents, water and ice, respectively, and T_{fi} was the initial freezing temperature (Gulati and Datta, 2013).

2.11.1.6 *Thermal conductivity*

Thermal conductivity represents the quantity of heat that flows per unit time through a food of unit thickness and unit area having unit temperature difference. Thermal conductivity relates the conduction heat transfer rate to the temperature gradient.

It depends on factors such as structure, composition and temperature of the food (ASHRAE Handbook, 2006). Various researchers have proposed using parallel and series models based on analogies to electrical resistance (Murakami and Okos, 1989) for determining the thermal conductivity of foods.

The thermal conductivity of an aqueous material generally increases as water changes into ice and continues to increase steadily with further decrease in temperature (Fennema *et al.,* 1973). Similarly, the thermal conductivity of reconstituted milk during processing was determined by Reddy and Datta (1994), and it was found to increase with increase in moisture content and temperature.

Jayakumar (1998) determined the thermal conductivity of khoa and paneer at different concentrations of TS and temperature. The author reported that thermal conductivity of paneer having moisture content of 41-58% varied from 0.212 to 0.353 W/m K (6-40°C range of temperature) and for khoa having moisture content of 32-68% it varied from 0.259 to 0.473 W/m K (10-90°C range of temperature). Thermal conductivity of chhana was measured by Asim (1999), and it was found to range from 0.331 to 0.442 W/m K for the temperature range of 41– 47°C.

For khoa:

$$k=0.115+0.435M+0.0009T \quad (2.27)$$

For paneer:

$$k = 0.603M + 0.00135T - 0.044 \quad (2.28)$$

Similarly, a model was proposed by Asim (1999) for predicting the thermal conductivity of chhana as follows:

$$k = 0.00994772M - 0.0036978F + 0.0025041P + 0.00452695T - 0.3441016 \quad (2.29)$$

Muramatsu *et al.* (2005) determined the thermal conductivity of WMP and SMP using transient heat source method. The authors reported that the thermal conductivity of WMP was 0.058-0.097 W/m K and SMP was 0.073-0.113 W/m K, respectively in the range of 10-50°C.

Two more models were found to predict the upper and lower bounds of the thermal conductivity of most food items (ASHRAE Handbook, 2006). The parallel model was the sum of the thermal conductivities of the food constituents multiplied by their volume fractions.

$$k = \sum x_i^v k_i \tag{2.30}$$

where, x_i^v was the volume fraction of constituent 'i'. The volume fraction of constituent 'i' and. could be determined from the following equation (Eq. 2.31), and 'k_i' was the thermal conductivity of each constituent.

$$x_i^v = \frac{\left(\frac{x_i}{\rho_i}\right)}{\sum\left(\frac{x_i}{\rho_i}\right)} \tag{2.31}$$

The perpendicular model (Eq. 2.32) was the reciprocal of the sum of the volume fractions divided by their thermal conductivities:

$$k = \frac{1}{\sum\left(\frac{x_i^v}{k_i}\right)} \tag{2.32}$$

Similarly, as described under specific heat (Choi and Okos, 1986), a set of completely empirical correlations also was developed based on food composition data (Eqs. 2.33-2.39) for thermal conductivity.

$$k_w = 0.57109 + 1.762 * 10^{-3} T - 6.7036 * 10^{-6} T^2 \tag{2.33}$$

$$k_{ice} = 2.21960 - 6.2489 * 10^{-3} T + 1.0154 * 10^{-4} T^2 \tag{2.34}$$

$$k_{prot} = 0.17881 + 1.1958 * 10^{-3} T - 2.7178 * 10^{-6} T^2 \tag{2.35}$$

$$k_{fat} = 0.18071 - 2.7604 * 10^{-3} T - 1.7749 * 10^{-7} T^2 \tag{2.36}$$

$$k_{carb} = 0.20141 + 1.3874 * 10^{-3} T - 4.3312 * 10^{-6} T^2 \quad (2.37)$$

$$k_{fibre} = 0.18331 + 1.2497 * 10^{-3} T - 3.1683 * 10^{-6} T^2 \quad (2.38)$$

$$k_{ash} = 0.32961 + 1.4011 * 10^{-3} T - 2.9069 * 10^{-6} T^2 \quad (2.39)$$

where,

'k' was the thermal conductivity of the food (W/m K)

'k_w' was the thermal conductivity of water (W/m K)

'k_{ice}' was the thermal conductivity of ice (W/m K)

'k_{prot}' was the thermal conductivity of protein (W/m K)

'k_{fat}' was the thermal conductivity of fat (W/m K)

'k_{carb}' was the thermal conductivity of carbohydrates (W/m K)

'k_{fibre}' was the thermal conductivity of fibre (W/m K)

'k_{ash}' was the thermal conductivity of ash (W/m K)

'T' was the temperature (°C)

From the above thermal conductivities of the individual constituents, the effective thermal conductivity of the composite food material could be predicted using the following equation (Eq. 2.40).

$$k = \sum x_i^v k_i \quad (2.40)$$

2.12 Heat Transfer Coefficient

The heat transfer coefficient 'h' is the ratio of heat flux 'q' (heat flow per unit area) to the difference between the temperature T_s of the surface and that of the cooling medium, T_a. Fricke and Becker (2002) calculated heat transfer coefficient during cooling of Mozzarella cheese, and the values were 7.59, 6.48 and 7.04 W/m^2 K, respectively for air temperature of 0.6, -23.3 and -34.4°C. Becker and Fricke (2004) reviewed the heat transfer data for cooling and freezing of foods and the authors claimed that the information would make possible a more accurate determination of cooling and freezing times and corresponding refrigeration loads. Kondjoyan (2006) reviewed the heat and

mass transfer coefficients that were needed in the mathematical simulation of chilling of food products. The author observed that CFD models were more and more often found to be suitable to calculate heat transfer coefficients on a single food product or packaged food.

Apart from all the work done, literature on preparation of *kulfi* from dry mix and cryogenic freezing of kulfi using LN_2 is not available. The data on heat transfer coefficient during cryogenic freezing of *kulfi* and melting characteristics of *kulfi* are very less. In order to meet the gap in this area, the cryogenic freezing of *kulfi* from concentrated milk and dry mix was taken up.

III MATERIALS AND METHODS

This Chapter describes the experimental techniques employed to fulfill the various objectives envisaged in this study. It includes preparation of *kulfi*, measurement of temperature profiles, freezing times, measurement of thermo-physical properties of *kulfi* concentrate, determination of heat transfer coefficients during freezing of *kulfi* and measurement of physico-chemical, melting, textural and sensory properties of *kulfi*. The methodologies and techniques used in the study are listed below, and are detailed in the following sections.

- Preparation of *kulfi*
- Freezing of *kulfi*
- Temperature profile during freezing
- Determination of freezing time of *kulfi*
- Measurement of thermo-physical properties of *kulfi* concentrate
- Prediction of thermo-physical properties using mathematical models
- Determination of heat transfer coefficient during freezing
- Physico-chemical properties of *kulfi*
- Colour of frozen *kulfi*
- Melting properties of *kulfi*
- Textural properties of *kulfi*
- Sensory evaluation of *kulfi* using fuzzy-logic approach

3.1 Preparation of *Kulfi*

Kulfi was prepared from condensed milk in the conventional manner and also from dry mix. The methodology of preparation is illustrated in the flow charts and the detailed procedure is given in the following paragraphs.

3.1.1 Raw materials

Fresh cow milk was collected from the Livestock Research Centre of SRS of ICAR-National Dairy Research Institute, Bengaluru. The fat content was determined by Gerber method and total solids (TS) were determined by gravimetric method (Giri *et al*.,

2013). The fat and SNF contents of milk were standardised to 5 and 8.5%, respectively. Other ingredients such as sugar were procured from local market and stabilizer was procured from HiMedia Laboratories Pvt. Ltd., Mumbai. Dry mix was produced by drying condensed milk in the pilot-scale spray dryer (model R&D Spray Dryer, Ganga-Tech Engineers, Bengaluru).

3.1.2 Preparation of *kulfi* from milk concentrate

In this method, the standardised raw milk was concentrated two times in a steam jacketed kettle (Fig. 3.1). Sugar was added to condensed milk at the rate of 15% and sodium alginate was added as stabilizer at the rate of 0.2% on weight basis of condensed milk. The resultant concentrate was frozen using deep freeze method to prepare *kulfi*. One set of samples was frozen using LN_2 to produce cryogenically frozen *kulfi*. The procedure of kulfi preparation using concentrated milk is outlined in the flow chart (Fig. 3.2).

Fig. 3.1. Steam jacketed kettle used for condensing milk

Raw milk
↓
Filtration using cheese cloth
↓
Standardization of milk (5% fat & 8.5% SNF)
↓
Concentration of milk (2:1) in steam jacketed kettle (117.68-147.1 kPa pressure)
↓
Addition of ground sugar (15% on condensed milk basis)
↓
Addition of sodium alginate (0.2% on condensed milk basis)
↓
Cooling of mix to 30°C
↓
Filling of *kulfi* concentrate into moulds
↓
Freezing using deep freeze method or LN_2 to -20°C
↓
Storage at -20°C
↓
Frozen *kulfi*

Fig. 3.2. Process flow chart for preparation of *kulfi* from concentrated milk

3.1.3 Preparation of *kulfi* from dry mix

3.1.3.1 *Preparation of dry mix for kulfi*

The *kulfi* dry mix was prepared by spray drying. Milk standardised to 5% fat and 8.5% SNF, and was concentrated in a single effect evaporator (model APV, Kolkatta) with a water evaporation capacity of 20 L/h to twice the TS concentration. Homogenisation was done in two-stage homogeniser at pressures of 17236.89 kPa in the first stage and 3447.38 kPa in the second stage. Sugar was added at 13% weight basis of condensed milk. Out of 13%, only one-fourth of the quantity of sugar was added before spray drying and remaining sugar ground into fine powder was dry blended with the spray-dried powder. The *kulfi* mix was dried in a locally fabricated pilot-scale spray drier at the inlet drying air temperature of 185°C and outlet air temperature of 75°C. This pilot-

scale dryer had water evaporation capacity of 5000 mL/h (model R&D Spray Dryer, Ganga-Tech Engineers, Bengaluru). Feed was pumped through a peristaltic pump at 30 mL/min and was sprayed through two-valve pressure nozzle. The operation of the spray drier was controlled through a microprocessor circuitry for each of the process conditions.

3.1.3.2 *Preparation of kulfi from dry mix*

The dry mix, which was prepared by spray drying in the pilot-scale spray dryer and having 97% dry solids, was used for preparation of *kulfi*. It was reconstituted to get 40% TS. After adding sugar, the level of TS, fat and SNF was maintained same as that of milk concentrate. The mix was pasteurised at 80°C for 25 s and frozen using LN_2. The flow chart for preparation of cryogenically frozen *kulfi* from dry mix is shown in Fig. 3.3.

Dry mix
↓
Addition of stabilizer (0.2% on mix)
↓
Addition of dry mix slowly to warm water (50°C) with continuous stirring
↓
Mixing / blending using hand blender
↓
Filtration using cheese cloth
↓
Pasteurization of mix (80°C for 25 s)
↓
Cooling of mix to 30°C
↓
Filling of concentrate into *kulfi* moulds
↓
Freezing using LN_2 to -20°C
↓
Storage at -20°C
↓
Frozen *kulfi*

Fig. 3.3. Process flow chart for preparation of *kulfi* from dry mix

3.2 Freezing of *Kulfi*

The samples of *kulfi* were frozen using both deep freeze and cryogenic (LN_2) methods. Cylindrical moulds made of galvanised iron (GI) were filled with the *kulfi* concentrate. The dimensions of the mould were: 31 mm dia, 83 mm height and 6.265x 10^{-5} m^3 volume. The moulds were placed on wooden racks and were subjected to freezing (Fig. 3.4). Cryogenic freezing was carried out by immersing the moulds in LN_2 contained in an insulated box.

Fig. 3.4. Moulds used for preparation of *kulfi*

3.3 Measurement of Temperature Profile during Freezing

The temperature profile during freezing of *kulfi* was recorded using the temperature data logger (model CENTER® 309, Ankom International, Bengaluru, India). K-Type thermocouples were used for recording the temperature, and data were acquired at 10 s intervals. One thermocouple was inserted inside the product at thermal centre (one third from bottom) and another was inserted inside the product at a distance two third from bottom. One more thermocouple was inserted inside the freezing medium to determine its temperature during freezing (Fig. 3.5). The length, breadth and height of the insulated box were 0.225, 0.225 and 0.2 m, respectively. The requirement of LN_2 for freezing of 1 L of *kulfi* concentrate was approximately 2 L.

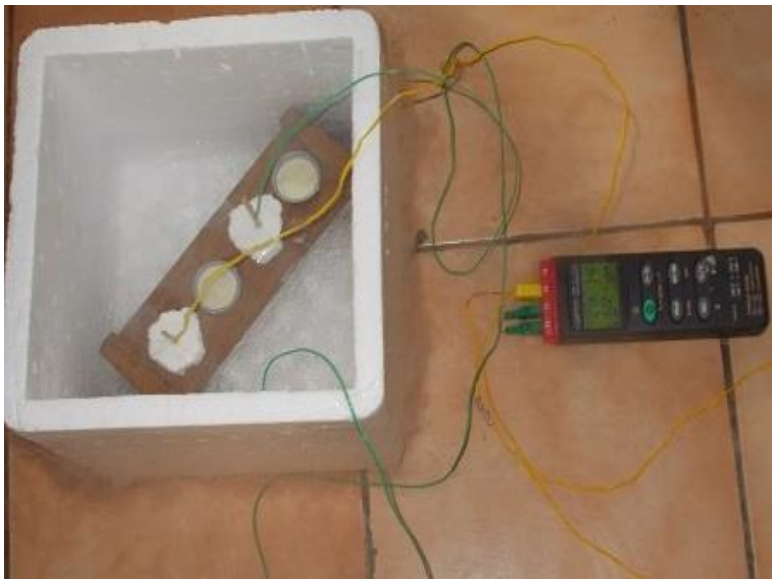


Fig. 3.5. Recording of temperature profile during freezing

3.4 Determination of Freezing Time

Freezing time is found to be a function of product size, temperature difference between the cooling medium and the product, heat transfer coefficient of the freezing system and thermal diffusivity of the product (Muthukumarappan and Marella, 2007). Freezing time was calculated using analytical, approximate and empirical approaches.

3.4.1 Analytical approach

The general approach for predicting freezing time is to seek approximate or empirical relationships, generally based on the Plank's equation (Plank, 1913) or by modification of the Plank's equation.

3.4.1.1 *Plank's equation*

$$\theta = \frac{L_f}{T_f - T_m}\left[\frac{PD}{h} + \frac{RD^2}{k_f}\right] \tag{3.1}$$

where,

'θ' was the freezing time of *kulfi* (s)

'L_f' was the volumetric latent heat of *kulfi* (J/m^3)

'T_f' was the initial freezing point of *kulfi* (^oC)

'T_m' was the temperature of freezing medium (^oC)

'P' was the constant (0.25 for cylinder)

'R' was the constant (0.0625 for cylinder)

'D' was diameter of mould used (m)

'h' was the heat transfer coefficient during freezing of *kulfi* (W/m^2 K)

'k_f' was the thermal conductivity of frozen *kulfi* (W/m K)

3.4.1.2 *Pham's equation*

One of the most recommended equations for predicting the freezing time of one-dimensional food stuffs is using the mean freezing temperature (T_{fm}) equation given below (Pham, 1986).

$$\theta = \frac{V}{hA_s}\left(\frac{\Delta H_1}{\Delta T_1} + \frac{\Delta H_2}{\Delta T_2}\right)\left(1 + \frac{B_i}{4}\right) \tag{3.2}$$

$$T_{fm} = 1.8 + 0.263T_c + 0.105T_m \tag{3.3}$$

$$\Delta H_1 = \rho_u \left(C_{pu}\left(T_i - T_{fm}\right)\right) \tag{3.4}$$

$$\Delta H_2 = \rho_f \left(L_f + C_{pf}\left(T_{fm} - T_c\right)\right) \tag{3.5}$$

$$\Delta T_1 = \frac{T_i + T_{fm}}{2} - T_m \tag{3.6}$$

$$\Delta T_2 = T_{fm} - T_m \tag{3.7}$$

where,

'θ' was the freezing time of *kulfi* (s)

'ρ_u'- density of unfrozen *kulfi* (kg/m^3)

'ρ_f'- density of frozen *kulfi* (kg/m^3)

'V' was the volume of *kulfi* (m^3)

'h' was the heat transfer coefficient during freezing of *kulfi* (W/m^2 K)

'A_s' was the surface area of the mould (m^2)

'L_f' was the volumetric latent heat of *kulfi* (J/m^3)

'T_c' was the final centre temperature of *kulfi* (°C)

'T_i' was the initial temperature of *kulfi* (°C)

'T_f' was the initial freezing temperature of *kulfi* (°C)

'T_m' was the temperature of freezing medium (°C)

'C_{pu}' was the specific heat of unfrozen *kulfi* (J/kg K)

'C_{pf}' was the specific heat of frozen *kulfi* (J/kg K)

3.4.1.3 *Modification of Plank's equation*

$$\theta = \left[C_{pu}(T_i - T_{if}) + \lambda X_w + C_{pf}\left(T_{if} - T_m\right)\right]\left[1 + 0.008\left(T_i - T_{if}\right)\right] \times \left[\frac{\rho}{T_{if} - T_m}\left(\frac{P \times D}{h} + \frac{R \times D^2}{k_f}\right)\right] \quad (3.8)$$

where,

'θ' was the freezing time of *kulfi* (s)

'T_i' was the initial temperature of *kulfi* (°C)

'T_{if}' was the initial freezing temperature of *kulfi* (°C)

'T_m' was the temperature of freezing medium (°C)

'C_{pu}' was the specific heat of unfrozen *kulfi* (J/kg K)

'C_{pf}' was the specific heat of frozen *kulfi* (J/kg K)

'λ' was the latent heat of fusion of ice (J/kg)

'X_w' was the water fraction in *kulfi*

'P' was the constant (0.25 for cylinder)

'R' was the constant (0.0625 for cylinder)

'D' was the diameter of mould (m)

'h' was the heat transfer coefficient during freezing of *kulfi* (W/m^2 K)

'k_f' was the thermal conductivity of frozen *kulfi* (W/m K)

3.4.2 Analytical and empirical methods

3.4.2.1 *Cleland and Earle model*

Cleland and Earle (1984) modified Plank's equation using non-dimensional numbers as follows:

$$\theta = \frac{\rho \Delta H_{ref}}{E_f \left(T_{if} - T_m\right)} \left(\frac{2P_1 R}{h} + \frac{4P_2 R^2}{k_f} \right) \left[1 - \frac{1.65 Ste}{k_f} \left(\frac{T_c - T_m}{T_{ref} - T_m} \right) \right] \quad (3.9)$$

$$P_1 = 0.5(1.026 + 0.5808 Np_k + N_{Ste}(0.2296 N_{Pk}) + 0.105) \quad (3.10)$$

$$P_2 = 0.125(1.202 + N_{Ste}(3.410 N_{Pk}) + 0.73360 \quad (3.11)$$

$$N_{Ste} = \frac{C_{pf} \left(T_{if} - T_m\right)}{\Delta H_{ref}}$$

(3.12)

$$N_{Pk} = \frac{C_{pu} \left(T_i - T_{if}\right)}{\Delta H_{ref}} \quad (3.13)$$

where,

'θ' was the freezing time of *kulfi* (s)

'ρ' was the density of *kulfi* (kg/m^3)

N_{Ste} –Stefen's number

N_{Pk} – Plank's number

ΔH_{ref} was the enthalpy at reference temperature (-20°C)

'D' was the diameter of mould (m)

'E_f' was the shape factor (2 for cylinder)

'h' was the heat transfer coefficient during freezing of *kulfi* (W/m^2 K)

'k_f' was the thermal conductivity of frozen *kulfi* (W/m K)

'T_c' was the final temperature of *kulfi* (°C)

'T_{if}' was the initial freezing temperature of *kulfi* (°C)

'T_m' was the temperature of freezing medium (°C)

'T_i' was the initial temperature of *kulfi* (°C)

'C_{pu}' was the specific heat of unfrozen *kulfi* (J/kg K)

'C_{pf}' was the specific heat of frozen *kulfi* (J/kg K)

3.5 Measurement of Thermo-physical Properties of *Kulfi* Concentrate

The thermal properties such as thermal conductivity and thermal resistivity of *kulfi*, prepared by the two methods, were measured using KD2 Pro thermal properties analyser (Decagon Devices Inc., Pullman, Washington, USA) (Fig. 3.6.). The thermal properties were measured in the temperature range of 30 to -20°C. Other properties such as density, specific heat, ice content, initial freezing point and enthalpy were determined using appropriate equations.

Fig. 3.6. KD2 Pro thermal properties analyser

3.6 Prediction of Thermo-physical Properties

3.6.1 Thermal conductivity

As described by Choi and Okos (1986), a set of empirical correlations developed based on food composition data was used for determination of thermal conductivity.

For water:

$$k_w = 0.57109 + 1.762 \times 10^{-3} T - 6.7036 \times 10^{-6} T^2 \quad (3.14)$$

For ice:

$$k_{ice} = 2.21960 - 6.2489 \times 10^{-3} T + 1.0154 \times 10^{-4} T^2 \quad (3.15)$$

For protein:

$$k_{prot} = 0.17881 + 1.1958 \times 10^{-3} T - 2.7178 \times 10^{-6} T^2 \quad (3.16)$$

For fat:

$$k_{fat} = 0.18071 - 2.7604 \times 10^{-3} T - 1.7749 \times 10^{-7} T^2 \quad (3.17)$$

For carbohydrate:

$$k_{carb} = 0.20141 + 1.3874 \times 10^{-3} T - 4.3312 \times 10^{-6} T^2 \quad (3.18)$$

For fibre:

$$k_{fibre} = 0.18331 + 1.2497 \times 10^{-3} T - 3.1683 \times 10^{-6} T^2 \quad (3.19)$$

For ash:

$$k_{ash} = 0.32961 + 1.4011 \times 10^{-3} T - 2.9069 \times 10^{-6} T^2 \quad (3.20)$$

From the above thermal conductivities of the individual constituents, the effective thermal conductivity (k) of *kulfi* was calculated using

$$k = \sum x_i^v k_i \quad (3.21)$$

where,

'k' was the thermal conductivity of *kulfi* (W/m K)

'k_w' was the thermal conductivity of water (W/m K)

'k_{ice}' was the thermal conductivity of ice (W/m K)

'k_{prot}' was the thermal conductivity of protein (W/m K)

'k_{fat}' was the thermal conductivity of fat (W/m K)

'k_{carb}' was the thermal conductivity of carbohydrates (W/m K)

'k_{fibre}' was the thermal conductivity of fibre (W/m K)

'k_{ash}' was the thermal conductivity of ash (W/m K)

'T' was the temperature of *kulfi* (°C)

3.6.2 Enthalpy

Enthalpy of unfrozen *kulfi* could be obtained as the weighted average of the enthalpies of its major constituents namely water, fat, carbohydrates, proteins, fibre and

ash (Mannapperuma and Singh, 1988). The Chen's equation (Eq. 3.22) used for computation of enthalpy is given below.

$$H = H_f + \left(t - t_f\right)\left(1.0 - 0.55x_s - 0.15x_s^3\right) \tag{3.22}$$

where,

'H' was the enthalpy of *kulfi* (J/kg)

'H_f' was the enthalpy of *kulfi* at initial freezing temperature (J/kg)

't' was the temperature of *kulfi*

't_f' was the initial freezing temperature of *kulfi*

'x_s' was the mass fraction of various solids of *kulfi*

The enthalpy of frozen *kulfi* was calculated using the following Schwartzberg's (2007) equation.

$$H = \left[C_f + \left(X_{wo} - BX_s\right)\left(\frac{\Delta H_0}{T_0 - T_R} \times \frac{T_0 - T_{if}}{T_0 - T}\right)\right]\left(T - T_R\right) \tag{3.23}$$

where,

'H' was enthalpy at given temperature 'T' (J/kg)

'C_f' was the specific heat of frozen *kulfi* (J/kg K)

'X_{wo}' was the water content in *kulfi*

$BX_s = 0.4X_p$

'X_p' was the protein content in *kulfi*

'ΔH_0' was the enthalpy of water at 0°C (J/kg)

'T_{if}' was the initial freezing temperature of *kulfi* (^oC)

'T_R' was the reference temperature (-40^oC)

'T' was the temperature of *kulfi* (^oC)

3.6.3 Specific heat

The specific heat of the unfrozen food 'c_u' was determined using the formula given below (Eq. 3.24).

$$c_u = \sum c_i x_i \tag{3.24}$$

where, 'c_i' was the specific heat of individual food constituents and 'x_i' was the mass fraction of the food constituents.

3.6.4 Initial freezing point

The equation proposed by Boonsupthip *et al.* (2009), based on average molecular weights of food constituents, was used for determination of initial freezing point (Eq. 3.25).

$$\frac{1}{T_{fi}} = \frac{1}{T_{fo}} - \frac{R}{\lambda_{ice} M_w} \ln\left(\frac{\frac{\left(X_w - X_b\right)}{M_w}}{\left(\frac{X_u - X_b}{M_w}\right) + \sum_i \left(\frac{X_i}{M_i}\right)} \right) \tag{3.25}$$

where,

'T_{fi}' was the initial freezing temperature of *kulfi* (K or °C)

'T_{f0}' was the freezing temperature of pure water (273.15 K)

'X_w' was the total amount of water

'X_b' was the mass fraction of bound water

'X_i' was the mass fraction of major food constituents

'M_w' was the molecular weight of water, and

'M_i' was the molecular weight of major food constituents

The mass of various constituents was calculated from the total mass of food excluding the amount of ice. This model predicted the initial freezing point of foods more accurately than other models (Boonsupthip *et al.,* 2009).

3.6.5 Ice fraction/ ice content

The empirical equation (Eq. 3.26) proposed by Tchigeov (1979) was used to estimate the mass fraction of ice.

$$\frac{X_{ice}}{X_w} = \frac{1.105}{1 + \left(\frac{0.70138}{\ln\left(T_{fi} - T + 1\right)} \right)} \tag{3.26}$$

where,

'X_{ice}' was the mass fraction of ice in *kulfi*

'X_w' was the mass fraction of water in *kulfi*

'T' was the temperature of *kulfi* (°C)

'T_{fi}' was initial freezing temperature of *kulfi* (°C)

3.6.6 Density

Density was calculated using the mass fraction and density of the individual food constituents. The density 'ρ' of *kulfi* was calculated using Eq. 3.27.

$$\rho = \frac{(1-\varepsilon)}{\sum \frac{x_i}{\rho_i}} \tag{3.27}$$

where,

'ρ' was the density of *kulfi* (kg/m^3)

'ε' was the porosity

'x_i' was the mass fraction of individual food constituents

'ρ_i' was the density of individual food constituents (kg/m^3)

3.7 Determination of Heat Transfer Coefficient

3.7.1 Assumptions for modeling of heat transfer during freezing of *kulfi*

- *Kulfi* samples were assumed to be cylindrical in shape
- The heat fluxes were directed along the radius
- The temperature of freezing medium was constant during freezing
- The initial properties and temperature distribution of *kulfi* concentrate were uniform

3.7.2 Lumped thermal capacity model

The model considered a lump product with surface area 'A', volume 'V', density 'ρ', thermal conductivity 'k' and specific heat 'C_p' having the initial temperature T_i and surrounded by a medium of temperature T_∞ . The transient response of the product was

determined by relating the internal energy with convective heat exchange at the surface as follows:

$$-\rho V C_P \frac{dT}{dt} = hA(T - T_\infty) \tag{3.28}$$

where, 'T' was the temperature, 't' was the time and 'h' was the convective heat transfer coefficient. By integrating the above equation and applying the boundary conditions $T = T_i$ at $t = 0$ and $T=T_t$ at $t = t$, Eq. 3.29 was obtained.

$$\ln\left[\frac{T_t - T_\infty}{T_i - T_\infty}\right] = -\left[\frac{hA}{\rho V C_P}\right] t \tag{3.29}$$

Linearization of above equation yielded Eq. 3.30

$$\left[\frac{T_t - T_\infty}{T_i - T_\infty}\right] = \exp\left[-\frac{hA}{\rho V C_P}\right] t \tag{3.30}$$

The Eq. 3.30 explains the variation in product temperature with time. The variation depends on the parameter $-\frac{hA}{\rho V C_P}$, and it was assumed that the product took infinite time to reach the surrounding temperature and thus attain steady state condition. The dimensionless term on the right hand side of Eq. 3.30 was rearranged as:

$$\left[\frac{hA}{\rho V C_P}\right] t = \left[\frac{hA}{kA}\right]\left[\frac{A^2 k}{\rho V^2 C_P} t\right] = \left[\frac{hl}{k}\right]\left[\frac{\alpha t}{l^2}\right] = Bi_h Fo_h \tag{3.31}$$

where, 'α' was thermal diffusivity $\left(\alpha = \frac{k}{\rho C_P}\right)$ and '*l*' was the characteristic length of the product.

Considering *kulfi* as a cylinder, the characteristic length was calculated using Eq. 3.32.

$$l = \frac{\text{Volume of the cylindrical } \textit{kulfi} \text{ sample}}{\text{Surface area of cylindrical } \textit{kulfi} \text{ sample}} = \frac{r}{2} \tag{3.32}$$

The lumped capacity model is applicable only when heat transfer Biot number is less than 0.1.

$$Bi_h = \left[\frac{hL}{k}\right] \leq 0.1 \text{ (Kumar, 2008)} \tag{3.33}$$

3.7.3 One-dimensional transient heat conduction equation

The surface heat transfer coefficient of a product having one dimensional geometry such as infinite slab, cylinder or sphere with an internal temperature gradient was determined from the one-dimensional transient heat conduction equation (Fricke and Becker, 2002) given below:

$$\left(\frac{1}{x^a}\right)\left(\frac{\partial}{\partial x}\right)\left[x^a \frac{\partial\left(T_t - T_\infty\right)}{\partial x}\right] = \frac{1}{\alpha}\left[\frac{\partial\left(T_t - T_\infty\right)}{\partial t}\right] \tag{3.34}$$

where, a = 1 for cylinder. The initial and boundary conditions were as follows:

$$T_{t=0} = T_i$$

$$\frac{\partial T}{\partial r_0} = 0$$

$$-k\frac{\partial T}{\partial r_0} = h(T_{r_0=r} - T_\infty) \tag{3.35}$$

For infinite cylinders, ‘r’ was the radius and r_0 was the radial distance (Fricke and Becker, 2002).

In order to non-dimensionalize the solution of Eq. 3.35, two dimensionless parameters were introduced namely, the Biot’s number (Bi) and Fourier’s (Fo) number.

Biot number is given by

$$Bi = \frac{hl}{k} \tag{3.36}$$

Fourier number is given by:

$$Fo = \frac{\alpha\theta}{l^2} \tag{3.37}$$

The infinite series solution for the dimensionless centre temperature distribution for Eq. 3.35 was given by Carslaw and Jaeger (1980) as follows:

$$\left(\frac{T_t - T_\infty}{T_i - T_\infty}\right) = \sum_{i=1}^{n} A_n B_n \tag{3.38}$$

where, Fourier and Bessel coefficients (A_n & B_n) were calculated using Eqs. 3.39 and 3.40.

$$A_n = \frac{2Bi}{\mu_n^2 + Bi^2 + J_0(\mu_1)} \tag{3.39}$$

$$B_n = \exp(-\mu_n^2 Fo) \tag{3.40}$$

where, μ_n was the characteristic coefficient, which was dependent on the geometry of the product. The characteristic equation for cylinder is given as Eq. 3.41.

$$\frac{J_0(\mu_1)}{J_1(\mu_1)} = \frac{\mu_1}{Bi} \tag{3.41}$$

The Biot number was obtained from appropriate equations given above, depending upon the geometry. Finally, the surface heat transfer coefficient 'h' was obtained through algebraic manipulation of the Biot number.

3.8 Physico-chemical Properties of *Kulfi*

3.8.1 Total solids (TS)

The TS content of *kulfi* samples was determined by AOAC method 941.08 (AOAC, 2005). About 5 g of sample was exactly weighed in a petri-plate. This sample was heated on a steam bath for 30 min and then the petri-plates were kept in a convection oven (Anamatrix Instrument Technologies Pvt. Ltd., Bengaluru.) set at 102±1°C. The final dried weight of the cooled sample was determined at the end of 5 h, and the TS content was determined using Eq. 3.42. Estimation of total solids was done in triplicate, and the mean value was computed.

$$TS(\%) = \frac{Dried\ sample\ weight}{Weight\ of\ sample\ taken} \times 100 \quad (3.42)$$

3.8.2 Titratable acidity

About 10 g of molten *kulfi* sample was accurately weighed and added to a conical flask and diluted with twice its volume of CO_2 free water. About 0.5 mL of phenolphthalein indicator was added. The solution was titrated against 0.1N NaOH to a persistent pale pink end point and titre value was noted. Titratable acidity of the product was calculated using the following formula. The titratable acidity of the samples was estimated three times and the mean values were computed.

$$\text{Titratable acidity (\% Lactic acid)} = \frac{9 \times N \times TV}{W} \quad (3.43)$$

'N'-Normality of NaOH

'TV'-Titre value

'W'-Weight of sample taken.

3.8.3 pH

Exactly 50 mL of molten *kulfi* rendered homogeneous was taken in a glass beaker. The sample was tested for pH at 30°C by direct immersion of electrode of the pH meter (model pH Tutor, Eutech Instruments Pvt. Ltd., Singapore) into the sample. The pH meter was calibrated using standard buffer solutions at 30°C. Estimation of pH was done in triplicate.

3.8.4 Fat

The fat content of *kulfi* was estimated using Mojonnier method (method 952.06, AOAC, 2005). About 10 g of accurately weighed sample was mixed with 2 mL of ethanol in a beaker. The sample was digested using 10 mL of concentrated HCl at 70-80°C in a water bath for about 1 h, and 10 mL of ethyl alcohol was added and cooled. The contents were transferred to Mojonnier fat extraction flask. Exactly 25 mL of diethyl ether was added to the above contents and the flask was closed with the cork stopper. The contents were then shaken vigorously for 1 min. Exactly 25 mL of petroleum ether was

added, and after mixing, the flask was allowed to stand for 30 min till the ethereal layer was completely separated from the aqueous layer. The supernatant layer was carefully decanted into a 250 mL previously weighed conical flask. The extraction was repeated two times using 15 mL each of diethyl and petroleum ethers. The solution was transferred to conical flask, and it was evaporated slowly on a steam bath to remove the solvent. The residual fat was dried in the oven (about 90 min) at 100±2°C to constant weight. The fat content of *kulfi* was calculated as:

$$\text{Fat content}(\%)=\frac{W_d - W_i}{W_s}\times 100 \tag{3.44}$$

where, 'W_s' was the weight of sample (g), 'W_i was the initial weight of conical flask and 'W_d' was the final weight of conical flask after drying (g). Estimation of fat content was done in triplicate for all samples.

3.8.5 Protein

The protein content of *kulfi* was estimated using micro-Kjeldahl method with slight modifications (method 930.33, AOAC, 2005). About 0.2 g of accurately weighed sample was taken in a 300 mL digestion tube, followed by addition of 5 g of digestion mixture and 15-20 mL of concentrated H_2SO_4. The samples were digested until a clear filtrate was obtained. Then the contents were cooled to room temperature, and about 25-30 mL of 50% (w/w) NaOH was added to make the solution alkaline. The contents were distilled and the liberated ammonia was collected in 25 mL of saturated boric acid solution containing 3-5 drops of mixed indicator (made by adding 10 mL of 0.1 % bromocresol green + 2 mL of 0.1% methyl red indicator in 95% ethyl alcohol). Distillation was continued until 65 mL (approx.) of distillate was collected, and the contents were titrated against 0.1N HCl till the pale pink end point was attained. The same procedure was followed for blank also. The percentage of protein in the sample was calculated as:

$$\text{Nitrogen, }\%=\frac{1.4007\times\left(V_s - V_b\right)\times M}{W} \tag{3.45}$$

where,

'V_s' and 'V_b' are mL of HCl used for titration of sample and blank, respectively

'M' was molarity of HCl solution and

'W' weight of sample taken, g

Protein, % = %Nitrogen x 6.38 (3.46)

The protein content of the samples was determined and the mean values were computed.

3.8.6 Lactose

Lactose content was estimated by Lane-Eynon method as described in BIS (BIS, 1981). About 25 g of molten *kulfi* was exactly weighed into a 250 mL beaker and 10 mL of lukewarm water was added. The contents were mixed and precipitated with neutral lead acetate solution and one drop of alumina cream. After 15 min, the excess lead acetate solution was precipitated with sufficient amount of saturated sodium oxalate solution and the contents were filtered through Whatman No.1 filter paper into a 250 mL volumetric flask. The precipitate on the filter paper was washed with hot water and the washings were collected in the volumetric flask. After cooling, the volume was made up to 250 mL with distilled water. The filtrate, which comprised of the sugar solution, was filled in the burette and titrated against a mixture of 5 mL each of Fehling's A and Fehling's B solution using methylene blue as indicator. The titration was carried out in boiling condition over a flame and end point was determined when the solution turned into clear brick red colour. The titre values were used to compute lactose content of the product. Estimation of lactose was done in triplicate for all samples.

$$\% \text{ Reducing sugars (\% Lactose)} = \frac{25 \times X}{W \times V} \quad (3.47)$$

where,

'X' was the lactose equivalent in 'mg' of standard lactose solution required for 10 mL of Fehling's solution.

'W' was the weight of sample taken

'V' was the volume of filtrate required for 10 mL of Fehling's solutions.

3.8.7 Sucrose

Sucrose content was estimated by Lane-Eynon method as described in BIS (BIS, 1981). Exactly 25 g of molten *kulfi* sample was accurately weighed into a 250 mL beaker and added with 10 mL of lukewarm water. The contents were mixed and precipitated with neutral lead acetate solution and one drop of alumina cream. After 15 min, the excess lead acetate solution was precipitated with sufficient amount of saturated sodium oxalate solution and the contents were filtered through Whatman No.1 filter paper into a 250 mL volumetric flask. Titration was carried out as discussed in case of lactose estimation for determination of reducing sugars before inversion. For determination of reducing sugars after inversion, 50 mL of filtered solution was transferred to a 200 mL graduated flask and 25 mL of water and 10 mL of 6.34 N HCl was added and mixed thoroughly. The contents were allowed to stand for 3 days at a temperature of approximately 20°C. It was then diluted to 200 mL. Titrations were carried out against Fehling's solution as described above.

Standard invert sucrose solution was prepared using sucrose, which was dried in vacuum desiccator overnight. Exactly 23.75 g of sucrose was taken in 1 L volumetric flask and 100 mL of water and 10 mL of 6.34 N HCl was added and mixed thoroughly. The reducing sugar of this solution was determined as discussed in the above paragraph. Estimation of sucrose content of the samples was done in triplicate.

$$\% \text{ Reducing sugars after inversion} = \frac{25 \times X}{W \times V} \qquad (3.48)$$

where,

'X' was the sucrose equivalent in 'mg' of standard invert sucrose solution required for 10 mL of Fehling's solution

'W' was the weight of sample taken

'V' was the volume of filtrate required for 10 mL of Fehling's solutions.

$$\text{Sucrose content, \%} = (\text{Reducing sugars after inversion} - \text{Original reducing sugar}) \times 0.95 \qquad (3.49)$$

3.8.8 Ash

The ash content of *kulfi* was determined by ashing the samples in the muffle furnace (Murophage Scientific Ltd., Mysuru) maintained at 550±2°C until light grey ash resulted. After ashing, the samples were cooled in a desiccator and the weights of crucibles were recorded. Three replications were done and the mean values were computed (method 945.46, AOAC, 2005). Estimation of ash content of the samples was done in triplicate.

$$\text{Ash content (\%)} = \frac{\text{Weight of ash (g)}}{\text{Sample weight (g)}} \times 100 \tag{3.50}$$

3.9 Colour

The colour of *kulfi* after freezing was measured using a computer-based image analysis technique. The samples were placed on a black sheet and images were captured using a 7.1 MP digital camera (model FMZ8, Panasonic Corporation, Tokyo, Japan). The images were then imported into Adobe Photoshop 7.0 software, and the 'L', 'a' and 'b' values were obtained from the histogram window. According to International Commission of Illumination (CIE, 1986), colour could be defined by three parameters namely L^*, a^* and b^*. The L^* value was a measure of lightness or luminance, which ranged from 0 (black) to 100 (white) and a^* and b^* were the two chromatic components, which ranged from -120 to 120 (a^* from green to red and b^* from blue to yellow) (Adobe Photoshop 7.0 User Guide for Macintosh and Windows, 1998). The Adobe software uses a scale, ranging from 0 to 255, to characterize L (lightness), 'a' and 'b'. These values were converted into machine independent CIELAB L^*, a^* and b^* values using the following formulae (Yam and Papadakis, 2004).

$$L^* = \left[\frac{L}{255}\right] \times 100 \tag{3.51}$$

$$a^* = \left[\frac{240a}{255}\right] - 120 \tag{3.52}$$

$$b^* = \left[\frac{240b}{255}\right] - 120 \tag{3.53}$$

Yellowness index (YI) and whiteness index (WI) were calculated from the L^*, a^* and b^* values using the following formula.

$$YI = 142.86\left[\frac{b^*}{L^*}\right] \quad \text{(Pagliarini } et\ al.\text{, 1990)} \quad (3.54)$$

$$WI = 100 - \sqrt{\left(100 - L^*\right)^2 + a^{*2} + b^{*2}} \quad \text{(Pagliarini } et\ al.\text{, 1990)} \quad (3.55)$$

where, L^*, a^* and b^* represented the colour values of *kulfi* after freezing. Colour of the samples were measured three times and the mean values were tabulated.

3.10 Melting Properties

The meltdown of ice cream and frozen desserts was quantified by determining the mass that drips from the product through a mesh screen as a function of time when the product was allowed to melt at a constant temperature (Bolliger *et al.*, 2000). The melting properties of *kulfi* were measured using two methods.

3.10.1 Melting rate

Melting rate is the rate at which the sample melts at a constant temperature. It is expressed as the mL of sample melted for 15 min of time. It was measured using the method described by Giri *et al.* (2013). In this method, 55 g of *kulfi* sample was taken and kept on the platform. The platform was positioned inside the incubator at 30°C to measure the time required to complete meltdown of the sample (Fig. 3.7.). Immediately after keeping the sample on metal mesh, the time taken for complete meltdown was noted. Melting rate was expressed as mL of sample melted in 15 min, and each sample was analyzed in triplicate.

3.10.2 Melting curve

Melting curve is a plot of weight percentage of product melted (y-axis) versus time (x-axis). It was measured by the method described by Goff and Hartel (2013). In this method, 55 g of *kulfi* sample was taken and kept on the platform. The platform included sample holder and a weighing balance upon which the beaker for collection of meltdown was placed. The sample was placed over a wire mesh having 120 openings per square

inch, which in turn was placed above the funnel (Fig. 3.8a). *Kulfi* was placed above the wire mesh and the whole arrangement was placed inside the incubator being set at 20°C (Fig. 3.8b). The weight of sample melted was recorded manually at every 5 min interval till it completely melted. The melting experiments were carried out in triplicate, and the mean of melted sample weight was calculated.

Fig. 3.7. Experimental setup for determination of melting rate

(a) (b)

Fig. 3.8. Experimental setup for determination of melting curve of *kulfi*

3.11 Textural Properties

Textural profile analysis (TPA) of *kulfi* was performed using TA.XT Plus texture analyser (Stable Micro Systems, Godalming, Surrey, UK) equipped with 50 kg load cell (Fig. 3.9). TPA was done to characterize the maximum force required to shear through the sample. Frozen *kulfi* samples of 31 mm diameter were cut using Warner-Bratzler blade (HDP/WBR) (Fig. 3.10). This rectangular slotted blade had a knife edge at one end and a flat Guillotine edge at the other. The blade was firmly held by means of the blade holder, which was screwed directly into the arm of the texture analyzer. The compression depth used was 15 mm and trigger force was 2 g. The maximum force realized at the point of return of the probe was measured as hardness of the sample. Each sample was analysed at least six times and the hardness values were averaged.

Fig. 3.9. TA.XT Plus texture analyzer

Fig. 3.10. Platform and probe used for Warner-Bratzler shear test

3.12 Sensory Evaluation of *Kulfi*

Kulfi samples were evaluated by a panel of experienced judges and the data obtained were used to compute the ranking of samples using fuzzy-logic approach. This is an important decision-making tool for comparing the samples. By using this, it is also possible to find out the reasons for low and high ranking of products as evaluated by the judges. The quality attributes selected for sensory evaluation were colour & appearance, flavour & taste, body & texture and melting characteristics. The judges were supplied with one control and two samples coded as S1, S2 and S3. The weight of each sample was approximately 55 g. Eleven judges were given the samples for sensory evaluation and the trials were done in triplicate.

The study was done in the sensory evaluation lab of the institute, and the trained panel consisted of faculty, technical staff and doctoral students. The age of the judges varied from 22-58 years, and the panel consisted of 12 members. All members had considerable experience in preparing and evaluating dairy products, particularly *kulfi*. The judges received a sample of 55 g, and testing was carried out in three sessions. The arbitrarily identified samples were ranked in order for colour and appearance, flavour and taste, body and texture and melting characteristics. The study was replicated three times, and the scores obtained were statistically analysed.

Judges were instructed to give tick (✓) mark in the respective fuzzy-scale factor for each of the quality attributes of the sample. The samples were rated as “Excellent”, “Good”, “Medium”, “Fair” and “Not satisfactory”. The judges were asked to indicate the weightage they would like to assign for each quality attribute of *kulfi* by putting a (✓) mark against the appropriate choice as ‘not important’, ‘somewhat important’, ‘important’, ‘highly important’, and ‘extremely important’. The set of observations was analysed using fuzzy comprehensive modeling of sensory scores.

A set of three numbers known as “triplet” was used to represent triangular membership function distribution pattern of sensory scores, and the distribution pattern of 5-point sensory scores consisting of “Not satisfactory/Not at all important,” “Fair/ Somewhat important,” “Medium/Important,” “Good/Highly important” and

"Excellent/Extremely important" was followed. The scorecard developed for sensory evaluation of *kulfi* by fuzzy-logic method is given in Appendix-I.

3.13 Statistical Analyses

Data on physico-chemical, melting and textural characteristics were analysed using One-way Analysis of Variance (ANOVA). The treatment means were compared using Tukey's Test of Honestly Significant Difference. The level of significance for comparison of the means was kept at 0.05.

IV RESULTS AND DISCUSSION

This Chapter deals with the presentation and discussion of results drawn from the various experiments conducted for fulfilling the objectives of the current study. It includes modeling of the freezing time of cryogenic freezing of *kulfi*, determination of heat transfer coefficient during cryogenic freezing and comparison of physico-chemical, sensory, melting and textural properties of *kulfi* prepared from concentrated milk and dry mix using liquid nitrogen (LN_2). Also, the freezing behaviour of *kulfi* milk concentrate frozen using deep freeze method was analysed and compared.

4.1 Freezing Performance

4.1.1 Freezing curve of *kulfi* from milk concentrate during deep freezing

The freezing curve of *kulfi* prepared from condensed milk and frozen in deep freezer is shown in Fig. 4.1. The time taken for reducing the temperature of *kulfi* milk concentrate from 30 to -20°C was 267 min. Freezing followed the normal freezing curve for foods.

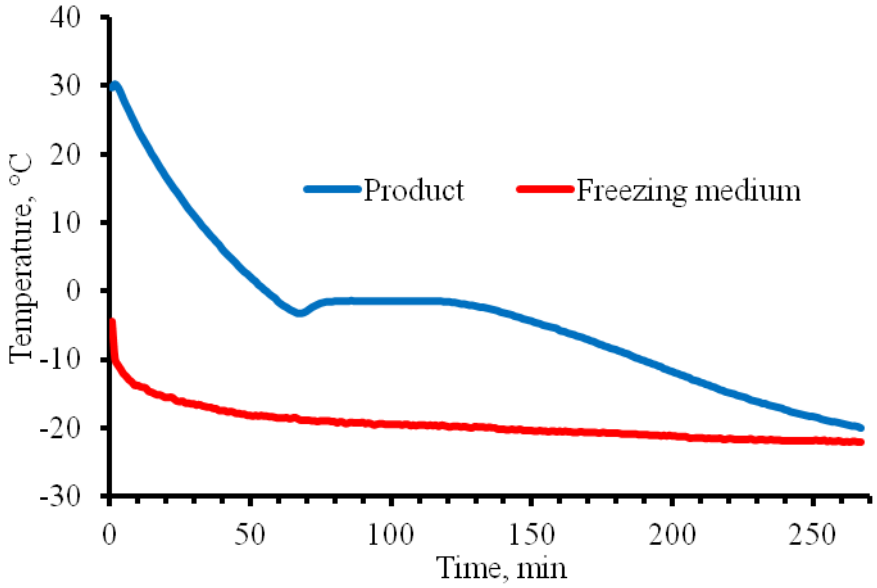


Fig. 4.1. Freezing curve of *kulfi* from milk concentrate in deep freeze method

4.1.2 Cryogenic freezing of *kulfi* prepared from milk concentrate

The freezing curve of *kulfi* prepared from *kulfi* milk concentrate and frozen using LN_2 is shown in Fig. 4.2. The temperature of *kulfi* almost declined steadily from the initial temperature to attain the freezing temperature of -20°C. The freezing curve matched the typical curves seen in other food products. The time required for freezing the milk concentrate from 30°C to -20°C was only 190 s as compared to 267 min in deep freeze method. Thus, cryogenic freezing was much faster as compared to conventional deep freeze method.

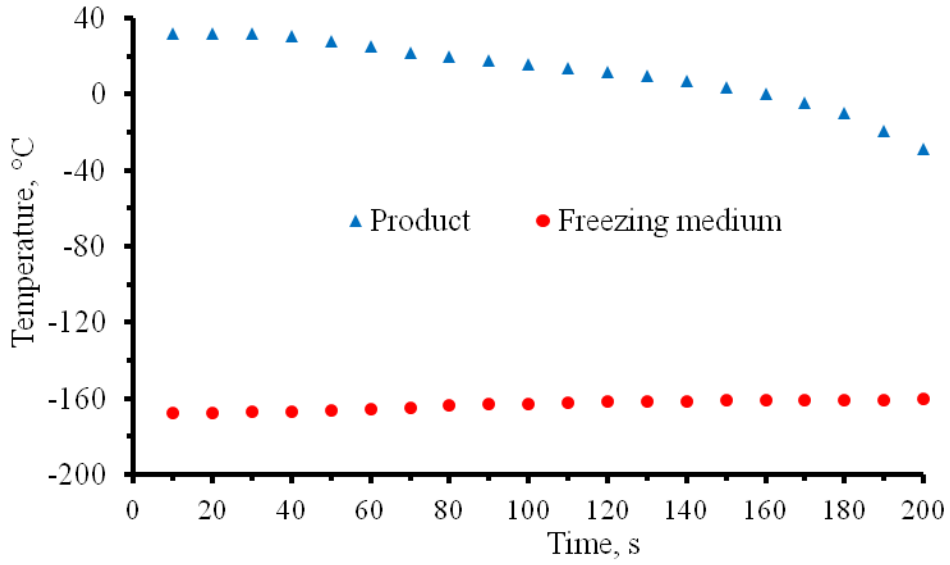


Fig. 4.2. Cryogenic freezing curve of *kulfi* prepared from milk concentrate

4.1.3 Cryogenic freezing of *kulfi* prepared from dry mix

The freezing curve of *kulfi* from dry mix and frozen using LN_2 is shown in Fig. 4.3. Similar to freezing of milk concentrate, there was a steady decline in the temperature of the product. The time required for reducing the temperature from 30 to -20°C was 185 s as compared to 190 s and 267 min for freezing of milk concentrate by cryogenic and deep freeze methods, respectively. The small reduction in freezing time of *kulfi* prepared from dry mix could be due to improved nucleation of the powder particulates.

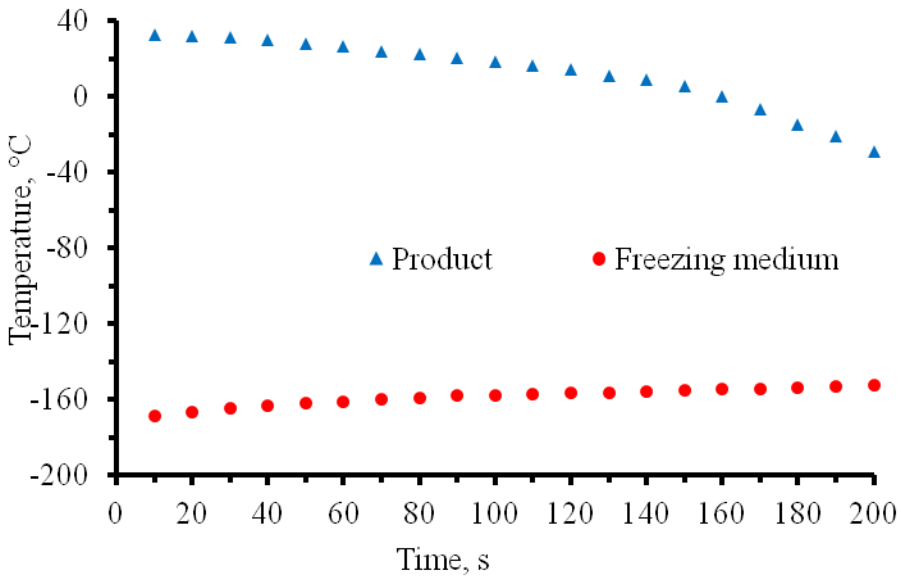


Fig. 4.3. Cryogenic freezing curve of *kulfi* prepared from dry mix

4.1.4 Freezing rate

The freezing rate (°C/s) (defined as the difference between the initial and the final temperature divided by the freezing time) of *kulfi* was much higher in cryogenic freezing than in deep freeze method. It was 0.263°C per second in cryogenic freezing as compared to 0.003°C per second in deep freeze method. Thus, the freezing rate was almost 84.31 times faster in cryogenic freezing.

4.1.5 Freezing time

The time required to freeze the product from an initial temperature to the required final temperature is called freezing time. In this study, the initial and final temperatures of freezing of *kulfi* were kept as 30 and -20°C, respectively. Breyer *et al*. (1966) reported that freezing of 23 cm thick apple pies from the initial temperature of 20 to -17.8°C took 192 min in air blast method while in case of cryogenic freezing, the time taken reduced to as low as 17.5 min.

4.2 Thermo-physical Properties of *Kulfi*

4.2.1 Thermo-physical properties of *kulfi* prepared from *kulfi* concentrate

4.2.1.1 *Density*

The density of *kulfi* prepared from milk concentrate was predicted by using Choi and Okos (1986) method as a function of temperature. As the density of ice is less than that of water, the density of a frozen food would be less than that of the unfrozen product (Singh and Heldman, 2009). The dependence of density on the temperature of *kulfi* frozen by three methods is presented in Fig. 4.4. As expected, the densities of *kulfi* prepared from milk concentrate at -20 and 30°C were 1057.59 and 1102.46 kg/m^3, respectively. The magnitude of change in density would be proportional to moisture content of the product (Singh and Heldman, 2009). Similar observations were also found in *kulfi* concentrate made from dry mix. From Fig. 4.5, it is evident that the density of the product decreased markedly in the temperature range of -5 to 2°C (over 7°C range). This drastic decrease in density could be attributed to phase change of water in the product.

The density decreased because of the way the hydrogen bonds in water were oriented in the frozen product. Specifically, in ice, the water molecules were pushed farther apart than they were in liquid water. The density of *kulfi* concentrate prepared from dry mix was 1058.19 and 1103.46 kg/m^3, respectively at -20°C and 30°C. However, as evident from Fig. 4.5, the phase change of *kulfi* concentrate prepared from dry mix occurred over a narrow temperature range of -7 to -3°C (4°C). Phase change over such a narrow temperature range confirmed that the powder particulates were involved in nucleation, which facilitated faster freezing of the product.

4.2.1.2 *Thermal conductivity*

The thermal conductivity of *kulfi* as a function of temperature was measured using KD2 thermal property analyser, and the plot is presented in Fig. 4.6. It could be seen that the thermal conductivity of the concentrate beyond 0ºC (0 to 30ºC) was almost constant at 0.437 W/m K. In contrast, the thermal conductivity of the *kulfi* milk concentrate below the freezing point (-20 to 0ºC) was as high as 1.395 W/m K. The thermal conductivity

changed sharply in the temperature region of -5 to 0°C due to phase transition from liquid to ice. Such increase in thermal conductivity was expected because the thermal conductivity of ice was approximately four times higher than the thermal conductivity of water (Singh and Heldman, 2009).

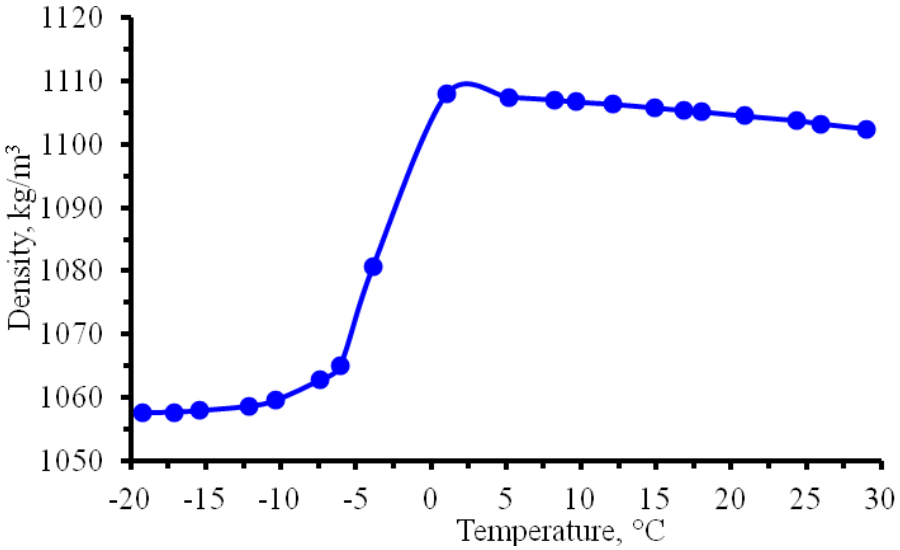


Fig. 4.4. Density of *kulfi* milk concentrate during freezing

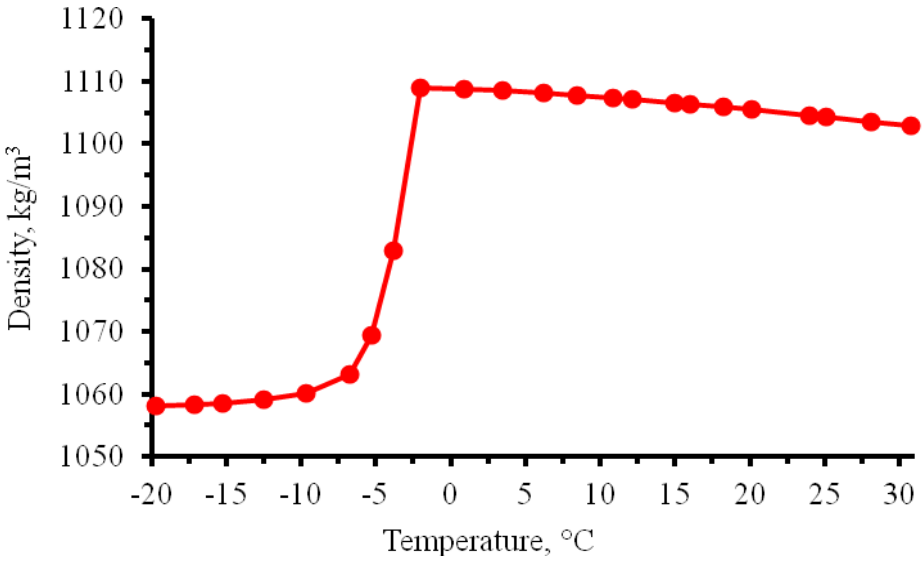


Fig. 4.5. Density of *kulfi* concentrate prepared from dry mix during freezing

The thermal conductivity continued to increase even after phase change from 1.13 W/m K at -5°C to 1.395 W/m K at -20°C. This increasing trend occurred due to the growth of ice crystal size and hardening of the crystals. The results are in compliance with those of apples as reported by Ramaswamy and Tung (1981) and that of lean beef by Heldman and Gorby (1975). Neckel and Mariani (2011) also reported similar trends while predicting the thermal conductivity of beetroot as a function of temperature using the model proposed by Choi and Okos (1986).

The thermal conductivity of *kulfi* concentrate from dry mix also showed similar behaviour during freezing (Fig. 4.7). The thermal conductivities at -20°C and 30°C were 1.294 and 0.471 W/m K, respectively. However, as seen with density changes, the thermal conductivity of *kulfi* concentrate from mix decreased markedly within a narrow temperature range. The thermal conductivity remained almost constant above the freezing point (0°C).

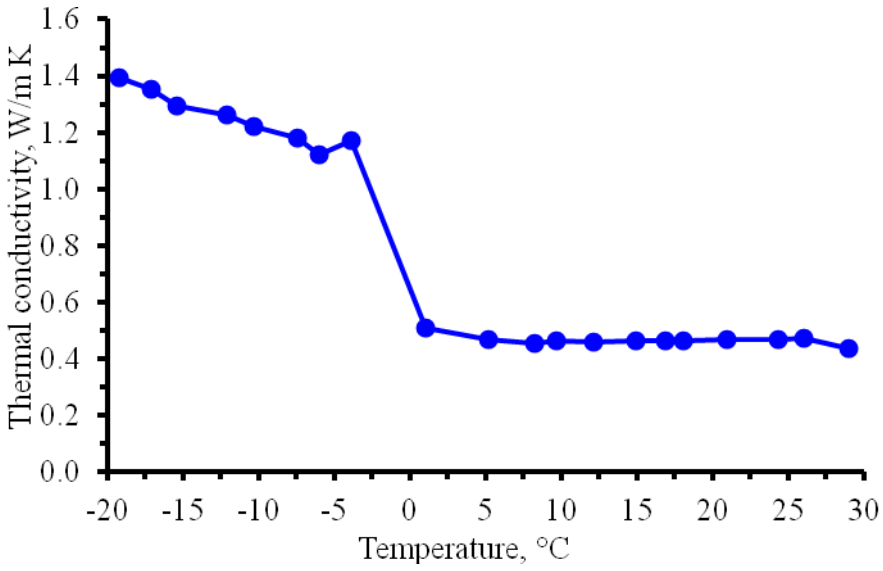


Fig. 4.6. Thermal conductivity of *kulfi* milk concentrate during freezing

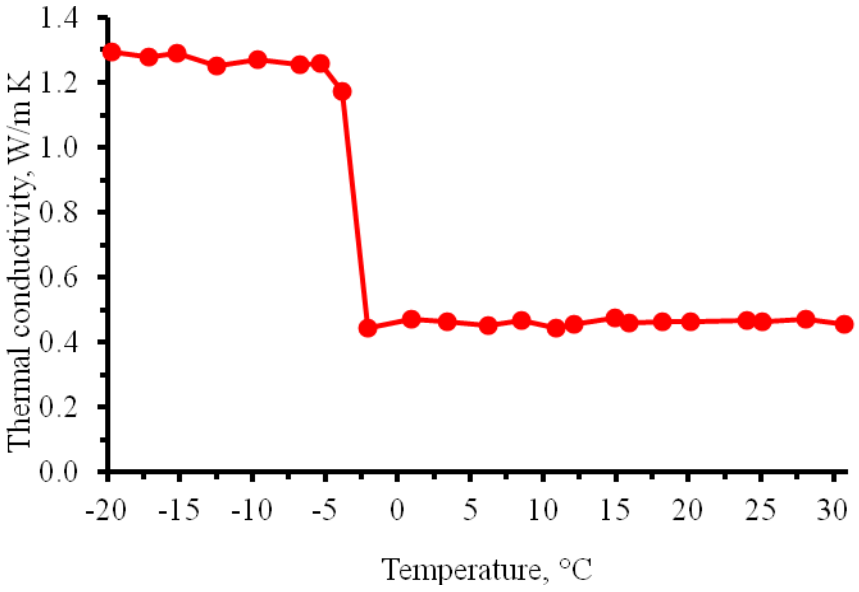


Fig. 4.7. Thermal conductivity of *kulfi* concentrate from dry mix during freezing

4.2.1.3 *Specific heat*

The specific heat of *kulfi* milk concentrate was determined using Choi and Okos (1986) equation as a function of temperature, and the results obtained are plotted in Fig. 4.8. The specific heat of *kulfi* milk concentrate at -20 and 30°C was 2018.79 and 3207.5 J/kg K, respectively. Similar values of *kulfi* concentrate from dry mix were 2014.37 and 3205.86 J/kg K at -20 and 30°C, respectively. There were differences in specific heat capacities because the specific heat of food materials at temperatures below the initial freezing point was expected to be less as compared to those above the initial freezing point. Specifically, the specific heats of water and ice are 4187 J/kg K and 2108 J/kg K, respectively.

The specific heat capacity of water was very high because energy given to water in liquid form was destroyed owing to molecular movement, while that given to ice was used to easily break the intermolecular bonds of its covalent molecular structure, thereby requiring more energy to raise the temperature for water. The results of this study followed the same trend observed for specific heat of frozen sweet cherries as a function of temperature (Heldman, 1982) below the initial freezing point. Neckel and Mariani

(2011) also obtained similar results while predicting specific heat as a function of temperature of beet using the models proposed by Choi and Okos (1986).

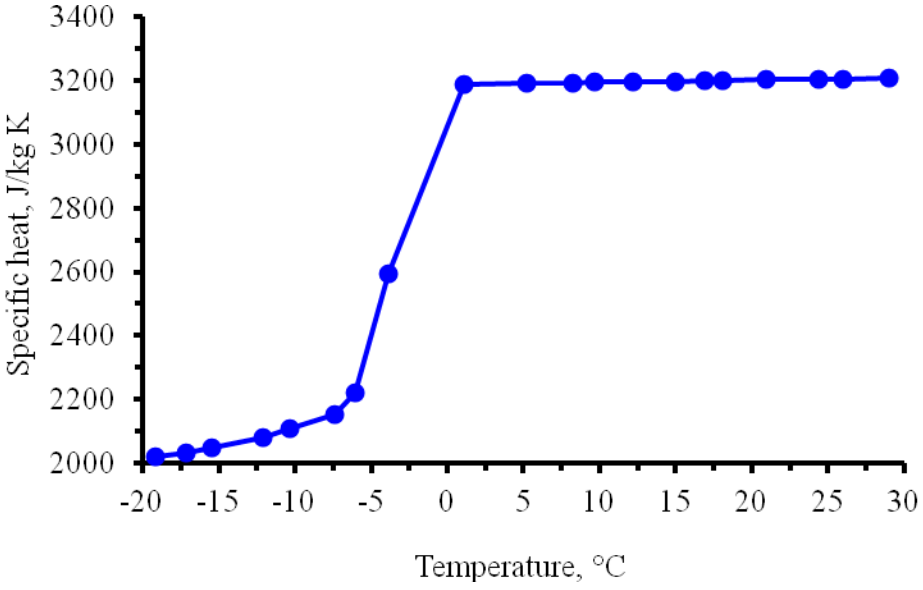


Fig. 4.8. Specific heat of *kulfi* milk concentrate during freezing

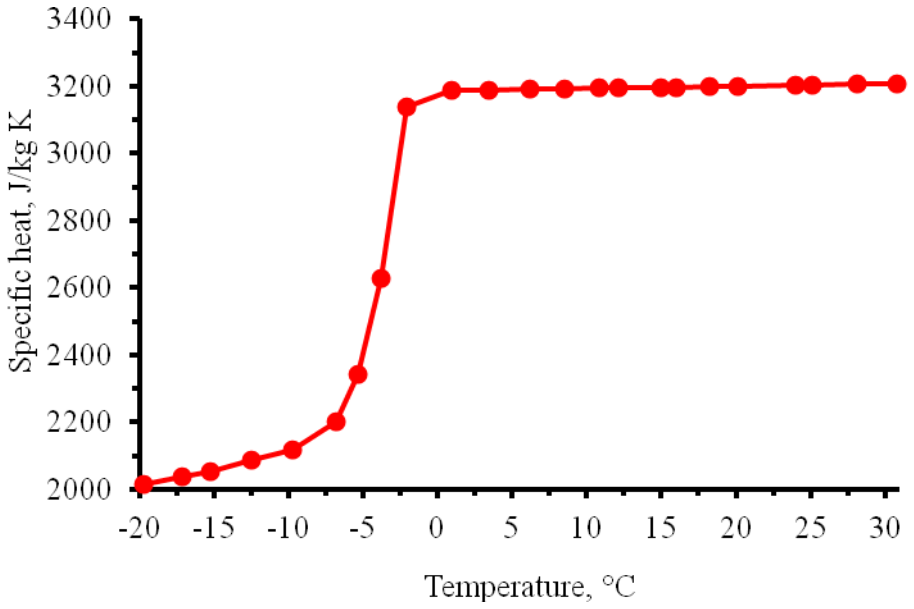


Fig. 4.9. Specific heat of *kulfi* concentrate prepared from dry mix during freezing

4.2.1.4 *Thermal diffusivity*

Thermal diffusivity is an important thermal property associated with the rate of changes in ice temperature. Higher the thermal diffusivity, the faster the propagation of heat into the medium. That is, substances with high thermal diffusivity rapidly adjust their temperature to that of their surroundings, because they could conduct heat quickly in comparison to their volumetric heat capacity.

Thermal diffusivity of *kulfi* milk concentrate at different temperatures was determined using the formula $\alpha=K/\rho\times C_p$, and the values as a function of temperature are presented in Fig. 4.10. The thermal diffusivity at temperatures below the initial freezing point was much higher compared to the temperatures above freezing point. The thermal diffusivities at -20 and 30°C were 6.53×10^{-7} and 1.24×10^{-7} m^2/s, respectively. The changes in thermal diffusivity below the initial freezing temperature followed the same trend as reported by Heldman (1983) for food products. In the freezing zone, the thermal diffusivity increased from the initial freezing point to -20ºC because of the decrease in porosity of ice. As the temperature decreased below initial freezing point, the porosity of ice decreased, thereby increasing the speed of propagation of heat, and consequently, the thermal diffusivity. The changes in porosity of ice were also reflected in its density, as evident from Figs. 4.4 and 4.5.

The thermal diffusivities of *kulfi* concentrate from dry mix at -20 and 30°C were $6.07\times10^{-7}$and 1.33×10^{-7} m^2/s, respectively and were quite similar to that of *kulfi* mix concentrate. However, from Figs. 4.10 and 4.11, it could be seen that the changes in thermal diffusivity near the initial freezing point region were very sharp in the concentrate from dry mix.

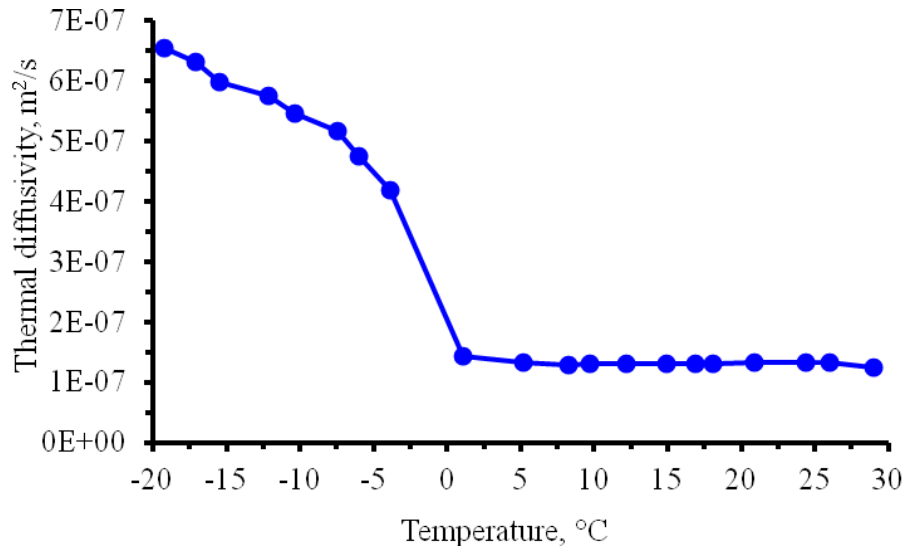


Fig. 4.10. Thermal diffusivity of *kulfi* milk concentrate during freezing

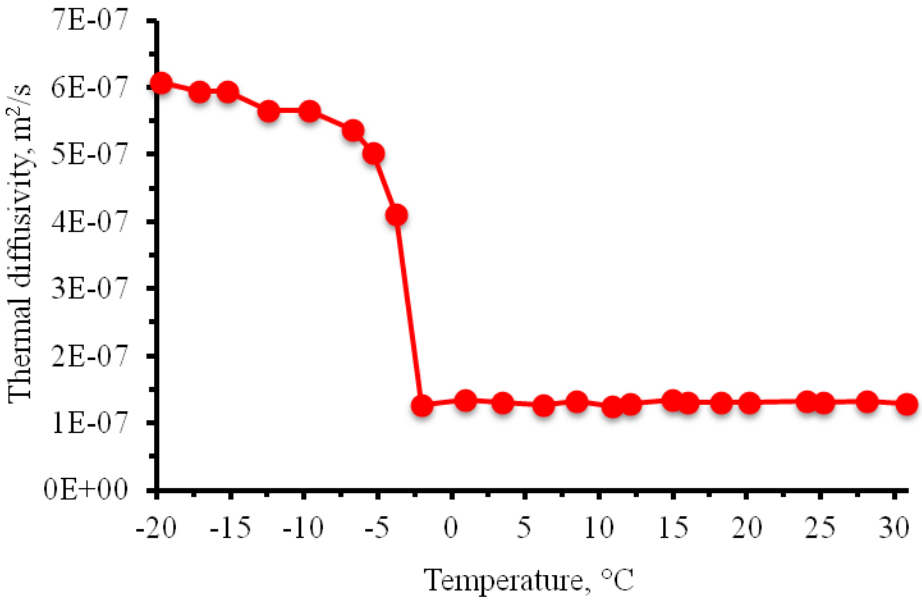


Fig. 4.11. Thermal diffusivity of *kulfi* concentrate from dry mix during freezing

4.2.1.5 *Ice content*

The ice content in the frozen *kulfi* milk concentrate was determined using the Tchigeov equation as a function of temperature below the initial freezing point (Fig. 4.12). The ice content was as high as 90% at -20ºC and was nearly constant in the temperature range of -20 to -10ºC. It decreased to as low as 9% at -3ºC. The results were

in compliance with the results of relationship between unfrozen water fraction and temperature in raspberries (Heldman, 1974). The ice content of *kulfi* concentrate from dry mix at different temperatures was quite similar to that of *kulfi* mix concentrate (Fig. 4.12). However, at -3ºC, the ice content was double that of *kulfi* milk concentrate. This could presumably due to the enhanced nucleation properties of particulates in the dry mix, facilitating the formation of ice.

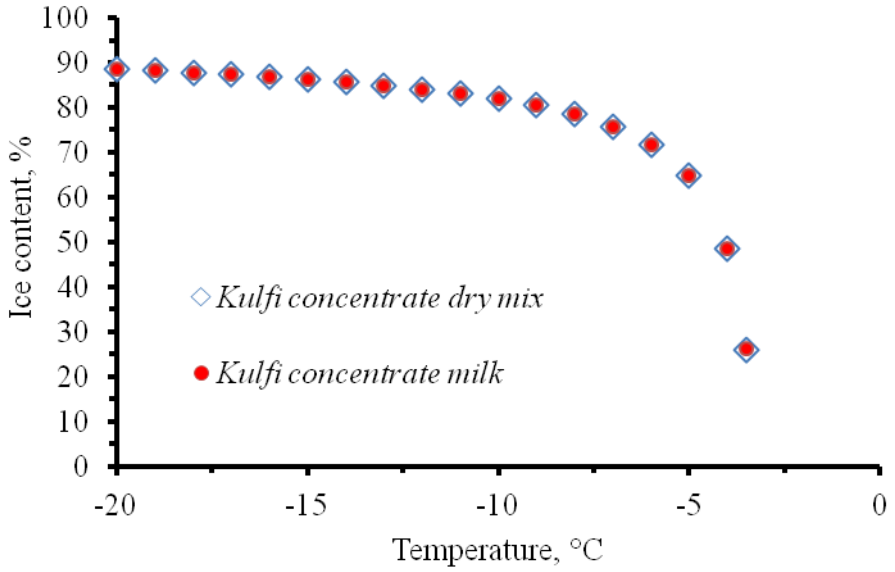


Fig. 4.12. Ice content of *kulfi* concentrates from milk and dry mix as a function of temperature

4.2.1.6 *Enthalpy*

The enthalpy of the *kulfi* milk concentrate was predicted using Schwartzberg equation and the data are presented in Fig. 4.13. As temperature increased towards the initial freezing point, the enthalpy of *kulfi* milk concentrate increased. The enthalpies at -20 and -3°C were 13.10 and 188.65 kJ/kg, respectively. The results were comparable with the enthalpy of sweet cherries as a function of temperature (Heldman, 1982). The enthalpy of *kulfi* concentrate from dry mix was also similar. The values at -20 and -3°C were 12.61 and 181.65 kJ/kg, respectively.

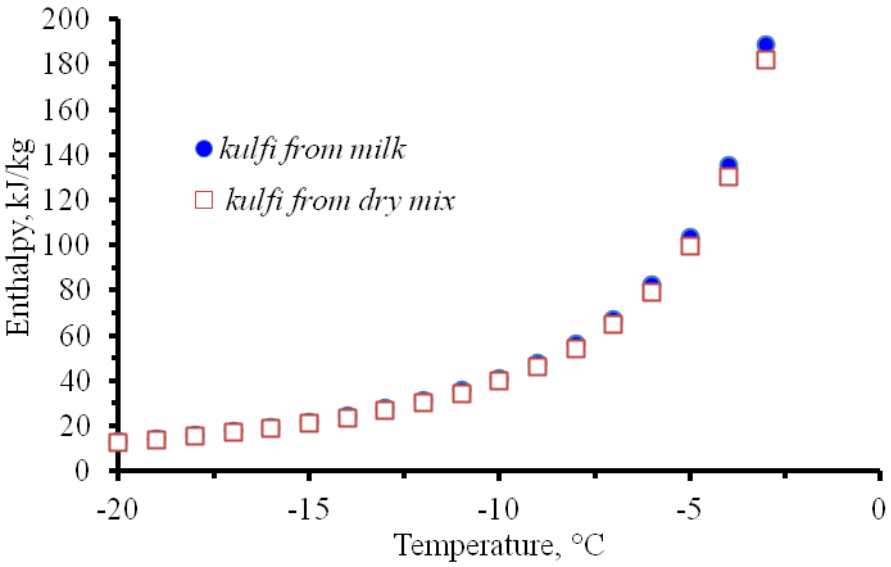


Fig. 4.13. Enthalpy of *kulfi* concentrates from milk and dry mix as a function of temperature

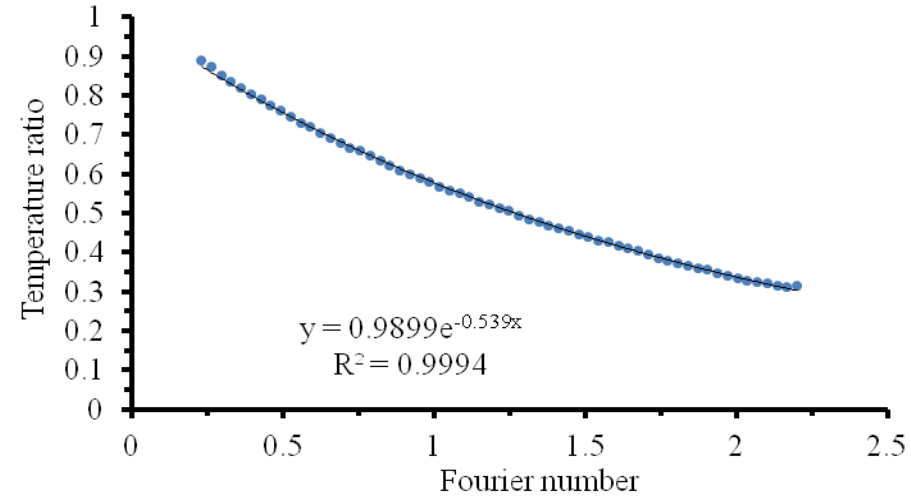
4.2.1.7 *Initial freezing point*

The initial freezing point of *kulfi* milk concentrate was predicted using the Boonsupthip equation (Boonsupthip *et al.*, 2009) as -3.38°C. As the TS content of *kulfi* milk concentrate was higher (as compared to water), freezing point depression occurred. In comparison, the initial freezing point of *kulfi* concentrate from dry mix was -3.25°C.

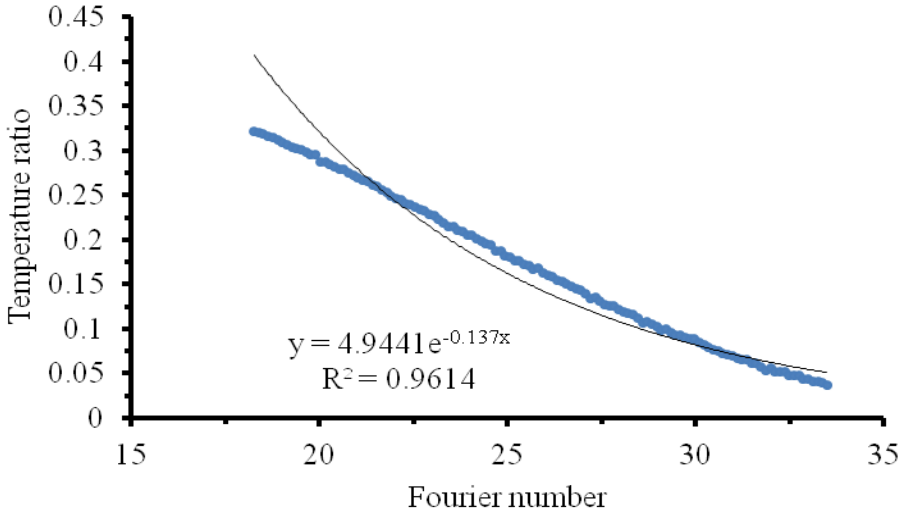
4.3 Determination of Heat Transfer Coefficient

4.3.1 Heat transfer coefficient of freezing of *kulfi* milk concentrate by deep freeze method

The heat transfer coefficient for deep freezing of *kulfi* from milk concentrate was determined using one-dimensional transient heat conduction equation. The heat transfer coefficient above freezing point was 4.57 W/m^2 K, while below freezing point it was 12.08 W/m^2 K. The mean heat transfer coefficient was calculated as 8.33 W/m^2 K.



(a)



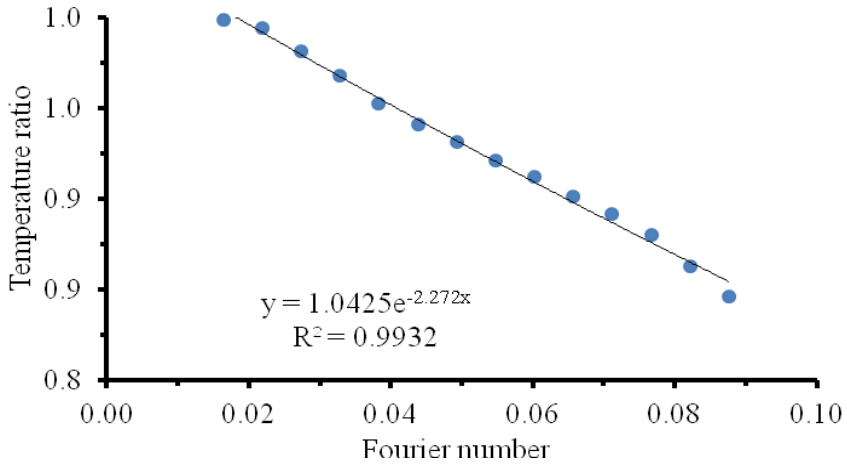
(b)

Fig. 4.14. Temperature ratio vs. Fourier number for freezing of *kulfi* milk concentrate using deep freeze method: (a) above freezing and (b) below freezing

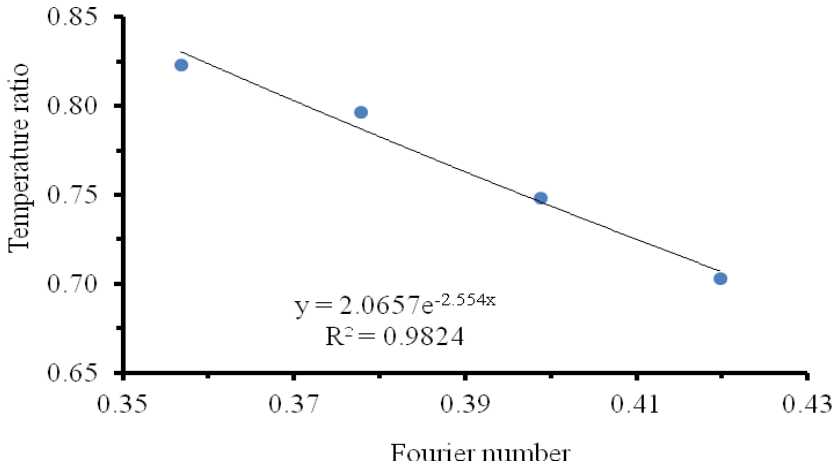
4.3.2 Heat transfer coefficient of freezing of *kulfi* milk concentrate using LN_2

The heat transfer coefficient for cryogenic freezing of *kulfi* from milk concentrate above freezing point was 98.62 W/m^2 K (Fig. 4.15a), while below freezing point, it was 322.53 W/m^2 K (Fig. 4.15b). The mean heat transfer coefficient was calculated as 210.58 W/m^2 K. The heat transfer coefficient was higher than the value of 170 W/m^2 K reported by Goswami (2010) for cryogenic freezing of shrimps. Thus, it could be stated that heat

transfer coefficient of cryogenic freezing of *kulfi* mix concentrate was much higher than that obtained using deep freeze method. The differences in heat transfer coefficient could be attributed to the differences in temperature between the product and freezing medium in the two cases. In case of deep freezing, the initial temperature difference between the product and freezing medium was only 60ºC (product at 30ºC and cold air at -30ºC). On the other hand, during cryogenic freezing, the initial temperature difference between the product and freezing medium was as high as 203ºC (product at 30ºC and LN_2 at -173ºC). Such large temperature difference between the product and freezing medium was expected to give relatively high heat transfer coefficient.



(a)



(b)

Fig. 4.15. Temperature ratio vs. Fourier number for freezing of *kulfi* milk concentrate using LN_2: (a) above freezing and (b) below freezing

4.3.3 Heat transfer coefficient of *kulfi* from dry mix during freezing using LN_2

In case of cryogenic freezing of *kulfi* from dry mix, the heat transfer coefficient above freezing was 98.22 W/m^2 K (Fig. 4.16a), while below freezing, it was higher at 335.46 W/m^2 K (Fig. 4.16b). The mean heat transfer coefficient was 216.84 W/m^2 K. The value was almost close to the heat transfer coefficient of 190 W/m^2 K reported by Awonorin (1989) for foods frozen using LN_2 for a mean temperature difference of 200 K. The heat transfer coefficient was much higher compared to the heat transfer coefficients by air freezing. Fricke and Becker (2002) calculated the heat transfer coefficient during freezing of Mozzarella cheese, and the values were 7.59, 6.48 and 7.04 W/m^2 K for air temperature of 0.6, -23.3 and -34.4°C, respectively.

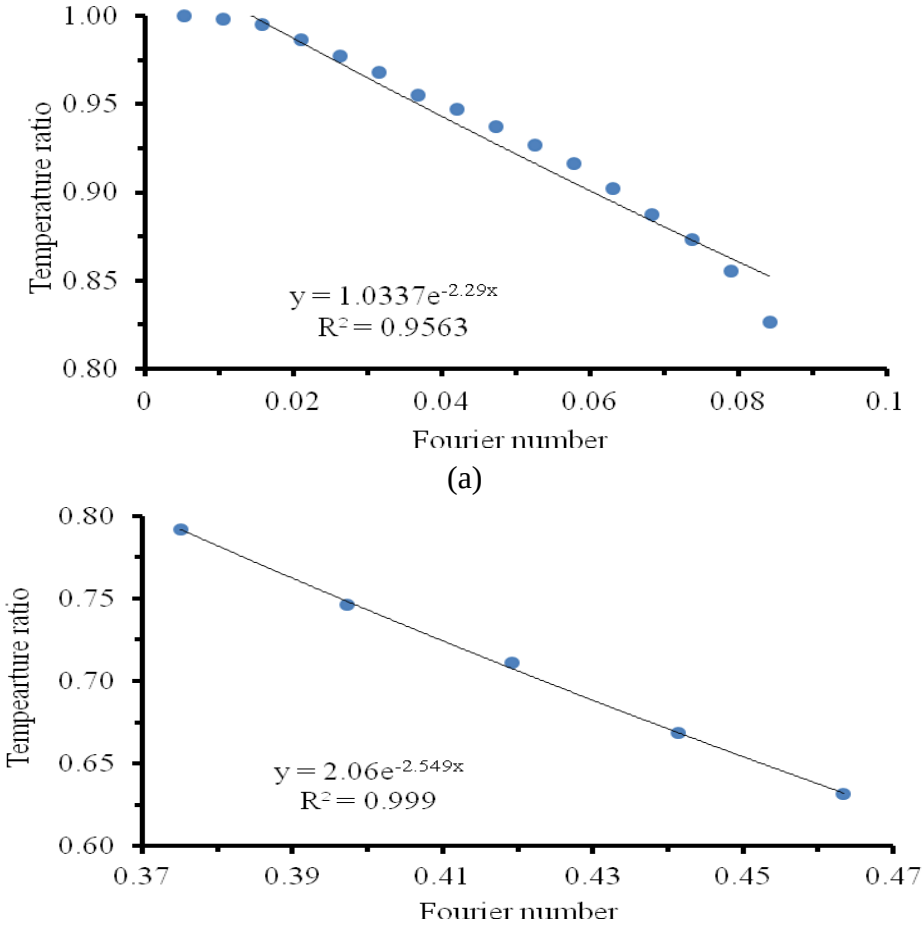


Fig. 4.16. Temperature ratio vs. Fourier number for freezing of *kulfi* concentrate from dry mix using LN_2: (a) above freezing and (b) below freezing

4.4 Prediction of freezing time

The prediction of freezing times of *kulfi* was done using mathematical models. The mathematical models used were Plank's, Modified Plank's, Pham's, and Cleland & Earle's models, the freezing time predicted by these models varies with each other. In case of *kulfi* prepared from milk concentrate and frozen using LN_2, the Plank's, Modified planks, Pham's, and Cleland & Earle's models, predicted the freezing time as 117.95, 271.93, 198.60, and 239.54 s, respectively compared to the actual freezing time of 190 s. In comparison, for *kulfi* concentrate prepared from dry mix and frozen using LN_2 the Plank's, Modified Plank's, Pham's, and Cleland & Earle's models predicted the freezing time as 119.21, 270.76, 194.86 and 230.74 s, respectively compared to actual freezing time of 185 s, the results were tabulated in Table 4.1.

Table 4.1. Predicted freezing time of *kulfi* prepared from milk concentrate and frozen using LN_2

Model	Predicted freezing time (s)	Actual freezing time (s)	% Error
Plank's	117.95	190	37.92
Pham's	198.60	190	4.53
Modified Plank's	249.87	190	31.51
Cleland & Earle's	239.54	190	26.07

Amongst the models tested, the Pham's model predicted the freezing times of *kulfi* using LN_2 with least error of 4.53%, followed by Cleland and Earle's, modified Plank's and Plank's models having an error of 26.07, 31.51 and 37.92%, respectively. The Plank's and modified Plank's models under-and over-predicted the freezing times, respectively.

In the case of *kulfi* concentrate from dry mix and frozen using LN_2, the Pham's model predicted the freeing time with an error of 5.33%, followed by Cleland and Earle's, modified Plank's and Plank's models having an error of 24.72, 34.03 and 35.56%, respectively.

Table 4.2. Predicted freezing time of *kulfi* concentrate prepared from dry mix and frozen using LN_2

Model	Predicted freezing time (s)	Actual freezing time (s)	% Error
Plank's	119.21	185	35.56
Pham's	194.86	185	5.33
Modified Plank's	247.97	185	34.03
Cleland & Earle's	230.74	185	24.72

Out of the four models tested, it could be concluded that the Pham's model predicted the freezing time with least error, and it best described the freezing of *kulfi* using LN_2. The results were comparable with those obtained by Ilicali and Icier (2010) for freezing of partially-dried papaya puree in infinite cylinder geometry where Pham's model predicted freezing time with 4.3% mean error and Cleland and Earle's model predicted freezing time with 14.2% mean error.

4.5 Physico-chemical Properties of *Kulfi*

4.5.1 Total solids

The gravimetric TS of *kulfi* prepared from milk concentrate and frozen by deep freeze method was 40.07%. Similarly, *kulfi* prepared from milk concentrate and frozen using LN_2 and for *kulfi* prepared from dry mix and frozen using LN_2 had TS contents of 40.06 and 40.05%, respectively. The TS content of *kulfi* was in the range of values reported by Yerriswamy *et al.* (1983) for both market (36.0-41.4%) and experimental samples (37.09-40.27%) samples, respectively and reported by Giri e*t al.* (2014) as 40.2 % for the *kulfi* which is used as control during preparation of reduced sugar *kulfi* with the addition of stevia.

4.5.2 Fat

The fat content of deep frozen *kulfi* prepared from concentrated milk was found to be 10.25%. The values for cryogenically prepared *kulfi* from milk concentrate and dry mix were 10.24 and 10.19%, respectively. The fat content of *kulfi* prepared in this study

met the standard of 10% (FSSA, 2006), but were slightly lower than the values reported by Giri *et al*. (2014). However, the fat content of *kulfi* fell in the range of 10.0-11.0% reported by Yerriswamy *et al.* (1983) for market samples and lower than the values of 13.05-14.12 % reported for experimental samples.

4.5.3 Protein

The protein content of *kulfi* prepared from milk concentrate and frozen by deep freeze method was 5.80%. The values for cryogenically prepared *kulfi* from milk concentrate and dry mix were 5.78 and 5.71%, respectively. The protein content of *kulfi* was higher than the values of 4.85-4.90 and 4.65-5.01% reported by Yerriswamy *et al.* (1983) for market and experimental samples, respectively. However, the protein contents of all three samples were slightly lower than the values reported by Giri *et al.* (2014).

4.5.4 Lactose

The lactose content, as estimated by Lane Eynon method, for *kulfi* prepared from milk concentrate and frozen by deep freeze method was 9.39%. The values for cryogenically prepared *kulfi* from milk concentrate and dry mix were 9.55 and 9.23%, respectively. The lactose content of *kulfi* prepared in this study was higher than the range of 5.74 to 9.30% reported by Ghosh (1991) for market samples.

Table 4.3. Chemical composition of *kulfi* prepared by different methods

Constituent, %	***Kulfi* prepared from milk concentrate and frozen in deep freezer**	***Kulfi* prepared from milk concentrate and frozen using LN_2**	***Kulfi* prepared from dry mix and frozen using LN_2**
Total solids	40.07 ± 0.09^{a}	40.05 ± 0.11^{a}	40.06 ± 0.10^{a}
Fat	10.25 ± 0.09^{a}	10.24 ± 0.11^{a}	10.19 ± 0.04^{a}
Protein	5.80 ± 0.11^{a}	5.78 ± 0.10^{a}	5.71 ± 0.05^{a}
Lactose	9.39 ± 0.04^{a}	9.55 ± 0.04^{b}	9.23 ± 0.04^{c}
Sucrose	12.64 ± 0.23^{a}	12.77 ± 0.16^{a}	12.71 ± 0.21^{a}
Ash	1.49 ± 0.02^{a}	1.45 ± 0.016^{a}	1.57 ± 0.02^{b}

*Same alphabet on superscript indicates no significant difference

4.5.5 Ash

The ash content of *kulfi* prepared from milk concentrate and frozen by deep freeze method was 1.49%. The values for cryogenically prepared *kulfi* from milk concentrate and dry mix were 1.45 and 1.57%, respectively. The ash content of *kulfi* was found to be slightly higher than the value of 0.99% reported by Giri *et al.* (2014). In contrast, the ash content of market *kulfi* samples reported by Ghosh (1991) varied from 1.37 to 1.80%.

4.5.6 Sucrose

The sucrose content, as estimated by Lane Eynon method, for *kulfi* prepared from milk concentrate and frozen by deep freeze method was 12.64%. The values for cryogenically prepared *kulfi* from milk concentrate and dry mix were 12.77% and 12.71%, respectively. These values were in the range of 10.9-16.0% reported by Ghosh (1991).

4.5.7 Titratable acidity

The titratable acidity of *kulfi* prepared from milk concentrate and frozen by deep freeze method was observed to be 0.28% lactic acid (%LA). In contrast, the titratable acidity of *kulfi* prepared from milk concentrate and frozen using LN_2 was 0.26% LA, while the *kulfi* prepared from dry mix had the acidity of 0.26% LA. The acidity of *kulfi* prepared by deep freeze method was slighter higher than its counterparts frozen by LN_2. The higher acidity in *kulfi* prepared by deep freeze method could be due to the physicochemical changes that took place before freezing occurred. However, the titratable acidity values were within the range (0.26-0.28) reported by Ghosh (1991).

4.5.8 pH

The pH of *kulfi* prepared from milk concentrate and frozen by deep freeze method varied from 6.37 to 6.39. The values for cryogenically prepared *kulfi* from milk concentrate and dry mix were in the range of 6.42-6.44 and 6.41 to 6.43, respectively. The pH of *kulfi* was slightly higher compared to the value range of 6.06 to 6.25 and 6.28 to 6.35 reported by Yerriswamy *et al.* (1983) for both market and experimental samples, respectively. However, the results matched with the values reported by Ghosh (1991).

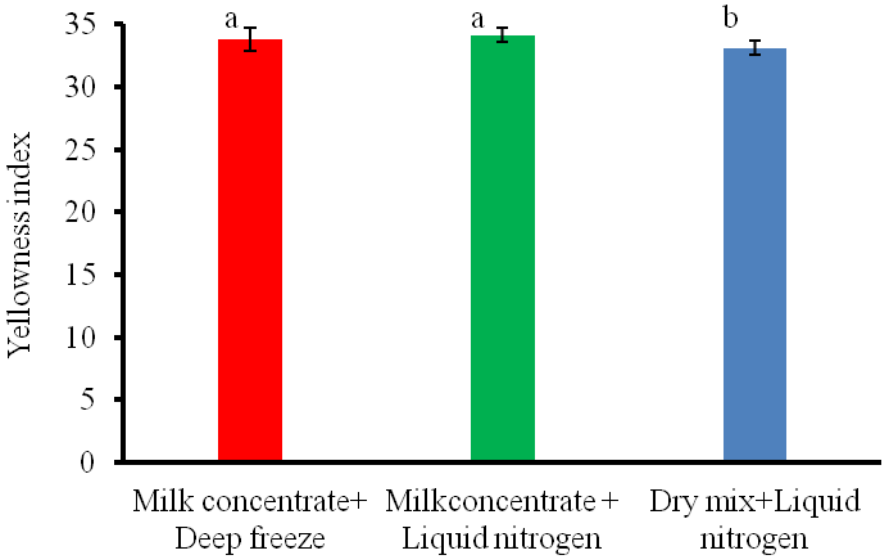
Table 4.4. Acidity and pH of *kulfi*

Sample	Acidity (% LA)	pH
Kulfi prepared from milk concentrate and frozen in deep freezer	0.28 ± 0.0045[a]	6.37-6.39[b]
Kulfi prepared from milk concentrate and frozen using LN_2	0.26 ± 0.0015[a]	6.42-6.44[a]
Kulfi prepared from dry mix and frozen using LN_2	0.26 ± 0.0019[b]	6.41-6.43[a]

*same alphabet on superscript indicates no significant difference

4.6 Colour of *kulfi*

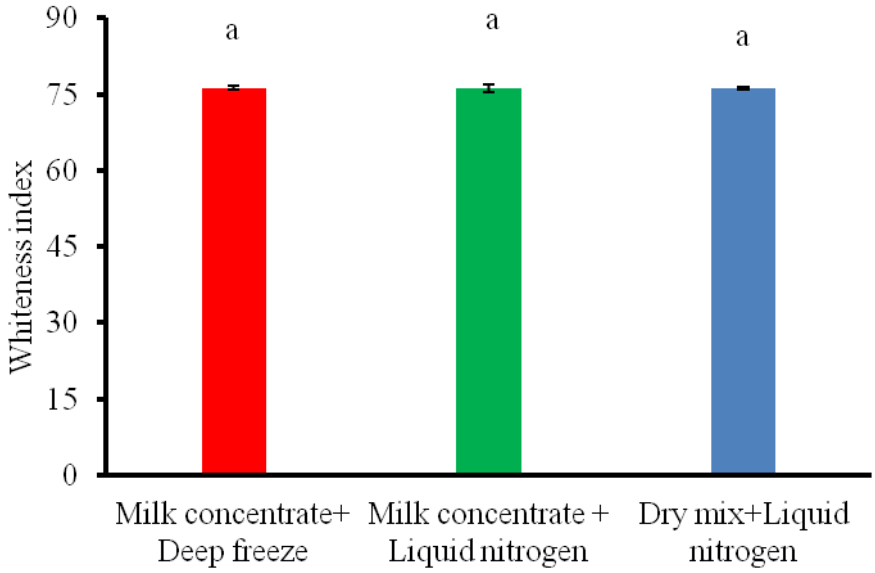
The yellowness Index (YI) and whiteness index (WI) of *kulfi* prepared using different methods are shown in Figs. 4.17 and 4.18, respectively. The YI of *kulfi* prepared by different methods varied significantly. The YI for *kulfi* prepared from milk concentrate and frozen by deep freeze method was 33.82. The values for cryogenically frozen *kulfi* prepared from milk concentrate and dry mix stood at was 34.11 and 32.80, respectively. The YI for cryogenic *kulfi* prepared from dry mix was significantly less due to the physic-chemical changes that occurred during spray drying.



*same alphabet indicates no significant difference

Fig. 4.17. Yellowness index of *kulfi* prepared by different methods

The WI for *kulfi* prepared from milk concentrate and frozen by deep freeze method was 76.28. The values for cryogenically frozen *kulfi* prepared from milk concentrate and dry mix stood at was 76.07 and 76.15, respectively (Fig. 4.18). There was no significant difference in the WI amongst the samples.



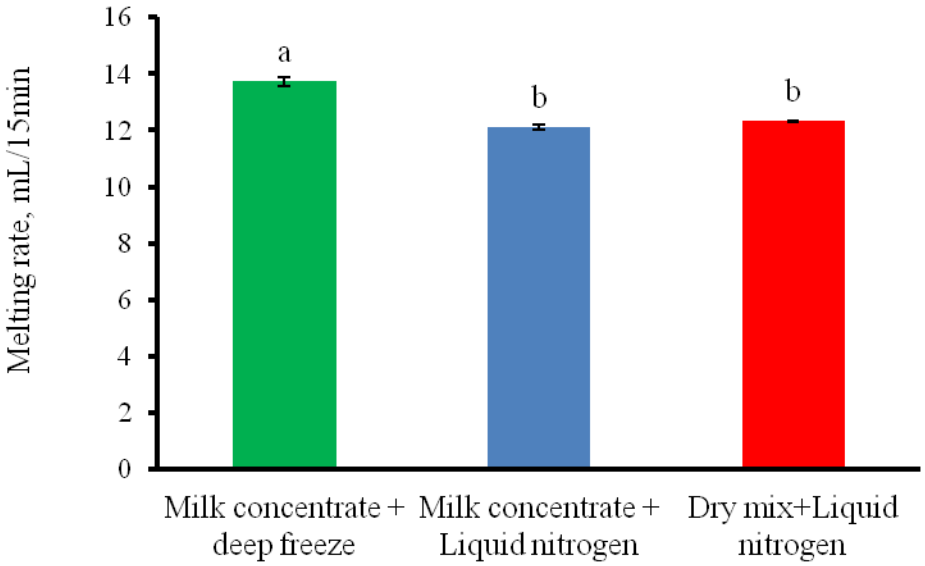
*same alphabet indicates no significant difference

Fig. 4.18. Whiteness index of *kulfi* prepared by different methods

4.7 Melting Properties of *Kulfi*

4.7.1 Melting rate

The melting rate of *kulfi* at 30°C is presented in Fig. 4.19. It could be observed that the melting rate of *kulfi* prepared from milk concentrate and frozen in deep freezer was 13.74 mL/15 min. It was slightly lower than the value of 14.81 mL/15 min reported by Giri *et al.* (2013) for deep freezing at -20°C for 8 h. In case of cryogenically frozen *kulfi* from milk concentrate, it was 12.11 mL/15min whereas for cryogenically frozen *kulfi* from dry mix, it was found to be 12.31 mL/15min. Thus, it could be stated that melting rate of *kulfi* frozen in deep freezer was significantly higher from that of cryogenically frozen *kulfi*. Cryogenic freezing led to increased surface hardness of ice, which required more time for the onset of melting, thereby lowering the melting rate.



*same alphabet indicates no significant difference

Fig. 4.19. Melting rate of *kulfi* prepared by different methods

4.7.2 Melting curve

The melting curve of *kulfi* prepared by different methods is presented in Fig. 4.20. The onset of melting was very fast in *kulfi* prepared from milk concentrate and frozen by deep freeze method, followed by cryogenically frozen *kulfi* from dry mix. In contrast, cryogenically frozen *kulfi* from milk concentrate had the least melting rate in the initial period. *Kulfi* made from condensed milk and frozen in deep freezer took 65 min for complete meltdown. In contrast, both cryogenically frozen samples took 70 min for complete meltdown. The differences in the melting rate of deep frozen and cryogenically frozen *kulfi* could be attributed to its differences in ice crystal size and hardness of the ice crystals. Cryogenically frozen *kulfi* was expected to have large number of small ice crystals with much higher hardness. Between cryogenically frozen *kulfi* from milk concentrate and dry mix, the melting rate of *kulfi* made from dry mix was faster up to 40% and thereafter the rate of melting marginally slowed down than that of cryogenic *kulfi* from milk concentrate.

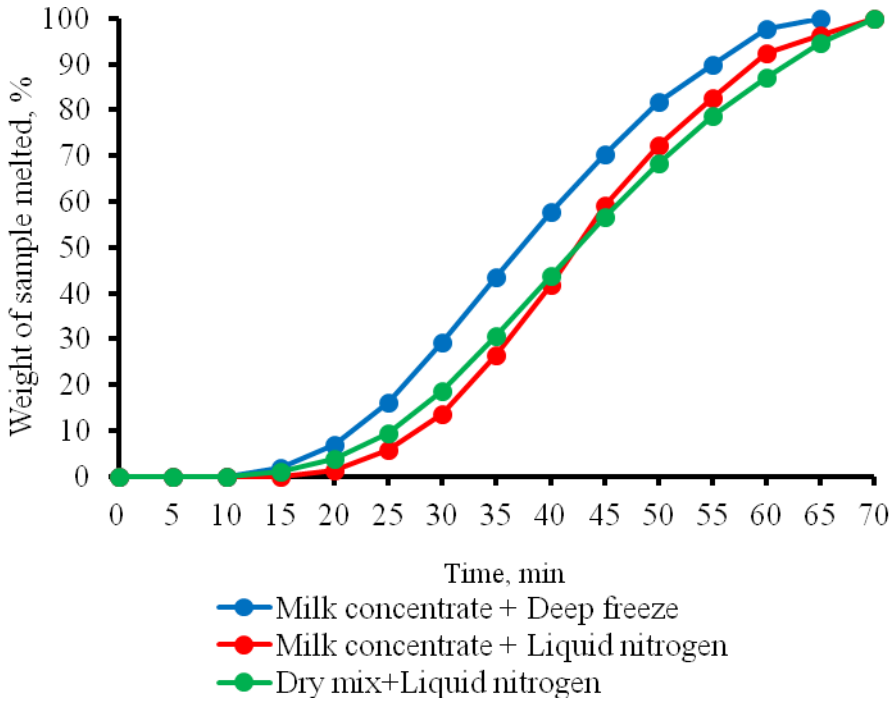
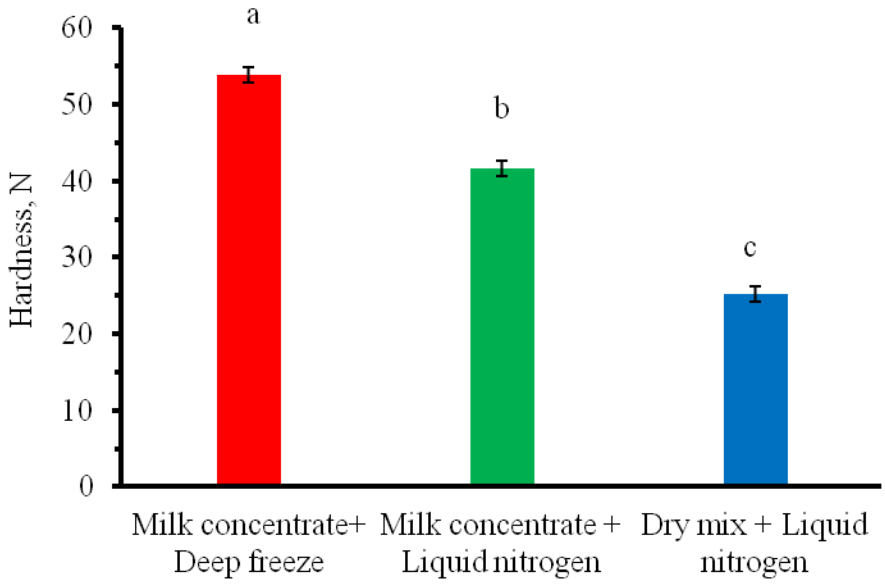


Fig. 4.20. Melting curves of *kulfi* prepared by different methods

4.8 Textural Properties of *Kulfi*

The hardness (N) of *kulfi* was measured using texture profile analyzer. The *kulfi* prepared using different methods was analysed, the results are shown in Fig. 4.21. The hardness (N) for *kulfi* prepared from milk concentrate and frozen in deep freezer was significantly higher compared to the one prepared from cryogenic freezing. This was due to the size and number of ice crystals produced during freezing methods. Freezing in deep freezer lead to large sized ice crystals resulting in a higher hardness and hence, this *kulfi* needed more force for Warner–Bratzler blade to shear through it, while in case of *kulfi* prepared from milk concentrate and frozen using LN_2 more number of small sized ice crystals were formed which lead to reduced hardness. In case of *kulfi* prepared using dry mix and frozen using LN_2, the hardness was still lower which may be due to the structural changes in proteins during drying and also due to freezing using LN_2.The hardness (N) of *kulfi* samples, prepared from milk concentrate and frozen using deep freeze method, and frozen using LN_2, and *kulfi* prepared from dry mix and frozen using LN_2 were 53.83, 41.56 and 25.17 N, respectively. The hardness values of *kulfi* prepared

from condensing the milk in an open pan and frozen by immersion in brine solution was 34 N (Nagajjanavar *et al.*, 2017).



*same alphabet indicates no significant difference

Fig. 4.21. Hardness (N) of *kulfi* using Warner-Bratzler shear test

4.9 Sensory Evaluation of *Kulfi* using Fuzzy-Logic Method

Sensory quality of *kulfi* was analysed by fuzzy-logic approach. In this approach, the samples were named as Sample 1, Sample 2 and Sample 3 for *kulfi* prepared from milk concentrate and frozen in deep freezer, and frozen using LN_2 and *kulfi* prepared from dry mix and frozen using LN_2, respectively.

4.9.1 Similarity values of *kulfi* samples

From Table 4.5, it could be observed that the similarity value for Sample 1 under "Poor" category was 0.0922, while the same under "Fair" was 0.3847, "Medium" was 0.6857, "Good" was 0.6298 and "Excellent" was 0.2046. Since similarity value under medium category was the highest, the overall quality of Sample I can be considered as "Satisfactory". Using similar reasoning, the overall quality of Sample 2 was considered as "Good" having similarity value 0.7068 and Sample 3 was also considered as "Good" with a similarity value of 0.7165. Comparing the similarity values of Samples 2 and 3, it

could be graded that Sample 3 was slightly superior to Sample 2. Thus, order of ranking of *kulfi* samples was Sample 3 (Good) > Sample 2 (Good) > Sample 1(Medium).

Table 4.5. Similarity values of *kulfi* samples

Grade	Sample 1	Sample 2	Sample 3
Poor	0.0922	0.0575	0.0542
Fair	0.3847	0.3079	0.3034
Medium	**0.6857**	0.6257	0.6267
Good	0.6298	**0.7068**	**0.7165**
Excellent	0.2046	0.2802	0.2825

4.9.2 Quality attributes ranking of *kulfi* in general

From Table 4.6, it was observed that similarity values for body & texture under highly important category (i.e. 0.9137) was the highest. This was followed by melting characteristics (highly important, 0.9139), flavour & taste (highly important, 0.8985) and colour & appearance (important, 0.7778). Thus, order of ranking of quality attributes of *kulfi*, in general, would be body & texture (highly important) > melting characteristics (highly important) > flavour & taste (highly important) > colour & appearance (important)

Table 4.6. Similarity values of quality attributes of *kulfi* in general

Ranking	Colour & appearance	Body & texture	Flavour & taste	Melting characteristics
Not important	0	0	0	0
Somewhat important	0.2976	0.0739	0.1158	0
Important	**0.7778**	0.6558	0.7368	0.2873
Highly important	0.2176	**0.9317**	**0.8985**	**0.9139**
Extremely important	0.0927	0.2858	0.2388	0.5574

For individual samples the similarity values of quality attributes were:

Sample 1: Flavour & taste (Highly important) > body & texture (Highly important) > melting characteristics (Important) > colour & appearance (Important).

Sample 2: Melting characteristics (highly important) > Flavour & taste (Highly important) > Body & texture (Important) > Colour & appearance (Important).

Sample 3: Melting characteristics (Highly important) > Body & texture (Highly important) > Flavour & taste (Important) > Colour & appearance (Important).

V SUMMARY AND CONCLUSIONS

Freezing is a very important step in the preparation of *kulfi* as it determines the characteristics of the frozen product. The thermo-physical properties of *kulfi* change during freezing, which consequently affects the heat transfer that takes place. The freezing method also affects the physico-chemical properties of *kulfi*. Newer techniques such as cryogenic freezing are available today for rapid freezing of dairy products such as ice cream and *kulfi*. This study was proposed with the following objectives:

- Analyze the heat transfer characteristics of cryogenically-prepared *kulfi* using dry mix.

- Determine the physico-chemical, melting, textural and sensorial properties of cryogenically frozen *kulfi*.

Kulfi was prepared using milk concentrate obtained by condensing milk and concentrate prepared from dry mix. The concentrates were frozen using deep freeze method at -30ºC and under cryogenic conditions using liquid nitrogen (LN_2) at -173ºC. During freezing, the temperature profile of *kulfi* was recorded using a data logger. The thermo-physical properties such as thermal conductivity, specific heat and thermal diffusivity of the concentrates were measured directly or indirectly using KD2 Pro thermal property analyser. Other properties namely, density, enthalpy, initial freezing point and ice content were predicted using appropriate equations.

The heat transfer coefficient during freezing of *kulfi* is very important as it affects the freezing characteristics and crystal growth. The heat transfer coefficient during normal deep freezing and cryogenic freezing of *kulfi* was modelled using one-dimensional transient heat conduction equation. The lumped thermal capacity model was found to be unsuitable. The process times during freezing of *kulfi* were predicted using four models, and their predictive performance was compared with experimental data.

The chemical composition of *kulfi* was determined using appropriate methods. For colour, images of the product were acquired using a digital camera and the L*, a* and

b* values were computed. Also, the yellowness and whiteness indices of *kulfi* frozen by both methods were measured. Melting characteristics such as melting rate and melting curve were determined using appropriate methodologies. The hardness of frozen *kulfi* was measured using TA.XT plus texture analyser fitted with Warner-Bratzler blade. Sensory evaluation of *kulfi* samples was done using fuzzy-logic approach.

1. The freezing rate of *kulfi* was 0.263°C per second in cryogenic freezing as compared to 0.003°C per second in deep freeze method. Thus, cryogenic freezing was 84 times faster than conventional deep freezing. Cryogenic freezing from 30 to -20°C was achieved in 190 and 185 s for *kulfi* from milk concentrate and dry mix, respectively as compared to 267 min in deep freeze method.

2. Thermo-physical properties of *kulfi* concentrates varied widely above and below freezing point. The density was lower below the freezing point as compared to the values above freezing point. Similarly, thermal conductivity of the concentrates below the freezing point was approximately four times higher than the near constant value obtained above freezing point. The thermal conductivity changed sharply in the initial freezing point region due to phase transition from liquid to ice.

3. Thermal diffusivity also followed the same trend as thermal conductivity. In contrast, specific heat was lower below the initial freezing point and it was higher above the freezing point. The changes in thermal properties near the initial freezing point region were very sharp in the concentrate from dry mix. The freezing points of both concentrates (milk and dry mix) were very similar.

4. Heat transfer coefficients during cryogenic freezing of *kulfi* from milk concentrate and dry mix were 210 and 216 W/m^2 K, respectively as compared to 8.33 W/m^2 K for deep freeze method. Large temperature difference between the product and freezing medium was expected to give relatively high heat

transfer coefficient. *Kulfi* from dry mix froze at a much faster rate than from milk concentrate because of the nucleation properties of the powder particulates.

5. The phase change of *kulfi* concentrate from dry mix occurred over a narrow temperature range of -7 to -3°C (4°C). In contrast, the phase change of *kulfi* milk concentrate occurred over a relatively broader temperature range of 7°C.

6. The freezing times of *kulfi* were predicted using Plank's, Modified Plank's, Pham's and Cleland & Earle's models. For cryogenic freezing of *kulfi* from milk concentrate, Pham's model predicted the freezing time with the least error of 4.53%, followed by Cleland and Earle's, modified Plank's and Plank's models having error of 26.07, 31.51 and 37.92%, respectively. The process time for cryogenic freezing of *kulfi* from dry mix was predicted using the same models. Among the models tested, Pham's model predicted the freeing times of *kulfi* using LN_2 with the least error of 5.33%, followed by Cleland and Earle's, modified Plank's and Plank's models, having error of 24.72, 34.03 and 35.56%, respectively. Pham's model was found to be the best for describing the cryogenic freezing behaviour of *kulfi*.

7. Melting rate (mL/15 min) for *kulfi* prepared from milk concentrate and frozen in deep freezer was 13.7, while for cryogenic freezing of *kulfi* from milk concentrate, it was 12.1. The value for cryogenic freezing of *kulfi* from dry mix was 12.3. The differences in the melting rate of deep- and cryogenically frozen *kulfi* could be attributed to the differences in ice crystal size and hardness of ice crystals. Cryogenically frozen *kulfi* was expected to have large number of small ice crystals with much lower hardness.

8. Hardness of *kulfi* prepared from milk concentrate and frozen by deep freeze method was 53.83 N, while for cryogenically frozen *kulfi* from milk concentrate it was 41.56 N. Similarly, the hardness of cryogenically frozen *kulfi* from dry mix was 25.17 N. The smaller ice crystals reduced the hardness of cryogenically frozen *kulfi*.

9. The yellowness index (YI) for *kulfi* prepared from milk concentrate and frozen by deep freeze method was 33.82, while the same for cryogenic freezing was 34.11. *Kulfi* prepared from *kulfi* dry mix and frozen using LN_2 had YI of 33.10. Similarly, the whiteness index (WI) for *kulfi* prepared from milk concentrate and frozen by deep freeze method was 76.28. The same for cryogenically frozen *kulfi* from milk concentrate and dry mix were 76.07 and 76.15.

10. Order of ranking of quality attributes of *kulfi* in general using fuzzy-logic approach was Body & Texture (Highly important) > Melting Characteristics (Highly important) > Flavour & Taste (Highly important) > Colour & Appearance (Important). Order of ranking of *kulfi* was cryogenically frozen *kulfi* from dry mix (Good) > cryogenically frozen *kulfi* from milk concentrate (Good) > deep frozen *kulfi* from milk concentrate (Medium).

The current study helped in analysing the feasibity of preparation of *kulfi* from instant dry mix and rapid freezing of *kulfi* using LN_2, with a better understanding of the freezing process and inherent changes in thermo-physical properties. After analysis of physico-chemical properties such as colour, chemical properties, melting properties, textural properties and sensory properties, it could be concluded that *kulfi* could be prepared using dry mix without affecting the properties of the product. Cryogenic freezing produced a superior product as compared to the product frozen by deep freeze method. The data derived from the present study will help in new equipment design for cryogenic preparation of *kulfi* and other frozen dairy desserts.

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APPENDIX-I

Please rate the samples for quality attributes by putting (✓) mark against the appropriate grade

Name of the Judge: Date:

SENSORY SCALE FACTOR	SENSORY QUALITY FACTOR				
	Excellent	Good	Medium	Fair	Poor
Colour and Appearance					
S1					
S2					
S3					
Body and Texture					
S1					
S2					
S3					
Flavour and Taste					
S1					
S2					
S3					
Melting Characteristics					
S1					
S2					
S3					

*S1-Sample1, S2-Sample2, S3-Sample3.

Please indicate the weightage you would like to assign for each quality attribute of *Kulfi* in general by putting a (✓) mark against the appropriate choice.

Quality attributes	Not important	Somewhat important	Important	Highly important	Extremely important
Colour& Appearance					
Body & Texture					
Flavour & Taste					
Melting Characteristics					

Signature of evaluator

APPENDIX-II

ANOVA for total solids

Sources of variation	DF	MS	F value
Between the *kulfi* samples	2	0.000	0.021
Error	6	0.010	
Total	8		

ANOVA for fat

Sources of variation	DF	MS	F value
Between the *kulfi* samples	2	0.004	0.520
Error	6	0.008	
Total	8		

ANOVA for protein

Sources of variation	DF	MS	F value
Between the *kulfi* samples	2	0.008	0.962
Error	6	0.008	
Total	8		

ANOVA for lactose

Sources of variation	DF	MS	F value
Between the *kulfi* samples	2	0.076	49.603*
Error	6	0.002	
Total	8		

ANOVA for sucrose

Sources of variation	DF	MS	F value
Between the *kulfi* samples	2	0.013	0.321
Error	6	0.041	
Total	8		

ANOVA for ash

Sources of variation	DF	MS	F value
Between the *kulfi* samples	2	0.013	44.082*
Error	6	0.000	
Total	8		

ANOVA for Yellowness index

Sources of variation	DF	MS	F value
Between the *kulfi* samples	2	0.803	3.231
Error	6	0.248	
Total	8		

ANOVA for whiteness index

Sources of variation	DF	MS	F value
Between the *kulfi* samples	2	0.032	0.132
Error	6	0.241	
Total	8		

ANOVA for hardness

Sources of variation	DF	MS	F value
Between the *kulfi* samples	2	620.327	75.114*
Error	6	8.255	
Total	8		

ANOVA for melting rate

Sources of variation	DF	MS	F value
Between the *kulfi* samples	2	2.311	221.292*
Error	6	0.10	
Total	8		

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CAREER OBJECTIVE	To work in a challenging and dynamic business environment and to keep adding value to the organization that I represent and serve, and to myself, while concurrently upgrading my skills and knowledge in the respective functional department of the organization.
AREA OF INTEREST	Process Engineering, Production engineering, production of dairy and food products.
QUALIFICATION	• Master of Technology (Dairy Engineering): ICAR-NATIONAL DAIRY RESEARCH INSTITUTE, SRS-BENGALURU: OGPA 8.8, 2015-17. • Bachelor of Technology (Dairy technology): Dairy Science college, Hebbal, Bengaluru: OGPA 8.37, 2011-15.
RESEARCH PROJECT	"Cryogenic preparation of *Kulfi* using dry mix and analysis of its heat transfer and melting characteristics"
PROFESSIONAL TRAINING	• Underwent Six months training (Jul-Dec, 2014) at Students Experimental Dairy Plant, Dairy Science College, Hebbal. • Underwent one month training (Jan, 2015) at Nandini Milk Products Limited. • Underwent two months training (Feb-Mar, 2015) at Mangalore Dairy, KMF. • Underwent one month training (May, 2015) at Tumkur Dairy, Tumakuru, KMF.
AWARDS/ ACHIEVEMENTS	• Secured 5TH RANK in ICAR's 20th All India Entrance Examination (AIEEA-PG-2015). • Awarded ICAR-Junior Research Fellowship in M.Tech programme. • Secured Merit Scholarships in B.Tech (D.Tech) programme.
SKILL SET	• Microsoft office utilities, General internet utilities.
EXTRACURRICULAR ACHIEVEMENTS	• Participated in 7th NATIONAL DAIRY AND FOOD QUIZ held at SMC College of Dairy Science, Anand Agricultural University (AAU) Anand, Gujarat. • Participated in the state level NSS Volunteer's Training Programme held at HK Veerannagowda College, Maddur, Mandya, District for 2 days. • Participated in Rural Dairy Work Experience Programme held at Melekote, Doddaballapur (Tq), Bengaluru Rural (D), for 15 days.
SEMINARS ATTENDED	**Attended national seminar on "QUALITY – A TOOL FOR VALUE ADDITION OF DAIRY PRODUCTS"**
PERSONAL DETAILS	• Date of Birth : 28th July 1992 • Father's name : Honnappa • Father's Occupation : Agriculture • Languages known : English, Kannada and Hindi • Permanent Address : s/o Honnappa, Gedlehalli(V), Bhyranayakanahalli (post), Tiptur (Tq), Tumkur (D), Karnataka(S), PIN-572201