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APPLICATION OF THERMOSONICATION TO IMPROVE SOAKING AND COOKING PROPERTIES OF CHICKPEA

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Supervisor
Prof. Dr. Mehmet Durdu ÖNER

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ABSTRACT

APPLICATION OF THERMOSONICATION TO IMPROVE SOAKING AND COOKING PROPERTIES OF CHICKPEA

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In this study, the effects of time, temperature and ultrasounds on soaking and cooking operations of chickpea were investigated. For moisture absorption, Fick's, Weibull, Peleg and Asymptotic first order models, for texture only Asymptotic first order model were used during soaking. Increase of soaking/cooking temperature, power of US and US treatment significantly ($P<0.05$) increased rate of moisture absorption, decrease texture of chickpea and affected the leaching characteristics of chickpea. High frequency US (40 kHz US) did not significantly ($P>0.05$) affect the water absorption of chickpea during soaking. Water diffusion coefficient (D_{eff}) value of chickpea from Fick's and Weibull models, Peleg rate constant (K_1) and hydration rate constant (k_H) of Asymptotic first order model increased with temperature and US (25 kHz 100 W, 40 kHz 100 W and 25 kHz 300 W). Texture model rate constant (k_F) also increased with temperature and 25 kHz 100 W, and 25 kHz 300 W US treatments. Degree of cooking of chickpea starch was investigated using DSC, unreacted-core model, electrical conductivity and birefringence images methods. The unreacted-core model very well fitted (R^2=0.8949-0.9727) gelatinization of the chickpea starch. There was a good linear relationship between degree of cooking and electrical conductivity data of cooking water and chickpea seeds. The cooking time (τ) of chickpea found as 240 min at 92 ^oC by birefringence images, DSC and EC of chickpea in contrast to unreacted-core model (183 min) due to different mechanisms of models. 25 kHz 100 W and 25 kHz 300 W US treatments represented a 40 min and 80 min decrease in cooking time of chickpea for every temperature, respectively.

Key Words: Chickpea, soaking, cooking, thermosonic, modeling

ÖZET

NOHUDUN SUDA ISLATMA VE PİŞME ÖZELLİKLERİNİN GELİŞTİRİLMESİNDE TERMOSONİK İŞLEM UYGULANMASI

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Bu çalışmada, süre, sıcaklık ve ultrasonik (US) dalgaların nohudun ıslatma ve pişme üzerindeki etkisi incelenmiştir. Su absorpsiyonu için Fick, Weibull, Peleg ve Asimptotik birinci derece modelleri, yapı için sadece Asimptotik birinci derece modeli kullanılmıştır. Nohudun ıslatma/pişirme sırasındaki sıcaklık artışı, US ve US güç artışı nem absorpsiyon hızını anlamlı olarak ($P<0,05$) arttırmış, yapı değerlerini azaltmış ve suya geçen madde özelliklerini etkilemiştir. Islatma sırasında, yüksek frekanslı (40 kHz) US nohudun su absorpsiyonu önemli ölçüde etkilememiştir ($P>0,05$). Nohudun su diffüzyon katsayısı (D_{eff}) değeri, Peleg hız katsayısı (K_1) ve Asimptotik birinci derece modelindeki hız sabiti (k_H) değerleri sıcaklık ve US uygulaması (25 kHz 100 W ve 25 kHz 300 W) ile artmıştır. Yapı modelindeki hız sabiti (k_F) ise sıcaklık, 25 kHz 100 W ve 25 kHz 300 W'lık US ile artmıştır. Nohudun pişme derecesi, DSC, kotiledonlardan beyaz kısmının azalmasının takibi, elektrik iletkenlik ve çift-kırma görüntü metotları kullanılarak bulunmuştur. Nohut nişastasının jelatinizasyonuna kotiledonlardan beyaz kısmının azalmasının takibi modeli iyi bir şekilde uymuştur (R^2=0,8949-0,9727). Nohudun pişme suyu ve tane kısmındaki pişme derecesi ile elektrik iletkenliği arasında iyi bir doğrusal ilişki bulunmuştur. Nohudun 92 ^oC deki pişme süresi (τ), çift-kırma görüntü yöntemi, DSC ve nohudun tane kısmının EC yöntemleriyle kotiledonlardan beyaz kısmının azalmasının takibi modelinin aksine (183 dakika) modellerin farklı mekanizmasından dolayı 240 dakika olarak bulunmuştur. 25 kHz 100 W ve 25 kHz 300 W US uygulamaları nohudun her sıcaklıktaki pişme süresinde sırasıyla 40 ve 80 dakikalık bir azalma sağlamıştır.

Anahtar Kelimeler: Nohut, ıslatma, pişirme, termosonik, modelleme

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LIST OF ABBREVIATIONS

a^*	CIELAB color degree (Red-green)
b^*	CIELAB color degree (Blue-yellow)
BI	Birefringes Imeges,
D	Diameter (m)
d.b.	Dry basis
D_c	Diameter of unreacted-core (m)
D_{eff}	Effective diffusion coefficient, (m^2/s)
D_g	Geometric mean diameter, (m)
DC	Degree of cooking (%)
DC-BI(%)	Degree of cooking by birefringes images
DC-DSC(%)	Degree of cooking by DSC
DC-EC-C(%)	Degree of cooking by electrical conductivity of chickpea method
DC-UC(%)	Degree of cooking by unreacted core model
D_o	Pre-exponential factor, (m^2/s)
D_{ref}	Reference hydration rate constant in Fick's and Normilized Weibull models
DSC	Differential Scanning Calorimeter
E_a	Activation energy of diffusion or water absorption, (kJ/mol)
EC	Electrical conductivity, (mS/cm or µS/cm)
EC-C(mS/cm)	Electrical conductivity of chickpea
EC-CW (mS/cm)	Electrical conductivity of cooking water
EC-CW-BI(%)	Electrical conductivity on the basis of Birefringes images
EC-CW-C(%)	Electrical conductivity on the basis of electrical conductivity of
EC-CW-DSC(%)	Electrical conductivity on the basis of DSC
EC-CW-UC(%)	Electrical conductivity on the basis of Unreacted core model
F	Force (N) at any time
F_e	Equilibrium predicted force (N)
F_{max}	Maximmum force (N)
F_o	Initial predicted force (N)
H_a	Hectare
HTST	High temperature short time
K_1	Peleg rate constant, s/% m.c (d.b)
K_2	Peleg capacity constant, 1/% m.c (d.b)
k_F	Rate constant of chickpea softening (s^{-1})
k_H	Rate constant of Asyptotic first order model (min^{-1}, s^{-1}, h^{-1})
k_{ref}	Reference hydration rate constant in Asymptotic first order
K_{ref}	Reference hydration rate constant in Peleg model
L^*:	CIELAB color degree (Lightness or luminance)
M_e	Saturation or equilibrium moisture content, % (d.b)
M_o	Initial moisture content, % (d.b)
M_t	Moisture content at time t, % (d.b)
n	Order of reaction

r	Radius, (m)
R	Universal gas constant (8.314 x10^{-3} kJ/mol ^{o}K)
R^2	Coefficient of determination
r_c	Radius of unracted-core (m)
R_g	Geometric factor in the Weibull distribution function
RMSE	Root mean square error
R_o	Initial rate of water absorption, g H_2O/kg dry matter,(s)
t	Soaking or cookin time, (min, s)
T	Temperature, (^{o}C, ^{o}K)
TDS	Total dissolved solid
t_e	Equilibrium softening time (min)
T_o	Onset temperature (^{o}C)
t_o	Reduced or pseudo soaking time, (min, s)
u	Sphericity
UC	Unreacted-core model
US	Ultrasound
α	Shape parameter of the Weibull model, dimensionless
β	Scale parameter of the Weibull model, (s)
ΔH_{gel}	Enthalpy of gelatinization
$\Delta H_{heat\text{-}treated}$	Enthalpy of heated sample
ΔH_{Raw}	Enthalpy of unheated sample
τ	Cooking time at 100% (min)
w/o	without
w/	with

CHAPTER I

INTRODUCTION

The role of legumes in the diet is increasing while the role of others appears to be decreasing around the world. Dry legumes are important ingredient of diet in many parts of the world. Nourishment from these sources is not always readily identified because legumes contribute the diet in multiple forms and at multiple stages of processing. Legumes are treated as in dehulling, milling, extruding, puffing, isolating, soaking, drying, roasting, frying, germinating, fermenting and cooking, among other things, before consumers encounter them as edible food. However, they continue to provide a stable, relatively inexpensive source of calories and protein for consumers around the world with some promising new developments in process. Grain legumes are considered to be good for health due to their mutual compatibility for their properties in disease prevention, including cardiovascular diseases, diabetes, obesity and, possibly, colon cancer. The nutritional potential of the seeds from this group of plants is based on their high level of protein and, depending on species, a high proportion of either starch or oil.

Legume grains occupy an important place in human nutrition, especially in the pattern of low income groups of people in developing countries. Legumes are prepared for consumption in many ways, such as whole legumes called grains or dehusked and split legumes, known as dehulled legumes. Similar to chickpea, expanded pigeon pea and horse gram and their flours may find applications in snack, confectionary, meat, bakery, and other traditional food and feed industries (Saeed et al., 2007; Torres et al., 2007).

Food processors are continuously trying to design new and better techniques for food legumes that will not only bring them profits but will also fill the needs of consumers. Consumer's food needs consist from not only of nutritional but also of satisfactory taste, variety, and convenience for their life style all at a price they are

willing and able to pay. Since food habits are always culture bound and difficult to change, a critical extension of technological changes in food production and processing is an examination of what foods consumers want, how they can best be informed about new choices, and how they can best be protected from current and yet unknown hazards to their health and safety. Consumer's welfare is ultimately changed by how well their preferences are met by the products they consume. Potential changes in consumers welfare resulting from activities in the the legume industries will be the focus (Kirsey, 1978).

Nowadays, legumes are essential raw material for the modern food industry in the production of protein concentrates, fats and starches, and functional food ingredients (protein isolates, protein hydrolysates, dietary fibres, lecithin and iso-flavones) (Salunkhe and Kadam, 1989; Linden and Lorient, 1994).

Legumes are economical sources of protein, energy, vitamins and minerals. Oil content ranges from almost none to high (6.9 %). Carbohydrate contents vary, but often include long chain carbohydrates that are difficult to digest and lead to flatulence. Most grain legumes contain antinutrients or poisonous substances and need to be thoroughly cooked before eating. In spite of their good nutritional qualities, legume consumption is declines worldwide. This could be due to extensive preparation and cooking, production of gastro-intestinal distress after ingestion and the presence of some nutritional problems. Economic problems due to the loss of an important functional property of the legumes and an energy problem for those areas (where fuel is costly and long cooking times are needed to soften the stored legumes) limit their utilization. In order to solve these problems, alternative methods should be used to process the legumes.

CHAPTER II

LITERATURE REVIEW

2.1. Legumes (Pulses) and Chickpea Production in the World

Legumes (Pulses) have been eaten around the world for more than 10,000 years - and even today they remain a popular, healthy and versatile food. Worldwide, most grown legumes are soybean, peanut, black, red, white, navy and kidney beans, peas, chickpeas and lentils (Salunkhe and Kadam, 1989). India is the biggest legume producer with a production of 800,000 metric tones in 2008. United Kingdom, Mozambique, Poland and Pakistan are the other legume producers, with 612,000, 151,000, 150,000 and 121,000 tones productions, respectively (FAO, 2008).

Chickpeas have been grown in Turkey since about 7000 B.C, and has been produced in semi-arid zones of India and Middle Eastern countries. Chickpeas belong to the family *Leguminosae*. It is a staple food crop in many tropical and subtropical countries (Chavan et al., 1986). Chickpea is the second most important pulse crop in the world with a harvesting area of 11,556,744 hectare (Ha) at 2008, grown in at least 33 countries in South Asia, West Asia, North Africa, East Africa, southern Europe, North and South America, and Australia. Acording to harvesting area; India, Pakistan, Iran, Turkey and Australia with 7,543,700, 1,106,800, 790,000, 486,199 and 298,000 Ha are major chickpea growers in the world (FAO, 2008). The total production of chickpea in India, Turkey, Pakistan, Australia and Iran was 5,748,600, 518,026, 474,600, 378,000 and 320,000 tones in 2008, respectively (FAO, 2008).

2.2. Legumes/Chickpea Seed Characteristics

Three different parts are recognised in the legume seeds: cotyledon, seed coat and embryonic axe, which represent, on average, 89%, 10% and 1% of the total seed weight, respectively. The cotyledon contains the main reserve substances, basically proteins and carbohydrates. The seed coat, which acts as a protective barrier for the cotyledon, has the highest concentration of phenolic compounds (Duenas, 2003;

Shahidi et al., 2001; Troszynska et al., 1997). Starch granules are held within the protein matrix in the cotyledons (Sayar et al., 2001). In simple terms, chickpea grain comprises starch granules embedded in a protein matrix covered by a seed coat (Sayar et al., 2003).

Earlier botanists had postulated several different origins. De Candolle (1883) traced the origin of chickpea to an area south of the Caucasus and in the north of Persia. Vavilov (1926) identified two primary centres of origin, south-west Asia and the Mediterranean, and one secondary centre of origin, Ethiopia. He noted that large-seeded lines were abundant around the Mediterranean basin while small-seeded lines were dominant eastward. There is linguistic evidence that large-seeded chickpea reached India via the Afghan capital Kabul about two centuries ago and acquired a name in Hindi as Kabuli chana (chana = chickpea) (Van Der Maesen, 1972). The small-seeded, dark chickpea is called desi (local), and these denominations are commonly used to distinguish the two main groups of cultivars (Singh, 1997). *Cicer* is in a tribe of its own, Cicereae Alef, (Kupicha, 1977). There are 43 species reported: 9 annual (including the cultivated one), 33 perennial, and 1 unspecified (Van Der Maesen, 1987).

2.3. Composion and Nutrition of Legumes/Chickpea

In general, legumes are sources of complex carbohydrates, protein and dietary fibre, having significant amounts of vitamins and minerals, and high energetic value (Chavan et al., 1986; Tharanathan and Mahadevamma, 2003). The cotyledons are the major source of nutrients in pulse grains. For chickpeas, cotyledons constitute 84% of the whole seed weight. The embryo has also considerable protein, fat and minerals but its contribution in total seed weight is meagre (Table 2.1). The seed coat contains most of the nondigestible carbohydrates and relatively higher proportion of calcium (Chavan et al, 1986). During dehulling in which seed coat is removed crude fiber and ash levels decrease while protein, total carbohydrates and lipids content increase (Table 2.1).

2.3. 1. Proteins

The protein content of chickpea seeds is influenced by genetic and environmental factors (Chavan et al., 1986; Swanson, 1990). Chickpeas are highly valuable and

economical source of vegetable protein, which includes essential amino acids (Clemente et al., 2000). Protein contents in legume grains range from 17% to 40%, contrasting with 7-13% of cereals, and being equal to the protein contents of meats (18–25%) (Genovese and Lajolo, 2001).

Table 2.1. Relative distribution of nutrients in different anatomical parts of chickpea seeds (%, d.b.) (Chavan et al., 1986)

Nutrient	Seed coat (14.5 %)		Cotyledon (84.0 %)		Embryo (1.5 %)		Whole seed (100 %)
	a	b	a	b	a	b	
Protein (Nx6.25)	3.0	2.0	25.0	95.5	37.0	2.5	22.0
Carbohydrates	46.0	11.0	66.0	88.0	42.0	1.0	63.0
Fat	0.2	0.6	5.0	94.0	13.0	5.0	4.5
Ash	2.8	15.0	2.6	81.0	5.0	3.0	2.7
Crude fiber	48.0	87.0	1.2	13.0	-	-	8.0
Phosporus	24.0 mg	1.5	290.0 mg	94.0	740.0 mg	4.5	260.0 mg
Iron	8.0 mg	20.0	5.5 mg	77.0	11.0 mg	3.0	6.0 mg
Calcium	1000.0 mg	72.0	70.0 mg	29.0	110.0 mg	0.8	200.0 mg

a)Nutrient content in each anatomical part b)Relative distribution of nutrients in whole seed (mg/100 g)

Table 2.2. Essential amino acids composition (g/16gN) and protein fractions (%, d.b.) of chickpea (Chavan et al., 1986)

Amino acid	Mean	FAO Stand. protein	Component	Albumin	Globulin	Glutenin	Prolamin
Isoleucine	4.3	4.0	Whole seed	12.6	56.6	18.1	2.8
Leucine	7.8	7.0	Seeed coat	3.5	22.8	33.2	3.4
Lysine	6.9	5.5	Cotyledon	15.9	62.7	17.7	2.3
Methionine + Cystine	2.9	3.5	Embryo	22.5	50.0	21.4	3.0
Phenylalanine + Tyrosine	8.4	6.0					
Thereonine	3.7	4.0					
Valine	4.6	5.0					
Tryptophan	0.95	1.0					

The storage proteins of chickpea seeds include albumins (water soluble), globulins (salt soluble), prolamines (alcohol soluble), glutelins (acid/alkali soluble) and residual proteins. The globulins, consisting mainly of legumin and vicilin, constitute the major storage protein (56%) followed by glutelins (18.1%), albumins (12.0%) and the least are prolamines (2.8%). The cotyledon is the largest component of a chickpea seeds (Table 2.2), hence, it contains the majority of the globulins, glutelins and albumins (Chavan et al., 1986). Studies have shown that the globulins do not

contain methionine and cystine (sulfur amino acids). While the albumins and glutelins have higher level of these two amino acids (Saxena and Singh, 1987; Clemente et al., 2000). Hence, the poor nutritive value of chickpeas is due to globulins fractions (Chavan et al., 1986). Studies have shown that legume protein fractions are mainly deficient in sulfurcontaining amino acids and tryptophan but they are rich in lysine, unlike cereals. Therefore, care must be applied to provide a good balance of amino acids in human nutrition by combination of legumes and cereals (Salunkhe et al., 1985). Table 2.2 shows that the limiting amino acids in chickpeas are sulfur-containing amino acids, followed by valine, threonine and tryptophan.

2.3.2. Carbohydrates

Legumes are good dietary carbohydrates sources. The total carbohydrates of dry legumes vary from 24 to 68%. These include mono-, oligo- and polysaccharides including starch. Starch is a polysaccharide, which is digestible by humans. Chickpeas contain 52.4 to 70.9% total carbohydrates that constitute a major portion of the seed (Table 2.3). Chickpeas have the lowest carbohydrate digestibility among the commonly used pulse grains. This was confirmed in both in vitro and in vivo digestibility determination. The isolated starch of kabuli type has exhibited more digestibility than desi type in vivo (Chavan et al., 1986).

Table 2.3. Carbohydrate composition of chickpeas (Chavan et al., 1986)

Constituent	Percentage (%, d.b.)
Total Carbohydrate	52.4-70.9
Starch	37.2-50.8
Amylose. % of total starch	31.8-45.8
Soluble sugars	4.8 - 9.0
Reducing sugars	0.1
Sucrose	0.7- 2.9
Raffinose	0.5 - 3.0
Verbascose	0.1 - 4.5
Stachyose	1.1 - 3.4
Manninotriose	2.3
Crude fiber	7.1-13.5
Cellulose	7.1 - 9.7
Hemicellulose	3.5 - 8.7
Pectic substances	1.5 - 3.8
Lignin	2.2 - 5.9
Dietary fiber	19.0- 22.7

2.3.2.1. Starch

Starch is the major component of chickpeas and constitutes 37.2 to 50.8% of the whole seed and 55.3 to 58.1% of the dehulled seed. The desi type has less starch content than the kabuli type. Chickpea starch contains 31.8 to 45.8% amylose and the rest is amylopectin. The amount of amylopectin is higher than amylose, making this starch useful for special applications. With starch being a long-chain molecule, it has lower digestibility and may cause flatulence in humans (Biliaderis et al., 1981). Legumes are important ingredients of a balanced human diet in many parts of the world due to their high protein and starch content. The production of legume protein can be of economic value only if their starch component is made profitable simultaneously. Legume starches have been recognized as a potential food ingredient. Legume starches contain a relatively high proportion of amylose (30-65%) when compared to cereal starches (Table 2.3) (Chavan et al., 1986).

2.3.2.2. Sugar

Table 2.3 shows that most of the remainder carbohydrates of chickpeas include reducing and non-reducing sugars and crude fiber. The kabuli type chickpeas have higher level of soluble sugar than the desi types. Among legumes, chickpeas contain high amounts of raffinose, stachyose, verbascose and manninotriose. These oilgasaccharides cause flatulence in humans, because they cannot produce α-galactosidase required for digesting them. Therefore, the presence of these oligosaccharides is one of the most important reasons, which inhibits its use as convenience food (Chavan et al., 1986).

2.3.2.3. Fiber

Fiber constitutes a considerable proportion in human nutrition. Crude fiber in chickpeas ranges between 7.1 and 13.5% and includes cellulose and hemicellulose, which are major crude fiber components (Table 2.3). Crude fiber is mainly concentrated in the seed coat. The kabuli type has higher calorific value and nutrients because it contains less hemicellulose and cellulose in the whole seed and dehulled seed than the desi type. Studies have shown that dietary fiber is useful in reducing blood cholesterol levels.

2.3.3. Lipids

Legumes generally contain higher level of lipids than cereals (Salunkhe et al., 1985). The total lipid content in whole and dehulled chickpeas range between 3.1 and 6.9 %, between 4.5 and 7.5%, respectively (Table 2.4) (Chavan et al., 1986). Unsaturated fatty acids constitute 67.13% of the total lipids that include oleic acid (21.84%), linoleic acid (43.29%) and linolenic acid (2.0%). Saturated fatty acids constitute 10.42% of the total lipids, which include palmitic acid (9.22%) and stearic acid (1.20%) (Salunkhe et al., 1985; Chavan et al., 1986).

In mature legumes, most of the lipids are stored in oil bodies or spherosomes or lipidcontaining vesicles, which are located in the cotyledons. Most of the legume lipids are a good source of essential fatty acids such as linoleic and linolenic acids (Mahadevappa and Raina, 1978; Salunkhe et al., 1985). Oleic and linoleic acids are the major fatty acids in chickpeas, peanuts, soybeans, lentils, garden peas and broad beans. The unsaturated fatty acids of legume lipids have been involved in lowering blood serum and liver cholestrol levels (Salunkhe et al., 1985; Chavan et al., 1986).

Table 2.4. Chemical composition of chickpeas (Chavan et al., 1986)

Composition (g/100, d.b.)	Whole seed		Dehulled seed	
	Range	Mean	Range	Mean
Protein. (Nx6.25)	12.40 – 30.60	21.50	20.50 – 30.50	25.50
Total Carbohydrates	52.40 – 70.90	61.70	63.00 – 65.00	64.00
Lipid	3.10 – 6.90	5.00	4.50 – 7.50	6.00
Ash	2.50 – 4.67	3.60	2.10 – 3.70	2.90
Crude fiber	1.20 – 13.50	8.00	0.90 – 1.50	1.20

2.3.4. Minerals

Food legumes are good sources of minerals. The most important minerals contained in chickpeas are calcium, phosphorus, magnesium, iron, copper, zinc, sodium and potassium (Table 2.5). Most of the seed calcium is located in the seed coat. Therefore, the consumption of whole seed would be useful in calcium-deficient diets. Chickpeas are also a good source of iron. They contain higher level of iron in comparison with other legumes (Tarek A. El-Adawy, 2002).

Table 2.5. Vitamin and mineral composition of chickpea (Chavan et al., 1986; Tarek El-Adawy, 2002)

Mineral	mg/100 g (d.b.)	Vitamin	µg/100 g (d.b.)
Phosporus	226.00	Thiamin	453.33
Calcium	176.00	Riboflavin	173.33
Magnesium	176.00	Pyridoxine	466.33
Iron	7.72	Ascorbic acid	5.43
Copper	1.10	Niacin	1602.67
Zinc	4.32	Carotene	0.12
Sodium	121.00	Folic acid	0.15
Potassium	870.00		
Manganese	2.11		

2.3.5. Vitamins

Food legumes are good sources of vitamins such as thiamine, riboflavin and niacin (Salunkhe et al., 1985; Chavan et al., 1986). The vitamin content of chickpeas are shown in Table 2.5. Chickpea contains considerable concentration of niacin (1602.67 µg/100) (Table 2.5).

2.4. Potential Disadvantages of Legumes

Some of the more common anti-nutrients and toxic or undesirable substances present in legumes are Hemagglutinins, Heterosides, Phytic Acid, Flatulence Factors and Protease Inhibitors. The hemagglutinins are heat-labile. The heterosides (goitrogens) are usually heat-labile. Flatulence factors are not a nutritional problem but are of concern in relation to the extensive utilization of legume products. Although pulse grains are a good source of protein, they do not have enough sulfur-containing amino acid such as methionine and cystine (Saxena and Singh, 1987; Tabil et al., 1995). The main limiting nutritional factors attributed to the low utilization of pulse grains in developed countries are poor digestibility and availability of nutrients, flatulence factors, inherent beany flavor and presence of antinutritional factors.

2.4.1. Antinutritional Factors

2.4.1.1. Inhibitors

Pulse grains contain protein inhibitors (trypsin, chymotrypsin) and antinutritional factors (phytic acid, oligosaccharides, tannins, lipoxygenase, lectins) (Salunkhe et al., 1985; Tabil et al., 1995). Considerable variation in the protease inhibitors contents of chickpeas genotypes has been reported (Chavan et al., 1986). Studies have shown

that albumins are mainly responsible of the poor bioavailibility of protein (Clemente et al., 2000). A number of researchers reported that poor susceptibility to proteolysis may be due to the presence of disulfide bounds in the formation of protein complex. In addition, some studies have shown that some indigestible peptides such as trypsin inhibitor are responsible for poor digestibility. Globulins do not have any trypsin inhibitor activity, while albumins show high inhibitor activity in chickpea protein fractions. Recently, studies on some products such as soybean have shown that a very low level of protein inhibitors is active and there is no significant correlation between protein digestibility and the level of trypsin inhibitors (Clemente et al., 2000). Hence, it was reported that it is mainly the chemical structure of the proteins, which is responsible for protein indigestibility. Heat treatment inactivates trypsin inhibitors by more than 50% (Clemente et al., 2000). They reported that the presence of inter- and intramolecular disulphide bonds seems to be the main factor affecting chickpea albumin digestibility. The chymotrypsin inhibitor activity in chickpeas is higher than in cowpea, pigeonpea, broad bean and lentil. The trypsin inhibitor activity of some legumes such as soybeans, cowpeas, chickpeas, pigeonpeas, blackgrams and butterfly peas, is higher than chymotrypsin inhibitor activity. As mentioned before, heat treatment decreases the protease inhibitor activities in chickpeas (Chavan et al., 1986).

2.4.1.2. Oligosaccharides

The microbial fermentation of some oligosaccharides such as raffinose, stachyose and verbascose of pulse grains in the large intestines of humans cause flatulence. The compositions of oligosaccharides for chickpea are given in Table 2.3. Among pulse grains, chickpeas produce more flatus than others, which may be because of the higher oligosaccharides content in chickpeas. Some processing methods such as soaking and fermentation reduce oligosaccharides in chickpeas (Chavan et al., 1986).

2.4.1.3. Tannins

Chickpea seeds (whole seed) contain 78 to 272 mg per 100 g tannins, while the cotyledons have only 16 to 38 mg per 100 g. Tannins are mainly located in the seed coat. There is a considerable variation in seed coat color among the various chickpeas cultivars. The polyphenols in cultivars, which have darker testa color, inhibit the digestive enzyme activity more than cultivars with lighter testa color

(Chavan et al., 1986). These components impart astringent flavors, which are not always desirable. Some processing treatments such as dehulling and cooking considerably reduce the level of tannins in legume (Chavan et al., 1986).

Tannins are polyphenol components prevalent in food legumes. Studies have shown that tannins interact with proteins, enzymes or nonenzymes, and form tannin-protein complexes, which decrease protein digestibility and protein solubility. This decrease in protein digestibility may be caused by either the inactivation of digestive enzyme or the reduction of the susceptibility of the substrate proteins after forming the complex (Chavan et al., 1986). Polyphenols are found to interact with proteins and cause either inactivation of enzyme such as trypsin and chymotrypsin or make protein insoluble. Polyphenols inhibit several enzymes including α-amylase, lipases, pectin esterases, cellulases and β-galactosidase (Salunkhe et al., 1985). In addition to this, tannins reduce the bioavailibility of vitamins and minerals (Chavan et al., 1986).

2.4.1.4. Lipoxygenase

The presence of lipoxygenase in raw legumes, even in low fat-containing legumes, causes off flavor development during storage. Off flavor development can be prevented by blanching for frozen storage. Acid extraction of isolated protein can inactive lipoxygenase and causes fewer secondary products of lipid oxidation in comparison with the alkaline extraction (Rackis and Sessa, 1979). Lipoxygenase oxidation in protein fractions also decreases its nutritive value, digestibility and solubility.

2.4.1.5. Lectins

Lectins, which are also known as phytohemagglutenins, are proteins present in a number of plants, especially legumes such as chickpeas. Lectins interact with glycoprotein components of red blood cells' surface causing agglutination (Valdebouze et al., 1980; Chavan et al., 1986). Owusu-Ansah and McCurdy (1991) reported that the toxic effects of lectins when ingested orally may be due to their ability to bind to specific receptor sites on the surface of intestinal epithelial cells which thus cause a non-specific interference with the absorption of nutrients across the intestinal wall. High-moisture heat treatment can completely destroy lectins (Chavan et al., 1986).

2.4.1.6. Phytates

Phytic acid is another antinutritional factor, which increases in concentration after dehulling but reduced by cooking (Tabil et al., 1995). A considerable proportion of phosphorus (60 to 80%) of food legumes is formed as phytic acid or complexed with protein. Phytates decrease the bioavailibility of minerals. Thus, the presence of phytates would increase the mineral requirement in human nutrition (Salunkhe et al., 1985).

2.4.1.7. Non-starch polysaccharides (NSP)

Polysaccharides are linear or branched chains of glycosidically linked sugar units, synthesized from a few types of hexoses, deoxy hexoses, pentoses and uronic acids. It is difficult to present a general description of the plant polysaccharides, partly because they are complex heterogeneous compounds and partly because they have been classified in a variety of ways, depending on the interests of the investigators. Englyst and Hudson (1996) grouped all polysaccharide components other than starch as non-starch polysaccharides. Non-starch polysaccharides are further classified into cellulose and non-cellulosic polysaccharides, the latter containing hemicelluloses, β-glucans, pectic substances in addition to the storage polysaccharides such as inulin, gums and mucillages. Legume NSPs are more complex in structure than those in cereals, containing a mixture of colloidal polysaccharides called pectic substances (Choct, 2006). The NSP of legumes can be found in Table 2.3 and 2.6.

Table 2.6. Soluble, insoluble and total NSP contents (g/kg, d.b.) of some grain legumes and soybean meal (Barneveld, 1999; Knudsen, 1997; 2001; Periago et al., 1997; Anguita et al., 2006; Englyst and Hudson, 1996; Gdala et al., 1997)

Legume	Soluble NSP	Insoluble NSP	Total NSP
Chickpea	20-30	74-76	96-107
Faba beans	50	140	190-209
Peas	25-59	129-322	173-347
Soybean meal	63-139	154-164	217-303
White Lupin (cotyledon)	14-134	170-244	244-280

Water-holding capacity is another characteristic of NSP that may influence its anti-nutritional properties of NSP (De Lange, 2000). The ability to absorb large amount of water and maintain normal motility of the gut becomes one of the most important attributes of insoluble NSP in monogastric nutrition (Stephen and Cumming, 1979).

Choct (2004) reported that insoluble NSP can affect not only the digesta transit time and gut motility, but it can also act as a physical barrier leading to lowered nutrient digestion.

2.4.1.8. Others

Allergens saponins, and low levels of estrogenic substances may also be present in plant proteins. If products are improperly processed or heat-treated, toxic compounds such as tysinoalanine may be produced or the protein nutritive value may be lowered. Other reactions, such as the conversion of methionine to methonine sulfoxide or sulfone may also ocur (Marable et al., 1980).

2.4.2. Hardness

Hardness of legumes is the most important factor and sometimes it is problem during processing. Hardness is related with some chemical compositions of legumes. Also, chemical fortifications that are used either texture or nutritional purposes. Storage of legumes at high temperatures and low humidity sometimes generates the hardshell condition. The level of water that hard to cook seeds imbibe is approximately the same as that of normal seeds, but the hard to cook legumes do not soften during cooking because the cotyledon cells do not separate. Hardshell legumes have a defective seed coat and fail to soften during cooking because they do not imbibe sufficient water.

Chickpeas, as other legumes, are prone to develop the hardening phenomenon known as hard to cook (HTC) defect when stored under adverse conditions of high temperature and high relative humidity ($\geq 25\ ^{o}C$, RH $\geq$ 65%) (Reyes-Moreno and Paredes-Lopez, 1993; Hussain et al., 1989; Liu et al., 1992). Hardening diminishes quality characteristics of grain legumes. The legumes with this defect are characterized by extended cooking time for cotyledon and seed coat softening; they are less acceptable to the consumer and are of lower nutritive value (Uma-Reddy and Pushpamma, 1986; Hentges et al., 1991; Reyes-Moreno et al., 1994). Several hypothesis have been proposed to explain the cause of legume hardening, but the mechanisms are still unknown (Reyes-Moreno and Paredes-Lopez, 1993; Liu et al., 1992; Liu, 1995).

The hard-to-cook defect had been partitioned into reversible and irreversible components using common beans, previously stored under a range of temp. (15, 30 and 45 ^{o}C) and aw (0.59, 0.75 and 0.86) that had been soaked and cooked in distilled water or a 5% (w/v) aqueous solution of Na_2(EDTA). Results of phytate analysis and fluorescence microscopy showed that these components reflect the pectin-phytate mechanism or reversible hardening, and the lignification mechanism or irreversible hardening. These data help to explain the multiple mechanism aspect of bean hardening (Valle and Stanley, 1995).

A study had been undertaken to assess protein denaturation and starch gelatinization in ground samples of common black beans exhibiting the hard-to-cook (HTC) defect. No significant differences in either gelatinization or denaturation temperature had been found between hard and soft beans, but tropical storage conditions produced significant increases in gelatinization enthalpy and reductions in denaturation enthalpy. Endotherms of cooked samples showed that as little as 34% of the protein had denatured in HTC beans, versus greater than 85% in soft beans. Micrographs of DSC indicated that the ground raw material had been composed of clumps of cotyledon cells; cooking soft beans produced cell separation, but this did not occur in HTC samples. These data supported the idea that bean hardening had been accompanied by limited water availability inside cotyledon cells, which could reduce cell swelling, starch gelatinization and protein denaturation, leading to textural toughness (Garcia Vela and Stanley, 1989).

In order to study the effect of various salts on the hard-to-cook phenomenon, black beans had been stored under tropical conditions to induce the defect, and soaked in various aqueous sodium salt solutions prior to cooking. Statistical analyses of hardness data had been showed that storage conditions and pH of soaking solutions did not produce significant effects but anion type had been important in inducing softness as follows: CO_3^{-2} greater than $EDTA^{-2}$ = NO_3^{-} greater than SO_4^{-2} = Cl^{-}. Softening had been also promoted by increasing the ionic strength of the soaking solution. Treated beans indicated that storage conditions contributed more to degree of cell separation after cooking than salt treatment, which had little effect. These results bring a mechanism based on chelation and ion exchange into question. Differential scanning calorimetry data had been interpreted as meaning that soaking

beans in salt solution caused a major reduction (10-15 ^{o}C) in temperature of protein denaturation. This suggests that aqueous salts influence storage proteins, perhaps by solubilization and rendering them more thermally labile (Garcia Vela and Stanley, 1991). Effect of using salt solutions to soak fresh and hard-to-cook beans [Phaseolus vulgaris] on cooking time and protein quality (PER and digestibility); sensory analysis had been also carried out after soaking and cooking. It had been found that by increasing the ratio of monovalent (Na^{+} and K^{+}) to divalent ions (Ca^{+2} and Mg^{+2}) in the salt solutions, cooking time of both fresh and hard-to-cook beans decreased significantly (P = 0.05). Protein quality had been lowered significantly at lower (0.30) and higher (9.80) monovalent to divalent ion ratios. Data obtained indicated the feasibility of implementing this process at industrial or population levels in order to decrease cooking time of both fresh and hardened beans. The most effective solution evaluated had a salt composition of 0.5% $NaHCO_3$ and 2.5% K_2CO_3 (w/v) (a ratio of 8.30 of monovalent to divalent ions) (Leon et al., 1992).

Effects of degree and type of salinity on characteristics of faba beans had been studied in a randomized complete block design experiment with 5 irrigation water salinity levels and 6 replicates. Control irrigation water had a salinity level (as measured by electrical conductivity) of 0.5 mmho/cm. The same water plus NaCl, $CaCl_2$ and $MgCl_2$ (2:1:0.5) had been used to obtain 30 and 60 m-equiv./l and other irrigation waters had been prepared by adding $CaCl_2$ at 30 and 60 m-equiv./l. Plants had been irrigated 6 times, dried for 5 days after harvest and properties of dry seeds and cooked beans (autoclaving in distilled water at 115.5 degree C for 2 h) had been studied. The linear effect of Ca ($CaCl_2$ treatments) on dry seeds had been significant for yield, swelling coefficient, seed weight, % seed coat and hydration coefficient; linear effect of salt (mixture) had been significant for yield and swelling coefficient only. Salinity had no effect on seed germination. Cooked faba beans had been examined for texture, hydration coefficient, and spesific gravity, volume and weight of cooking liquor. Effects of salt (mixture) had been not significant, but effects of Ca had been significant for all properties except spesific gravity of the cooking liquor. Cooked faba beans from the Ca treatments had been harder in texture and had lower hydration coeff. than those from other treatments. Phytate, pectic substances and mineral contents of dry faba beans and cooking liquor had been affected by soil ions but there had been no significant correlation with the texture of cooked beans except

in the case of K content and some pectic fractions. Ash content of dry beans had been significantly correlated with texture of cooked beans and soil ions. Texture of cooked faba beans had been correlated negatively with soil pH and HCO_3 but correlated positively with electrical conductivity, Cl, total anions, total cations, Ca and Mg. Results indicate that effects of soil ions on cooking properties of faba beans may be due to changes in functional, biochemical or other properties of chemical constituents (El Tabey Shehata et al., 1988).

For comparison of the effects of processing with solutions of $CaCl_2$, $MgCl_2$, $NaHCO_3$ and a local (Nigerian) tenderizer known as `Kanwa' (sodium sesquicarbonate) on pectin losses and cooked texture of the cowpeas had been processed in double distilled water and local tap water. Analysis included total pectin, calcium and magnesium content, leached solids, texture and water absorption. The results show that $CaCl_2$, $MgCl_2$ and the local tap water increased firmness, Ca and Mg content in the cooked beans compared to distilled water; however, water absorption, leached solids and pectin solubilization had been decreased by these salts. Kanwa and $NaHCO_3$ increased water absorption, leached solids and softness in the cooked beans and also increased pectin solubilization but decreased Ca and Mg when compared to distilled water or the other salts (Uzogara et al., 1990)

In another study, model aqueous systems had been used for the study of the cooking quality of beans. These systems had been created using graded contents of calcium and magnesium ions, in a ratio of 4:1, to prepare aqueous media with cation content corresponding to 0-400 mg/L of calcium carbonate. The model systems had been used to measure the quality of boiled beans in water of low and high divalent cation content. A boiling time of 60 min had been used and an Instron Universal Testing Machine had measured the hardness of the boiling beans. Cooking of beans in water of low divalent cation content equivalent to 0-50 mg/litre $CaCO_3$ resulted in well-boiled beans for both types (easy-to-cook and hard-to-cook) of beans. Boiling in water of high divalent cation content led to the formation of very hard beans for both types of bean, while boiling in water of moderate divalent cation content (normal drinking water: 150-250 mg/L $CaCO_3$) differentiated between the two categories of beans. These results had been further tested by adsorption experiments with divalent cations, on beans boiled (a) in different proportions of boiling water, and (b) in

model aqueous systems. The divalent cation content of boiling water and the phytic acid content of the beans proved to be the crucial factors in the hard-to-cook phenomenon of beans (Kyriakidis et al., 1997).

In order to determine the synergistic effects between salt and hydrogen ion concentration (acidity or alkanity) on softening during cooking had been tested by modifying solutions in which pods of snap beans had been heated. Ca displacement had been minimized by soaking heated pods in 0.2M $CaCl_2$ before measuring firmness. Softening had been increased independently by the presence of salts and when pH had been raised from 5.2 to 6.2. Cations decreased firmness in the order Li greater than Na = K greater than NH_4 and Ca greater than Mg. Anions decreased the firmness in the order SO4 greater than acetate greater than Cl greater than NO_3. Firmness differences persisted at long heating times. Results support the hypothesis that pectin beta-elimination had been the principal softening reaction (Buren et al., 1990).

Two common bean had been seeded in the same location, harvested and cleaned. 3 hardening procedures had been used (soaking in acetate buffer, pH 4.1 at 37 degree C for 5 h; storage at 37 degree C, 100% RH for 28 days; and storage at 31-33 degree C, 76% RH for 120 days) to have seeds in a hard-to-cook (HTC) state. The adverse effects of HTC condition, in terms of cooking time as assessed by a Mattson bean cooker, had been eliminated by soaking seeds in salt solutions (1% NaCl + 0.75% $NaHCO_3$, and 0.75% $NaHCO_3$) instead of only water. Ultrastructural changes of cotyledon cells from fresh, HTC and softened seeds had been observed. Results of this study may be used for the development of a technological procedure to utilize properly HTC beans generated by inefficient storage systems (Paredes et al., 1991). In addition, winged bean seeds had been soaked for 24 h in distilled water, 30 or 50 g/L rice husk ash suspension or solutions of 10 or 20 g/L baking soda, or 5 or 10 g/L $NaHCO_3$, then boiled for 30 min in these solutions, either had been held and resoaked in distilled water, or peeled, washed for 24 h and resoaked for 24 h in distilled water. pH and level of leached solids increased during boiling. Boiling in distilled water or rice husk ash suspensions did not render the bean sufficiently soft, whereas boiling in the alkaline solutions produced adequately soft seeds. There had been no significant difference in tenderness of beans given further processing by

resoaking or peeling and resoaking, compared with boiling. Nature of the cooking liquid had no significant effect on the protein content of the seeds (Buckle and Sambudi, 1990).

Effect of alkali treatments on the stability of antinutritional factors (tannins, phytates and trypsin inhibitors), vitamins (niacin and riboflavin) and on protein quality of kidney beans had been studied. Samples had been processed by soaking for 24 h, in alkali solutions of sodium hydroxide (0.005 and 0.01M), sodium carbonate (0.025 and 0.05M) and sodium bicarbonate (0.05 and 0.01M). At low temperature sodium carbonate, and at high temperature sodium bicarbonate had been found to be the most effective treatments for the extraction of tannins. At both low and high temperature sodium carbonate had been found to be more efficient for the destruction of phytates. Extraction of trypsin inhibitors at both low and high temperature with sodium bicarbonate had been the most effective alkali treatment. Retention of niacin and riboflavin in beans had been greatest with sodium hydroxide treated beans. With all treatments pressure-cooking further reduced levels of antinutritional factors and vitamins (Jyothi and Sumathi, 1995)

2.5. Nutritional and Health Advantages of Legumes/Chickpeas

In general, legumes are sources of complex carbohydrates, protein and dietary fibre, having significant amounts of vitamins and minerals, and high energetic value (Table 2.1-6) (Tharanathan and Mahadevamma, 2003).

Several reports claim that inclusion of legumes in the daily diet has many beneficial physiological effects in controlling and preventing various metabolic diseases such as diabetes mellitus, coronary heart disease and colon cancer. Currently, the role of legumes as therapeutic agents in the diets of persons suffering from metabolic disorders is gaining interest (Shehata et al., 1988; Simpson et al., 1981). The consensus of recent opinion on healthy eating habits favors an increase in the proportion of legume-based polymeric plant carbohydrates including starch in the diet. Legumes belong to a group that elicits the lowest blood glucose response. Biological value, protein efficiency ratio, digestibility coefficient and net protein utilization of chickpea have been found as in the range of 0.520-0.850, 1.2-2.64, 0.760-0.928 and 0.870-0.920, respectively (Chavan et al., 1989).

The iron, folic acid, calcium, magnesium, potassium and B vitamins found in legumes help meet daily vitamin and mineral requirements. Legumes are also high in dietary fibers, low in saturated fat, and cholesterol free. Cereal proteins are deficient in certain essential amino acids, particularly lysine (Amjad et al., 2003). On the other hand, legumes have been reported to contain adequate amounts of lysine, but are deficient in S-containing amino acids (methionine, cystine and cysteine) (Farzana and Khalil, 1999).

Table 2.7. Nutritional and energy content of some cereals and legumes (d.b.) (Woleung et al., 1968; Gopalan et al., 1980: FAO food tables: Morriso, 1956: Chavan et al., 1986; Webb, 1987)

Food type	Energy (kcal/100g)	Protein (g/100g)	Fat (g/100g)	Carbohydrates (g/100g)	Fiber (g/100g)
Barley	374	12.7	1.8	84.6	5.4
Wheat	386	13.2	1.9	80.8	2.6
Rice (white)	363	6.7	0.4	80.4	0.3
Peas	381	24.7	1.2	69.7	2.3
Lentil	302	17.9	1.3	67.8	5.0
Chickpea	347	22.2	6.7	70.6	8.0
Dry bean	340	22.1	1.2	62.0	5.5
Soya bean	403	40.3	19.9	30.2	5.2

Viveros et al, (2001) determined the apparent metabolisable energy values of chickpea cv *Kabuli* and cv *Desi* to be 12.6 and 10.5 MJ/kg, respectively. The lower energy availability of the *Desi* types was attributed to its higher fibre content (97 g/kg) compared to Kabuli types (34 g/kg). The the apparent metabolisable energy value of chickpeas (cv *Amethyst*) to layers has been reported by Perez-Maldonado (1997) to be 10.6 MJ/kg.

Ravindran et al. (2005) reported that the digestibility coefficient of amino acids ranged from 0.58 for cystine to 0.84 for arginine (Table 2.4). The poor digestibility of cystine is probably related to the lowest concentration of this amino acid in chickpea. The mean amino acid digestibility coefficient was determined to be 0.74. The importance of dietary fiber in normal and therapeutic diets has been acknowledged by Schneeman (1987) and Brand et al. (1990) in recent years. Dietary fiber consists mainly of soluble and insoluble fiber fractions which exert different physiological effects on human health. Soluble fiber lowers serum cholesterol and helps to reduce the risk of heart attack and colon cancer (Trowell, 1972; Burkitt et

al., 1974 and Kelsey, 1978). However, cellulose, hemicellulose and lignin are the main components of insoluble dietary fiber which prevent or relieve constipation in humans due to absorption of water from the digestive track (Hill, 1974). Similarly, dietary fiber in human diets also reduces the risk of obesity, blood pressure, appendicitis, and many other diseases (Spiller, 1986; Brand et al., 1990).

Experimental, epidemiological and clinical studies show correlations between the consumption of food legumes and decreasing incidence of several diseases, such as cancer, cardiovascular diseases, obesity and diabetes (Kushi et al., 1999; Bhathena and Velasquez, 2002; Kris-Etherton et al., 2002). Antioxidant activities and phenolic compounds in raw legumes have been reported in several earlier communications (Amarowicz et al., 2003; Xu et al., 2007). Food processing not only improves flavor and palatability of foods but also increases the bioavailability of nutrients, by inactivating antinutritional factors, growth inhibitors and haemagglutinins (Chau et al., 1997).

2.6. Processings of Legumes for Digestibility

2.6.1. Blanching

Blanching usually refers to the immersion of foods in boiling water or steam for a short amount of time, and is typically applied to legumes after soaking. Blanching is a pretreatment process to decrease the cooking time of legumes. High temperature short time (HTST) blanching has been shown to minimise nutrient losses in soybeans (Song et al., 2003) when compared with longer time and lower temperature blanching. As well as influencing nutritional aspects of foods, blanching also affects water intake characteristics. Abu-Ghannam and McKenna (1997) found that blanching could enhance hydration rates of kidney beans during soaking.

Blanching is conventionally applied to legumes after soaking, however the results show that it would be beneficial to apply blanching prior to soaking. Pre-blanching significantly reduced initial microbial counts on dry soybeans. This would decrease the risk of further microbial proliferation during the soaking process. Secondly, blanching increased the hydration rate for soybeans, thus reducing the soaking time required. Soaking time could be decreased by up to two hours by applying a pre-blanching step. The blanching pre-treatment was most effective for soaking at

temperatures below 50 ^{o}C. During the blanching process, the soybean seed coat is plasticized, allowing for faster moisture intake during the subsequent soaking process. Soaking at and above 55 ^{o}C effectively blanches the soybean, making pre-blanching unnecessary.

2.6.2. Soaking

Soaking process is generaly applied to legumes before cooking or during cooking in order to decrease the cooking time and increase the leached materials. Soaking consists of hydration of the seeds in water, usually until they reach maximum weight, with or without discarding of the soaking medium, and the results obtained depend on factors such as legume genus, species and variety, process duration, temperature, pH, salinity of the soaking media, and also the storage conditions undergone before processing.

Numerous studies indicate that soaking can reduce the levels of total sugars, α-galactosides, minerals, phytic acid and proteolytic enzyme inhibitors (Frias et al., 2000) which can be partly or totally solubilised and eliminated with the discarded soaking solution. During soaking some metabolic processes can take place and usually affect the soluble carbohydrate and riboflavin contents (Vidal-Valverde et al., 2002).

Increasing the temperature of the soaking has been the most common method for reducing the soaking time. This has been quite effective and soaking time was reduced from 16 hr at room temperature to 1 hr at 90 ^{o}C. Increase of soaking temperature increased in loss of total solids, nitrogeneous compounds, sugars, oligosaccharides, Ca, Mg and water soluble vitamins (thiamine, riboflavin, and niacin) (Kon, 1979). The effects of soaking beans at room temperature for various durations on the cookability of Ghanaian cowpeas have been reported (Sefa-Dedeh et al., 1978). Soaking is an important step, since sufficient water content is crucial to secure an adequate gelatinization in the subsequent steaming step (Bello et al., 2006). Soaking of soybeans is an essential step in the production of traditional soyfoods such as soymilk and tofu. Also, the soaking process is thought to change the texture characteristics of soybeans and also facilitate the extraction of soyprotein. It is known that textural changes of soybeans resulted from water absorption during

soaking affect the subsequent grinding and soymilk extraction processes (Lo et al., 1968; Liu, 1997). As the soaking time increases, the amount of water absorbed increases with an increase in temperature (Wang et al., 1979; Sopade and Obekpa, 1990; Chopra and Prasad, 1994). Soaking may also reduce the firmness of cooked soybeans (Gandhi and Bourne, 1991).

In the Mediterranean Basin, the chickpea is soaked overnight in order to reduce the necessary time for reaching an adequate texture in the cooking process (Clemente et al., 1998). In other legumes such as beans, the seeds are soaked until they are saturated with absorbed water, and heat is introduced to induce softening (Hincks et al., 1989). Sefa-Dedeh et al. (1978) found a strong correlation between water absorbed and texture of cooked cowpeas at room temperature. Youssef et al. (1982) reported a significant correlation between the hydration coefficient and cookability index in faba bean. Williams et al. (1983) noticed that swelling capacity and hydration capacity were related to cooking time in chickpea. Other beneficial effects of a pre-soaking period include a softer drained texture, and partial removal of stachyose and raffinose, which are related to flatulence (Nelson & Hsu, 1985).

2.6.3. Chemical Soaking

Pre-soaking pulses in salt solutions before cooking has been suggested as a means of shortening cooking time (Rockland et al., 1979; Singh et al., 2000). Results from their study showed that pre-soaking in sodium chloride, sodium bicarbonate and sodium tripolyphosphate solutions all considerably reduced cooking time for whole seeds. Soaking reduced both the cooking time and its variation for chickpea and lentil (Singh et al., 1988). According to the authors, soaking with $NaHCO_3$ further decreased cooking time for chickpea and lentil. Paredes-Lopez et al. (1991) reported that adverse effects of the hard-to-cook condition in common beans were practically eliminated by soaking seeds in salt solutions consisting of 1% NaCl and 0.75% $NaHCO_3$ instead of only water. When legumes have to be processed for human nutrition by soaking alone; acidifying the soaking media improves the vitamin retention in most cases and the addition of sodium bicarbonate increases vitamin loss, discarding the soaking liquids leads to certain loss of thiamin and a considerable loss of niacin, especially in chickpeas. It was found that the same conditions produced the best retentions in other nutrients, such as starch, glucose, fructose,

sucrose and a greater destruction of antinutrients, such as α-galactosides and trypsin inhibitors in chickpeas (Frias et al., 2000). It is noticed from these previous reports that besides autoclaving, soaking the seeds in sodium bicarbonate ($NaHCO_3$) solution also reduced significant levels of antinutritional compounds of underutilized legume seeds.

It is notable that the soaking in $NaHCO_3$ solution is effective in reducing certain heat stable antinutritional compounds such as tannin, phytic acid and oligosaccharides by leaching into the soaking medium. Several studies have reported the beneficial effects of soaking in salt before cooking or using various salt solutions such as improvement of protein digestibility of legume seeds without affecting the nutritional components (Chavan et al., 1983; Erskine et al., 1985; Williams and Singh, 1987; Black et al., 1998).

Soaking of soybeans for 24 h, in alkali solutions of sodium hydroxide, sodium carbonate and sodium bicarbonate affected the extraction of tannins, the destruction of phytates and trypsin inhibitors. Retention of niacin and riboflavin vitamins in beans had been greatest with sodium hydroxide treated beans. Rockland et al. (1979) have developed a method for the preparation of quickcooking beans (*P. vulgaris*) based on soaking the beans with a mixture of four salts (sodium chloride, sodium tripolyphosphate, sodium carbonate and sodium bicarbonate), rinsing and drying.

2.6.4. Cooking

Cooking is probably the oldest treatment for making legumes edible. Usually it includes a previous soaking of the seeds and a subsequent cooking in boiling water until they become completely soft. During the cooking of legume seeds, two simultaneous processes occur inside and outside the cotyledon cells. Gelatinization of intracellular starch and denaturation of proteins are accompanied by softening of the seeds as a result of plasticization or partial solubilization of the middle lamella, which leads to separation of individual cotyledon cells (Rockland, 1978). In general, cooking produces denaturalisation of proteins and their diffusion to the liquid phase (Haytowitz and Matthews, 1983), inactivation of heat-sensitive factors, such as trypsin inhibitors (Frias et al., 2000), decrease of phytic acid (Iyer et al., 1989; Khalil and Mansour, 1995) and α-galactoside contents (El-Adawy, 2002). Also, the cooking

process can cause considerable losses in some essential nutrients, such as water soluble vitamins, due to their high solubility and thermal instability (Edijala, 1980; Abdel-Hamid, 1983; El-Adawy, 2002).

The chemical composition and nutritive value of chickpea proteins are both affected by processing methods (Singh, 1985). Chickpea seed is processed and cooked in a variety of forms depending upon traditional practices and taste preferences. Different domestic processing methods (decortication, soaking, sprouting, fermentation, boiling, roasting, parching, frying, steaming) remove anti-nutritional factors and increase the protein digestibility of chickpea seed (Attia et al,, 1994). Data are scarce for the effect of heating on the nutritive quality of chickpea proteins. Gonzalez et al. (1960) reported a decrease of certain amino acids, especially lysine, cystine and arginine, when chickpea seeds are cooked. Increasing the time and temperature of cooking was reported to reduce the availability of lysine in chickpea seed (Rama Rao, 1974). To minimise amino acid losses, cooking of chickpea in an autoclave (121 °C) for 1 h has been suggested (Youseff, 1983). An increase of in vitro protein digestibility of legume seeds after heat treatment has been reported, probably resulting from protein denaturation and inactivation of protease inhibitors (Tan et al., 1984; Khokhar and Chauchan, 1986; Salunke and Kadam, 1989).

During the soaking/cooking, measurement of color could give idea about the overall leaching of pigments and water-soluble vitamins into the water from the chickpea. The main pigments of chickpea fall into the carotenoids class although often small amounts of chlorophyll are also present. Water-soluble vitamins in mature whole soybeans are thiamine, riboflavin, niacin, pantothenic acid, pyridoxine, biotin, folic acid, inositol, cholin and ascorbic acid (Synder and Kwon, 1987). The chickpea seeds contain carotenoids such as beta-carotene, cryptoxanthin, lutein and zeaxanthin in amounts above the engineered betacarotene-containing ‘‘golden rice’’ level (Abbo et al., 2005).

During thermal processing, the food material may be exposed to temperatures which have an adverse effect on quality and make these products susceptible to color deterioration (Avila and Silva, 1999; Barreiro et al., 1997; Ibarz et al., 1999; Lozano and Ibarz, 1997; Rhim et al., 1989). It has been reported that many reactions can

affect color during processing of foods. Among them, the most common are pigment degradation, (especially carotenoids and chlorophyll), browning reactions (such as Maillard condensation of hexoses and amino components), change of ingredient distribution and structure (swelling, salt or sugar distribution), recrystallization of some compounds (sugar, salt etc.), phenol polymerisation and oxidation of ascorbic acid (Abers and Wrolstad, 1979; Aguilera et al., 1987; Barreiro et al., 1997; Cornwell and Wrolstad, 1981; Lee and Coates, 1999; Lozano and Ibarz, 1997; Maskan, 2001b; Maskan et al., 2002; Petropakis and Montgomery, 1984; Resnik and Chirife, 1979; Reynolds, 1965). Other factors affecting color include acidity, processing temperature and time, cultivars and heavy metal contamination (Abers and Wrolstad, 1979; Garcia-Viguera et al., 1999).

2.6.4.1. Cooking in water

Legume seeds are commonly cooked in boiling water at extended periods of 1 to 4 hours following overnight soaking. Cooking is generally done to produce a tender, edible product, to develop the aroma and to inactivate antinutritional factors present in the legume seeds. Cooking can be achieved at atmospheric or high pressure. Other cooking methods include roasting, extrusion cooking, and drum drying. Prolonged cooking results in destruction of amino acids, change in protein structure, and the reduction in the digestibility of proteins (Salunkhe et al., 1985).

2.6.4.2. Pressure cooking

Pressure cooking is common practice in many areas of the world for cooking whole seeds or dehulled seeds. Bressani (1993) reported that pressure cooking of black beans for 10 to 30 min at 121ºC improved the utilization of black bean, as compared to raw beans. Bressani (1993) also reported that the in vitro digestibility of navy beans improved by mild heat treatment. Excessive heating reduced the nutritive value of the beans due to the destruction or inactivation of certain essential amino acids.

2.6.4.3. Roasting

This process involves the application of dry heat to legume seeds using a hot pan or dryer at a temperature of 150 to 200 ºC for a short time, depending on the legume or the recipe to be made. Roasting produces a better product as far as protein quality is

concerned than one produced by common wet cooking under pressure. Subjecting legumes to heat for varying periods of time, namely toasting and roasting, is widely practised as a method of food processing. Roasted chickpea is a traditional snack food which is consumed in several countries of the Middle East. The method of preparation may show considerable variation in different countries. A special type of roasted chickpeas, called leblebi has been eaten in Turkey and neighboring countries for many years. Large-seeded chickpeas are used preferentially in the production of leblebi (Gülümser, 1988; Aydın, 2000; Bilgir, 1976; Köksel, 1998).

The traditional Turkish household practice for roasting or parching legumes includes first sprinkling the grains (wheat, dent corn etc.) or legumes (chickpeas, soybeans, etc.) with a little water. Then mixing the legumes with preheated sand or preheated edible salt in a roasting pan kept on an open fire and maintained at a temperature from 200 to 250 ^{o}C, depending on the legume or grain species. Roasting whole grains directly on a hot metal surface is also a common traditional process, but it has been little studied, with less published scientific data available (Koksel, 1998). Singh et al. (1992) suggested parching of chickpea at 190 ^{o}C for 40 s and repeating the operation twice after resting periods of 5 min between the parching operations. The roasted legumes or grains are separated from the sand (or edible salt) by sieving. Roasted kernels become sugary, yellowish, swollen, and softened; and they can be easily crushed between fingers at the end of the first roasting process. The second roasting is done using the roasting and speckling equipment until the surfaces of the chickpeas are slightly speckled (Aydın, 2000; Gülümser, 1988; Bilgir, 1976; Köksel, 1998).

2.6.4.4. Puffing and Popping

Legumes may be puffed by subjecting them to high temperatures for a short time. At the home level, gentle heating to around 80ºC and then moistening with 2% water, which is absorbed overnight, may do this. The following day, the grain is roasted with hot sand at 250 to 300ºC at which point the cotyledons puff and split the husk, which is then removed by gentle abrasion. At the cottage industry level, puffing is accomplished with husk-fired furnaces and large toasting pans operated by a number of people. Fully automated, continuous oil-fired and electric roasting machines are also available. Chickpea is the most common of the puffed legumes (Salunkhe et al.,

1985). Among legumes, chickpea (Cicer arietinum) and peas (Pisum sativum) are most commonly used for popping in many countries due to their ideal cell wall polysaccharide composition, starch properties and relatively high content of oil (Pratape & Kurien, 1986). Popped/expanded chickpea and its flour are being used extensively in food products (Kurien, 1987; Ravi and Bhattacharya, 2004).

2.6.4.5. Microwave cooking

In contrast to conventional heating systems, microwaves (electromagnetic spectrum between frequencies of 300 MHz and 300 GHz) penetrate into a food product, and heating extends throughout the entire food material. The absorption of microwaves by a dielectric material results in the microwaves giving up their energy to the material, with a consequential rise in temperature. The composition of food material affects how it heats in the microwave field. The moisture content of food directly affects the amount of microwave absorption. If the food material is highly porous with a significant amount of air, then due to low thermal conductivity of air, the material will act as a good insulator and show good heating rates in microwaves (Singh and Heldman, 2001). The shape of the food material is important in obtaining uniformity of heating. Non-uniform shapes result in local heating; similarly sharp edges and corners cause non-uniform heating. Heating is a consequence of interactions between microwave energy and a dielectric material (Singh and Heldman, 2001).

El-Adawy (2002) reported that microwave cooking resulted in the greatest retention of all minerals followed by autoclaving and boiling. Cooking of chickpea by microwave has been shown to reduce antinutritional factors and has positive effects on protein digestibility in other legumes. For soybeans, microwave processing has been used to eliminate the unpleasant flavour, and destroy trypsin inhibitors and increase solubility, digestibility and metabolism of soy protein (Hafez et al ., 1983, 1985). An increased protein efficiency ratio of microwave-heated soybeans, cowpea bean and chickpeas has been reported in comparison with raw legumes (Sanchez et al ., 1981; Dario and Salgado, 1994; Hernandez-Infante et al ., 1998).

2.6.4.6. Infrared cooking (Micronization)

Micronization is a short time high temperature process that utilises electromagnetic radiation in the infrared region (wavelength of 1.8–3.4 nm) to rapidly heat materials (Zheng et al., 1998). Use of infrared heating (micronization) in food processing is rapid and economical methods for processing of food products with high organoleptic and nutritional value. It also helps in efficient heat transfer to the food, and reduces processing time and energy costs and uniform heating is achieved in food products. The process has been shown to considerably reduce the cooking time of legumes, such as cowpeas, lentils and split peas (Arntfield et al., 2001; Cenkowski and Sosulski, 1998; Mwangwela et al., 2006).

Kouizeh-Kanani et al. (1983) and Van Zuilichem and Van Der Poel (1989) reported the effect of infrared heating on the antinutritional factors in soybeans and peas, respectively. The effect on physical and mechanical properties of legume seeds namely, kidney beans, green beans, black beans, lentil and pinto beans when subjected to infrared heating was studied (Fasina et al., 1997 and 2001). Significant changes in the properties of the seeds in terms of increased volume, lower rupture point and toughness, higher water uptake, and higher leaching losses (when seeds were soaked in water) were obtained in comparison to unprocessed seeds. The changes in the physical and mechanical properties of the seeds were attributed to seed cracking during infrared heating (Fasina et al., 1997). Cenkowski and Sosulski (1996) investigated the effect of infrared heating on the physical and cooking properties of lentil. They found that cooking time was shortened from 30 to 15 min for lentils adjusted to 25.8% moisture content when infrared heated to 55ºC. Micronization procedure has a theoretical or operational efficiency of 90%, while during practical application, efficiency can reach about 65% (Wray et al., 1996).

2.6.5. Freeze drying

Freeze drying or lyophilisation is a two-step dehydration process, in which the solvent and/or the medium of suspension is first crystallized at low temperatures and then sublimated from the solid state directly to the vapour phase. The main advantages of freeze drying is preservation of most of the initial properties of the raw material such as shape, taste, colour, flavour, biological, or pharmaceutical activity (Genin et al., 1996). Foods produced by freeze drying are characterized by high-

quality characteristics, such as low bulk density, high porosity, superior taste and aroma retention, and beter rehydration properties compared with products of alternative drying processes such as air, vacuum, microwave and osmotic drying (Krokida et al, 1998). Low processing temperature, the absence of liquid water and rapid transition from a fully hydrated to nearly completely dehydrated state minimize the deterioration reactions that occur normally in drying processes, such as non-enzymatic browning, protein denaturation, and enzymatic reactions (Liapis and Bruttini, 1995). Freeze drying also gives porous, nonshrunken dried products as a result of the structural rigidity afforded by frozen water where sublimation occurs; hence it gives a high rehydration capacity to freeze dried products (Liapis and Bruttini, 1995; Genin et al., 1996).

Insoluble dietary fibre increased for all freeze-dried cooked legumes in relation to the raw samples. It is known that slow freezing leads to irreversible damage to the food structure. Variation in rate of freezing affects ice crystal size and hence pore size in the product and so can be expected to influence the characteristics of the product, particularly its reconstitutability. The heat to be removed is the heat of crystallization. Crystal growth rate increases moderately as temperature of the product is decreased (Kutos et al., 2003).

2.6.6. Peeling (dehulling)

Legumes are generally dehulled to improve their cooking and nutritional qualities. Dehulling of these legumes also helps to remove antinutritional compounds such as polyphenols located in the seed coat. Pre-dehulling treatment for loosening the husk from the cotyledons is one of the important steps in dehulling of legumes. Loosening the hulls during dehulling is traditionally achieved either by wet or dry methods (Kurien, 1977). Predehulling treatments may also involve heat treatment alone or soaking in water, chemical solutions, tempering followed by hot dehulling (Phirke and Bhole, 2000; Phirke, et al., 1992; Ramakrishnaiah and Kurien, 1983; Srivastva, et al.,1988). The chemical nature of the mucilage and gums present in the interface between the husk and cotyledons (Sreerama et al., 2008). Dehulling of legume seeds and splitting the cotyledons are often carried out for better product profile and acceptability. Dehulling reduces cooking time and it shows a negligible effect on the total protein content and amino acid composition (Bressani and Elfas, 1980).

As the chickpea dehulling portion increased, the protein and sugar content decreased and the starch content increased in dehulled fractions. The protein, soluble sugars and ash content of powder fractions of chickpeas had been higher, and the starch content lower than those of dehulled after a given dehulling time. The Ca, Fe, Zn, and Mn content of powder fractions had been higher than that of dehulled. Albumin and glutelin fractions had been higher in the powder fraction; the globulin fraction had been higher in the dehulled fraction. Dehulling resulted in a net protein loss, but the quality of protein did not appear to vary in the powder and dehulled fractions. Results suggest that loss of the outer portions of chickpea cotyledons during dehulling considerably reduces the protein, sugar, ash, Ca, Fe, Zn, and Mn of chickpea (Singh et al., 1992). A study was extended to investigate the effect of dehulling on the quality of chickpea from both desi and kabuli types. Aditionally the dietary fibre content of product is reduced by dehulling (Coşkuner and Karababa, 2004).

Dehulling leads to a considerable loss in dry matter but has the advantage that with the seedcoat removed, pulses cook more quickly (Kon et al., 1973). On a domestic level, especially in the less-developed countries, dehulling is normally carried out manually using a pestle and mortar, although in industry large-scale machinery is used. The main nutrient lost in dehulling process is Ca. As tannins are mainly confined to the hull, they are also removed during dehulling; Elias et al. (1979) found that the presence of tannins lowered protein quality of beans (*P. vulgaris*) by reducing digestibility.

2.6.7. Irradiation

Gamma irradiation is a food preservation technique that offers potential to protect cereal grains and legumes from insect infestation and microbial contamination during storage. Besides its protective role against insects, gamma irradiation may also have important effects on the functionality and various quality criteria of food legumes (Rao and Vakil, 1985; Sabularse et al., 1991). Both dry and wet cooking times for Gamma irradiated legumes (chickpea, lentil and bean) could decreased due to alteration of physicochemical properties of macromolecules (Köksel and Çelik, 2001). Reddy et al. (1979) reported that nutritive value of beans is significantly improved by gamma-irradiation due to inactivation of anti-nutritional factors. The rates of

digestibility of proteins and α-amylolysis of starch were shown to increase by gamma-irradiation in red gram samples (Nene et al., 1975a, b). The irradiation treatment is also shown to be effective for reduction of flatulence causing oligosaccharides in green gram samples (Rao and Vakil, 1983).

Sattar et al. (1989 and 1990) observed decreases in the trypsin inhibitor (TI) activity during soaking and germination of irradiated legumes. Other antinutrients, namely phytic acid, α-amylase inhibitor and oligosaccharides, were inactivated to a considerable extent when the legume samples were subjected to irradiation (Siddhuraju et al., 2002). Also, an irradiation dose of up to 10 kGy has been found to be effective in the depolymerisation of NSPs such as β-glucans in oat and barley, which improved the nutrient absorption in chicken by increased β-glucan solubility and reduced the extract viscosity (Campbell et al., 1986 and 1987). Irradiation has been used for disinfestation of legumes and is reported to aid the retention of seed quality of pigeon peas during storage (Nene et al., 1975a, b).

2.6.8. Fermentation

Fermented foods may be defined as those foods which have been subjected to the action of microorganisms or enzymes so that desirable biochemical changes cause a significant modification to the food (Campbell, 1987). Fermentation is one such important process which significantly lowers the content of antinutrients (Sharma and Kapoor, 1996; Sripriya et al., 1997) and thereby improves the nutritive value of food grains. Fermentation encourages the multiplication of selected organisms and their metabolic activities in food. If the fermentation is carried out with probiotic organisms, it might have spefic added advantages apart from the improvement of nutritive value. Both single as well as sequential culture fermentations with probiotic organisms were elective in enhancing the nutritional quality of the indigenously developed food mixture. Antinutrients like phytic acid and trypsin inhibitor activity were completely eliminated due to sequential culture fermentation (Sangeeta et al., 2001). In some Mediterranean countries fermented chickpea is being used as a leavening agent to make traditional breads and rusks. By the addition of fermented chickpea in the wheat flour, besides to the enhancement of the nutritional quality, the product's shelf life is also expanded (Tulbek et al., 2003).

2.6.9. Germination

Germination is one of the most common and effective processes for improving the quality of legumes, and germinated legumes are widely consumed all around the word. The process is influenced by external factors such as germination time and presence or absence of light both of which aid or inhibit the germination process in relation to the reserve materials of the seed (Ridge, 1991). Soaking legume seeds in water must precede germination. During germination, some of the seed reserve materials are degraded and used for respiration and synthesis of new cell constituents of the developing embryo, therefore causing significant changes in the biochemical, nutritional and sensory characteristics of these legumes. It is known that the germination process generally improves the nutritional quality of legumes, not only by the reduction of antinutritive compounds, but also by augmenting the levels of free amino acids, available carbohydrates, dietary fiber, trypsin and chymotrypsin inhibitors and other components, and increasing the functionality of the seeds due to the subsequent increase in the bioactive compounds (Danisova et al., 1995; Ayet et al., 1997; Lopez-Amoros et al., 2001; Frias et al., 2002; Vidal-Valverde et al., 2002, 2003; Martin-Cabrejas et al., 2008). Germination involves the breakdown of seed reserves owing to increased enzyme activity. Upon germination, the content of vitamins also increases considerably (Vijayaraghavan, 1981). Increase in enzyme activities (amylase, invertase, lipase and protease) and decrease in protein, lipid and carbohydrate content of chickpea have been found during the germination of chickpea (Rahman et al., 2008). The main effect of germination besides the loss of dry matter reported by Kon (1979) is to increase the content of vitamin C. Hsu et al. (1980) showed that for three pulses, the vitamin C content is between 600-800 mg/kg dry weight of seed after 4 days of germination, while the ungerminated seed contained negligible quantities. Additionally, as would be expected, the phytic acid content of seed is reduced during germination (Tabekhia and Luh, 1980; Rozan et al., 2000; Prodanov et al., 1997; Sierra and Vidal-Valverde, 1999).

2.6.10. Extrusion Cooking

Extrusion cooking has advantages including versatility, high productivity, low operating costs, energy efficiency and shorter cooking times. Extrusion cooking application to legume processing has developed quickly during the last decade, and can now be considered as a technology of its own right. Legume extrusion cooking

would allow reduction of antinutritional factors and therefore improve the nutritional quality at a cost lower than other heating systems (baking, autoclaving, etc.) due to a more efficient use of energy and better process control with greater production capacities (Reimerdes, 1990; Alonso et al., 1998; Quintana et al., 1998; Alonso et al, 2000b).

2.6.11. Frying

Cereals, legumes, millets, tubers and animal foods in various forms have been processed by frying. Among the legumes, chickpea is the most common raw material for making a variety of fried snacks. The fiber content of chickpeas fried in vegetable oil, a snack food commonly consumed in Spain, has been modified during frying. The total dietary fiber level decreased 3.6% from that of raw chick peas and 4.7% from that of soaked peas. The insoluble fraction has been reduced slightly, the soluble fractions as a result modified during frying. Varo et al. (1983) and Augustin et al. (1989) found higher insoluble dietary fiber values in other fried food. The nitrogen residue in fried chickpeas was larger than the residue in raw and soaked chickpeas. The amount of total dietary fiber increases (from 16.8 to 25.1%) after cooking and a decrease (from 16.8 to 13.2%) after frying. The insoluble dietary fiber fraction is responsible for the increase with boiling.

Ultrasounds and Applications

2.7.1. Ultrasounds

Ultrasound is a form of energy generated by sound waves of frequencies that are too high to be detected by human ear, i.e. above 16 kHz (Jayasooriya et al., 2004). Ultrasound when propagated through a biological structure, induces compressions and depressions of the medium particles and a high amount of energy can be imparted. In dependence of the frequency used and the sound wave amplitude applied a number of physical, chemical and biochemical effects can be observed which enables a variety of applications (Got et al., 1999; Knorr et al., 2004).

The amplitude can be expressed in terms of a number of different physical properties of the material that vary in the presence of an ultrasonic wave, such as the displacement of the layers from their equilibrium position, the velocity or acceleration of the layers, or the local energy, pressure, density, or temperature

within the material. An ultrasonic wave is characterized by its amplitude and frequency, which are chosen by the investigator, and its wavelength and attenuation coefficient, which are (frequency-dependent) characteristics of a material. The attenuation coefficient is a measure of how rapidly the amplitude of a wave decreases as it travels through a material: the higher attenuation coefficient, the more rapid the reduction in amplitude. The ultrasonic velocity is related to the wavelength and frequency (velocity = wavelength x frequency), and so it is also a characteristic property of a material. Measurements of the ultrasonic velocity and attenuation coefficient are the basis of most ultrasonic techniques used to evaluate the properties of foods (McClements , 1997)

The upper limit of ultrasound frequency is one, which is not sharply defined but is usually taken to be 5 MHz in gases and 500 MHz in liquids and solids. To avoid possible confusion, it is helpful to point out that there are two distinctly different types of application of ultrasound in the food industry: *high*- and *low*-intensity applications. The power levels used for low-intensity ultrasounds are so low (typically less than 1 W/cm^2) that they cause no alteration in the physical or chemical properties of a food once the ultrasonic wave is removed (i.e., they are nondestructive). On the other hand, high-intensity applications use power levels that are so high (typically between 10 and 1000 W/cm^2) that the properties of a food material are changed, often permanently (McClements, 1997).

When ultrasonic waves propagate into liquid media, alternating compression and expansion cycles are produced. During the expansion cycle, high intensity ultrasonic waves make small bubbles grow in liquid. When they attain a volume at which they can no longer absorb enough energy, they implode violently. This phenomenon is known as cavitation. The bubbles have a larger surface area during the expansion cycle, which increases the diffusion of gas, causing the bubble to expand. Cavitation can result in the occurrence of micro streaming which is able to enhance heat and mass transfer (Jayasooriya et al., 2004; Zheng and Sun, 2006). The ability of ultrasound to cause cavitation depends on ultrasound characteristics (e.g. frequency, intensity), product properties (e.g. viscosity, surface tension) and ambient conditions (e.g. temperature, pressure). The frequency is inversely proportional to the bubble size. High frequency ultrasounds generate small cavitation bubbles resulting in lower

pressures in the cavitation zone. As the frequency increases the cavitation zone becomes less violent and no cavitation is observed anymore. The ultrasound intensity required to cause cavitation increases markedly above about 100 kHz (Williams, 1983).

When high-intensity acoustic energy travels through a solid medium, the sound wave causes a series of rapid and successive compression and rarefaction, with rates depending on its frequency. In turn, the material is subjected to a rapid series of alternating contractions and expansions, much like when a sponge is squeezed and released repeatedly. This mechanism, known as "rectified diffusion", is very important in acoustic drying and dewatering and noticeable moisture migration takes place overall (Ensminger, 1988). In more dense materials that are practically incompressible, the alternating acoustic stress facilitates dewatering by either maintaining existing channels for water movement or creating new ones. Dense materials usually "fracture" under acoustic stress. Microscopic channels are created in directions normal to wave propagation during rarefaction, or parallel to wave propagation during compression (Floros and Liang, 1994).

High-intensity ultrasound in low-viscosity liquids and gases produces violent agitation, which can be utilized to disperse particles (Ensminger, 1988). At liquid/solid or gas/solid interfaces, acoustic waves cause extreme turbulence known as "acoustic streaming" or "micro streaming" (Nyborg, 1965). This reduces the diffusion boundary layer, increases the convection mass transfer, and considerably accelerates diffusion in systems where ordinary mixing is not possible.

For food processing purposes it is important to address the generation of heat due to ultrasound applications and the related cavitation (implosion of gas bubbles) caused by a rapid change of heating to 5500 ^{o}C and pressure increase to 50 MPa (Leighton, 1998). The temperature and pressure indicated are generated during a very short periods of time at the point were cavitation occurs with an order of temperature variation of 109 ^{o}C/s (Suslick, 1991). Shock waves are generated due to cavitation, which are contributed to the ultrasound effect. Formation and behaviour of the bubble of cavitation upon the propagation of the acoustic waves constitute the

essential events which induce the majority of the acoustic effects (Dahnke et al., 1999; Leighton, 1998; Save et al., 1994, 1997; Thakur and Nelson, 1997).

2.7.2. Application of Ultrasounds in Food Technology

In the literature ultrasounds have been appiled to edible oils, dairies (milk), sugar solutions, sugars, molasses, yeast production, chocolate crumb, peas, potato crisp, dough and float suspended in a solution of alcohol/water, soups, jams, brewing, orange juice or other juices, fruit juice (both concentrate and diluted), water, custard, sugar beet, peanut, sauces, gravies, mayonnaises, salad creams, synthetic creams, frozen-food industry, cereals and meat industry. Low energy ultrasound applications include stimulation of activity of living cells, surface cleaning of foods, effects on enzymes, ultrasonically assisted extraction, crystallization, emulsification, filtration, drying and freezing processes as well as tenderization of meat. In general, ultrasonic cavitation in liquids may cause fast and complete degassing; initiate various reactions by generating free chemical ions (radicals); accelerate chemical reactions by facilitating the mixing of reactants; enhance polymerization/depolymerization reactions by temporarily dispersing aggregates or by permanently breaking chemical bonds in polymeric chains; increase emulsification rates; improve diffusion rates; produce highly concentrated emulsions or uniform dispersions of particles; assist the extraction of substances such as enzymes from animal, plant, yeast, or bacterial cells; remove viruses from infected tissue; and finally, erode and break down susceptible particles, including micro-organisms (Povey and McClements, 1988; Mason et al., 1996; Mason and Luche, 1996; Behrend and Schubert, 2001; Dolatowski and Stasiak, 2002; Stasiak, 2005).

Ultrasounds have been used in fish tissues, chicken and raw meat mixtures related to its composition (Simal et al., 2003). High-intensity ultrasound has been used for many years to generate emulsions, disrupt cells and disperse aggregated materials. More recently various areas have been identified with greater potential for future development, e.g. modification and control of crystallization processes, degassing of liquid foods, enzymes inactivation, enhanced drying and filtration and the induction of oxidation reactions (Knorr et al., 2004; McClements, 1995; Roberts, 1993; Zheng and Sun, 2006).

When a liquid is irradiated by ultrasound, micro bubbles can appear, grow and oscillate extremely fast and even collapse violently if the acoustic pressure is high enough. These collapses occurring near a solid surface will generate microjets and shock waves (Suslick et al., 1987). Moreover, in the liquid phase surrounding the particles, high micro mixing will increase the heat and mass transfer and even the diffusion of species inside the pores of the solid (Contamine et al., 1994).

The possibility of using low-intensity ultrasound to characterize foods was first realized over 60 years ago; however, it is only recently that the full potential of the technique has been realized (Povey and McClements, 1988). Applications of ultrasound in food technology are found in the location of foreign bodies in food, the analysis of droplet size in emulsions of edible fats and oils and the determination of the extent of crystallization in dispersed emulsion droplets (Mason et al., 1996). Ultrasounds have been also used in dairy industry for the degree of homogenisation of fat within milk. It is possible to determine factors such as the degree of "creaming" of a sample, i.e. the movement of solid particles/fat droplets to the surface. The combination of velocity and attenuation measurements shows promise as a method for the analysis of edible fats and oil as well as for the determination of the extent of crystallization and melting in dispersed emulsion droplets (Mason et al., 1996).

One of the earliest use of ultrasound in processing is in emulsification. Emulsions generated with ultrasound are often more stable than those produced conventionally and often require little, if any, surfactant (Mason et al. 1996). Investigations have shown that the use of ultrasound as a processing aid can reduce the production time of yoghurt of up to 40%. Moreover, sonication reduced the normal dependence of the process on the origin of milk as well as improved both the consistency and the texture of the product. It also found that fish egg exposure to ultrasound of frequency 1 MHz for 35 min, three times a day resulted in the reduction in hatch time for loach from 72 to 60 hours. Several reports in the literature suggest that ultrasonic treatment of seeds before sowing is an effective method of improving crop yield (Mason et al., 1996).

One of the original uses of ultrasound in biochemistry is related to break down biological cell walls to liberate the contents. Subsequently it has been shown that power ultrasound can be used to activate immobilized enzymes by increasing the transport of substrate to the enzyme. As far as enzymes are concerned, ultrasound can also be employed as a method of their inhibition (Mason et al., 1996). Chambers (1937) reported that pure pepsin is inactivated by sonication probably as a result of cavitation. By applying ultrasound for over three hours, the original activity of peroxidase, responsible for the development of off-flavours and brown pigments, was progressively reduced by 90% (Mason et al., 1996).

The use of ultrasound significantly improves the extraction of organic compounds contained within the body of plants and seeds. The mechanical effects of ultrasound provide a greater penetration of solvent into cellular materials and improve mass transfer (Mason et al., 1996). Additional benefit results from the disruption of biological cell walls to facilitate the release of contents. Combined with this effect is enhanced mass transfer, due to the effects of microstreaming which results in a more efficient method for sugar extraction (Chendke and Fogler, 1975). The sonication accelerated sugar diffusion and gave the higher level of dry matter content and sugar content in juice (Stasiak, 2005). By using of ultrasound extraction of tea solids from leaves was improved by nearly 20%. Zayas (1986) reported that an increased yield of the enzyme rennin from calf stomachs has been achieved by using ultrasound. Power ultrasound has proved to be extremely useful in crystallization processes. It serves a number of roles in the initiation of seeding and subsequent crystal formation and growth (Mason et al., 1996; Stasiak and Dolatowski, 2007). Ultrasound has also been applied to filtration (Mason et al., 1996). Another example of ultrasound application of potentially great commercial importance is acoustic drying. By employing ultrasound the heat transfer between a solid heated surface and a liquid is increased by approximately 30-60% (Ensminger, 1988).

Power ultrasound has proved itself an effective method in assisting food freezing and its benefits are wide-ranged. In addition to its traditional application in accelerating ice nucleation process, it can also be applied to freeze concentration and freeze drying processes in order to control crystal size distribution in the frozen products. Application of power ultrasound can also benefit ice cream manufacture by reducing

crystal size, preventing incrustation on freezing surface, etc. (Zheng and Sun, 2006). Among other applications are improvements in the extraction of flavourings, filtration, mixing and homogenization and the precipitation of airborne powders, destruction of foams which cause general difficulties in process control e.g. in fermentation. As a result of continued research interest and development in instrumentation, novel applications such as oxidation of unsaturated oils, aging of alcoholic beverages, hydration of acetylene, decalcification of bone, hydrolysis of esters have been developed (Mason, 1999; McClements, 1995).

High power ultrasound is known to damage or disrupt biological cell walls which will result in the destruction of living cells. Unfortunately very high intensities are needed if ultrasound alone is to be used for permanent sterilization. Thermosonic (heat plus sonication), manosonic (pressure plus sonication), and manothermosonic (heat plus pressure plus sonication) treatments are likely the best methods to inactivate microbes, as they are more energy efficient and effective in killing microorganisms. The advantages of ultrasound over heat pasteurization include: the minimizing of flavour loss, greater homogeneity and significant energy savings (Mason et al., 1996; Piyasena et al., 2003). A considerable amount of data exists regarding the impact of ultrasound on the inactivation of microorganisms (Piyasena et al., 2003). Bactericidal effects of ultrasound were observed while suspended in culture medium (Davies, 1959). According to Lillard (1993) Salmonellae attached to broiler skin were reduced upon sonication in peptone at 20 kHz for 30 min. Results of research carried out by Dolatowski and Stasiak (2002) proved that ultrasound processing was having a significant influence on microbiological contamination of meat.

Some studies show increased tenderness of meat with low frequency ultrasound (22-40 kHz) treatment (Dickens et al., 1991; Dolatowski, 1988; 1989). Zayas and Gorbatow (1978) also reported the improvement of the tenderness of meat immersed in brine, sonifying at frequency of 22 kHz and 1.5-3 W/cm^2 (Dolatowski and Twarda, 2004). Ultrasound treatment caused fragmentation of myofibrils and disintegration of other cellular components (Dolatowski, 1988). Ultrasound-assisted process of meat tumbling caused the significant improvement of the yield, tenderness and juiciness of the end product (Dolatowski and Stasiak, 1995). Pre- and post-rigor

ultrasound treatments had small effects on raw meat texture, with ultrasound treated meat having a slightly softer raw meat texture after three to six days ageing (Got et al., 1999). Research in the last decade has shown the potential benefits of ultrasound treatment as an alternative technology for modifying properties of meat and meat products (Jayasooriya et al., 2004).

There are an increasing number of industrial processes that employ power ultrasound as a processing aid including the mixing materials; foam formation or destruction; agglomeration and precipitation of airborne powders; the improvement in efficiency of filtration, drying and extraction techniques in solid materials and the enhanced extraction of valuable compounds from vegetables and food products (Dolatowski et al., 2007).

Some of the simplest ultrasonic measurements involve the detection of the presence/absence of an object or its size. This approach can be used to detect (or image) the presence of fluid in a pipe, fouling on the inside surface of a pipe (Withers, 1996), the fill level of a tank, the presence of glass fragments at the bottom of a beverage container (Zhao et al., 2003), or to measure the thickness of a fat layer in an animal and thereby estimate carcass composition (Fisher, 1997). Ultrasound has also been widely used in the measurement of the solids content of semicrystalline fats (McClements and Povey, 1988). The speed of sound in fat decreases with temperature, while it increases in most aqueous solutions. Commercial ultrasonic particle sizers are widely available and enjoy the important advantage of working well with turbid food colloids (Dukhin and Goetz, 2001). Some intriguing applications of ultrasound have involved attempts to measure fluid viscosity. The flow profile generated can then be used to calculate fluid viscosity (10 MHz) (Choi et al., 2002). Some examples of ultrasonic application include measurements of the texture of cheese (Benedito et al., 2000; Cho et al., 2001) and cooked vegetables (Nielsen and Martens, 1997) and the ripeness of fruit (Flitsanov et al., 2000).

High energy ultrasound has been applied for degassing of liquid foods, for the induction of oxidation/reduction reactions, for extraction of enzymes and proteins, for enzyme inactivation and for the induction of nucleation for crystallization (Roberts, 1993; Thakur and Nelson, 1997; Villamiel and De Jong, 2000a). Further, heat, pressure, ultrasound combinations have been reported to inactivate heat

resistant enzymes (Vercet et al., 1997). Also a considerable amount of data exists regarding the impact of ultrasound on the inactivation of micro-organisms in conjunction with chemical antimicrobials (Phull et al., 1997), with heat or with heat and moderate pressure (Ciccolini et al., 1997; Sala et al., 1995; Villamiel and De Jong, 2000a).

The potential of ultrasound in beer processing was also analysed. Ultrasonic treatment at the beginning of the mashing process results in enhanced mash filtration. The increased filtrate flow occurred in the initial period of the filtration process. Apart from a better filterability, an increase in extraction yield was achieved by ultrasonic treatment. An increase of 0.5% was observed when the mash was ultrasonicated with 48 kJ/kg (Buckow et al., 2001). Ultrasound has been used for many years in the study of proteins. The major application of the technique has been determination of pseudo-adiabatic compressibility for which the technique is uniquely suited. The compressibility of solute molecules in solution is determined in the dilute limit from measurements of the concentration dependence of the speed of sound and density. Such studies have been used to estimate protein hydration and to infer changes in protein conformation. These parameters may be related to functional properties of proteins in foods such as solubility, foaming capacity and flexibility (Gekko and Yamagami, 1991)

Power ultrasound (20 to 100 kHz and high power), has proved to be useful in the formation of ice crystals during the freezing of water (Li and Sun, 2002b). Under the influence of power ultrasound, a much more rapid and even seeding occurs and this leads to shorten the time between the initiation of crystallisation and the complete formation of ice, and reduce cell damage. This may be mostly due to acoustic cavitation, which consists of the formation, growth and violent collapse of small bubbles or voids in liquids (Simal et al, 1998a), the cavitation bubbles acting as nuclei for crystal growth or by the disruption of nuclei already present (Mason, 1998). Furthermore, other studies (Lima and Sastry, 1990; Sastry et al., 1989) have showed that power ultrasound enhanced liquid to particle convective heat transfer. These damages in plant tissues would result in loss of function in cell membrane, disruption of metabolic systems, protein denaturation, permanent transfer of intracellular water to the extracellular environment, enzyme inactivation, and

extensive cell rupture. Properties that reflect freshness and turgidity would also lose in frozen food, because they depend largely upon the structural arrangement and chemical composition of the cell wall and the intercellular spaces where pectic substances are the primary constituents (Cano, 1996). In comparison with the microstructure for the potato tissue by immersion freezing, the cells with ultrasound treatment under power of 7.34 W remain integral, which is of importance to the textural properties and nutritive values of plant tissue. The application of power ultrasound is effective in improving the structure of frozen-then-thawed potato tissue (Floros and Liang, 1994).

A combination of consecutive ultrasound and high pressure treatment caused a slightly increased inactivation of E. coli, which can be attributed to the additional effect of ultrasound. Generally, most microorganisms showed greater sensitivity to ultrasound at increased temperature over 50 ^{o}C (Earnshaw et al., 1995; Zenker et al., 1999; Villamiel and De Jong, 2000a). The application of ultrasonic waves generating cavitation in suspensions which contain microorganisms and enzymes often has a lethal result and deactivating action (Suslick, 1988). Effects of ultrasound (32 kHz; 20; 50 and 65 ºC) had investigated that combined use of ultrasonic and thermal treatment, especially at 65 ºC, provided ultrasonic effect in addition to thermal effect on the microbial inactivation of strawberries (Bozkurt and İçier, 2009). Generally the ultrasound treatment are not much effective on small and round cells (Allinger, 1975), for example, Gram-positive bacteria, such as *Staphylococcus* aureus and *Enterococci* (Ordonez et al., 1984) are quite resistant and even more resistant are bacterial spores (Ahmed and Russell, 1975; Boucher and Lechowich, 1979). The combined effect of ultrasonic waves and heat treatment applied simultaneously appears instead more effective (Ciccolini et al., 1997) and even more are treatments which use the combination of heat and ultrasound under pressure (Raso et al., 1994). The same combination of effects has been demonstrated to have a quite effective deactivating action on various enzymes of interest in food technology (Lopez and Burgos, 1995a). The decimal reduction time decreases exponentially by increasing the power intensity and decreases faster the lower the frequency of the ultrasound.

The use of acoustic energy to assist solid–liquid separation processes has been explored in different ways, the majority of them oriented to obtain drying effects. In

fact, the pioneering authors in the use of acoustic energy to remove moisture from a product applied air-borne ultrasound and considered that the main effect was to increase the rate of evaporation (Brun and Boucher, 1957; Greguss, 1963). Tarleton & Wakeman (1998) reviewed the state of the art of acoustic dewatering and drying. High-intensity ultrasonic fields may be effective in the release of the residual moisture. Ultrasonic energy directly coupled to the cake to be dried causes alternative contractions and expansions in a similar way to a sponge when it is squeezed and released repeatedly (Gallego-Juarez et al., 1999).

The ultrasonic applications extend to all types of food products such as vegetables and fruits, meat and fish, drinks, oils and also to the dairy industry. In these applications the change in the physicochemical characteristics, such as textural properties or sugar content, has been related to ultrasonic parameters such as velocity and attenuation. Ultrasonic techniques have also been used to determine the beef carcass value and quality attributes (Cross and Belk, 1994). The composition of milk, wine, sugar solutions and oils has also been determined through the use of low intensity ultrasounds (Winder et al., 1970). The low intensity ultrasons can be applied to several stages of the cheesemaking process. Gunasekaran and Ay (1996) found that the ultrasonic velocity increased during coagulation while attenuation decreased. These changes increase cheese firmness thus increasing the ultrasonic velocity. Elasticity and firmness were the sensory attributes that best related to the ultrasonic velocity. In practice, the ultrasonic velocity increases during maturation, thus allowing to classify the pieces from a single ultrasonic measurement. The ultrasonic velocity increases in line with temperature in water, but decreases in fat (McClements,1997; Povey and McClements, 1988; Mulet et al., 1999). High intensity ultrasounds was used to isolate rice starch without causing undue starch damage (Wang and Wang, 2004).

The application of ultrasound and High Hydrostatic Pressure during soaking appeared to promote the leaching of oligosaccharides, whereas their effectiveness in oligosaccharide reduction of legumes during soaking varied among legume species. Ultrasound and High Hydrostatic Pressure could reduce the soaking time required to reduce oligosaccharide content. The higher oligosaccharide content of cooked legumes without presoaking compared with that of uncooked legumes was probably

due to the release of bound oligosaccharides and leaching of other soluble compounds, including mono and disaccharides, and soluble fiber (Han and Baik, 2006).

The structure and function of biological molecules can be changed by the ultrasound irradiation. The most common interaction mechanisms which involved in this case are either heat or chemical effects and acoustically induced cavitational activity. In addition to these, acceleration the rate of influx or uptaking of a substance into a seed by ultrasonication can also be caused by mechanical effects, i.e. shear stress developed by eddies arising from shock waves. Sonication have applied treating the extensive range of the seed types (Toma et al., 2001; Shimomura, 1990; Aladjadjiyan, 2002; Hebling and Silva, 1995; Weinberger and Measures, 1968). The effects of ultrasound (20 kHz) as emerging technology were investigated on germination stimulation, amount of alpha-amylase activity on dry barley seeds before steeping stage of malting process. It has been found that when malting barley is irradiated with an ultrasonic power, astimulating effect occurs as to the enzyme activity (Yaldagard et al., 2008).

Ultrasonic pre-treatment prior to airdrying on dehydration of bananas had studied to allowed estimating the water diffusivity in the air-drying process for bananas submitted to ultrasound. Results showed that the water diffusivity increases after application of ultrasound and that the overall drying time was reduced by 11% (Fernandes and Rodriques, 2007). The use of ultrasound in the food industry is new and few studies have addressed the use of ultrasound (Fuente-Blanco et al., 2006; Gallego-Juarez et al., 1999; Mason et al., 1996; Zheng and Sun, 2006). Few studies have addressed drying of fruits and most have used ultrasound to assist osmotic dehydration (Carcel et al., 2007b; Simal et al., 1998a).

Ultrasound-assisted extraction of oil from flaxseed has reported. It has been found that ultrasound-assisted extraction requires a shorter extraction time and a reduced solvent consumption. The yield of flaxseed oil has been found to increase with the increase of the ultrasonic power and to decrease as the temperature is increased (Zhang et al., 2008).

Elmehdi and Kovacs (2009) had reported that ultrasound has been used to investigate the structural and functıonal properties of wheat gluten. The results demonstrated that ultrasonic techniques can be used to measure changes in the physical, chemical and biological properties of wheat proteins, particularly the thermal transitions which relate to noodle, pasta and bread quality. Physical properties of soy proteins such as in texture model, mean diameter, volume-surface area, gelling, conductivity, solubility, emulsion activity index increased with ultrasound 20 kHz probe and ultrasound baths (40 and 500 kHz) system. Flowing behaviour of samples greater influenced by ultrasound treatment (Jambrak et al., 2009).

2.7. The Aim of This Study

It has been shown that for legumes, a soaking operation prior to cooking is necessary to eliminate the toxic factors contained in the raw seed and to decrease the cooking time. In order to benefit from the protein digestibility and time economy, soaking at above ambient temperature is recommended. However, the only pre-soaking may not be enough for decreasing cooking time of legumes.

Ultrasonic waves can cause a rapid series of alternative compressions and expansions, in a similar way to a sponge when it is squeezed and released repeatedly (sponge effect). The forces involved by this mechanical mechanism can be higher than surface tension which maintains the moisture inside the capillaries of the legume seed creating microscopic channels which may ease moisture uptake. Deformation of porous solid materials, such as legumes, caused by ultrasonic waves is responsible for the creation of microscopic channels that reduce the diffusion boundary layer and increase the convective mass transfer in the legume.

There are a number of reasons for the current interest in ultrasound for application in legumes. The food industry is becoming increasingly aware of the importance of developing new analytical techniques to study complex food materials, and to monitor properties of foods during processing; ultrasonic techniques are ideally suited to both of these applications. Ultrasound has advantages over other traditional analytical techniques because measurements are rapid, non-destructive, precise, fully automated and might be performed either in a laboratory or on line. But, in literatures

there is no research for ultrasonic application of legumes to decrease the cooking time of chickpea. Ultrasonic treatment method can be applied to soften the legumes (chickpeas) and to make them cook easily.

Therefore, the aim of this study was ;

- to study the soaking of chickpea at 20-97 ^{o}C with and without ultrasounds of 25-40 kHz 100 W and 25 kHz 300 W at atmospheric pressure,
- to investigate the effect of the soaking time, temperature, ultrasounds and power of ultrasounds on the moisture absorption of chickpea for the optimum soaking conditions,
- to study modeling of chickpea water absorption,
- to follow soaking of chickpea using textural measurements,
- to study modeling of chickpea texture,
- to study the atmosferic cooking of chickpea without and with ultrasound (25 kHz 100 and 300 W) at 87, 92 and 97 ^{o}C temperatures,
- to follow cooking of chickpea using conductivity, turbidity and color measurements,
- to determine the cooking degree of chickpea using Unreacted core model, Birefringes images, Differential Scanning Calorimeter (DSC) and conductivity methods,
- to determine the optimum cooking procedure and parameters for chickpea.

CHAPTER III
MATERIALS AND METHODS

3.1. Materials

Certified chickpea (İnci-2003) with initial moisture content of 11.58 (% g/g, d.b.) and an average diameter of 8.00 (±0.27) mm (measured with Mutitoyo No. 505–633, Japan, digital micrometer) obtained from Çukurova Agricultural Research Institute (Adana, Turkey), was used throughout this study. After removing foreign materials and damaged seeds, they sieved to standardize the sizes, 7.5 mm to 9 mm.

3.1.1. Chemicals

Concentrated sulphuric acid (H_2SO_4, d=1.83-1.84), boric acid (4%), phenolphthalein (70% in alcohol, 1%), methylene red (95% in alcohol, 1%), sodium hydroxide (NaOH, 33%), cupper sulphate ($CuSO_4$), potassium sulphate (K_2SO_4), zinc granules, hydrocloric acid (HCl, 0.1 M) were used to find the protein content of chickpea. All chemicals were at least analytical grade (Merck, Darmstadt, Germany).

3.1.2. Instrumentations

Ultrasonic tanks (Intersonik, Turkey) were used for conventional and ultrasonic operations (soaking and cooking), respectively. The dimensions of ultrasonic tanks were 240x140x150 mm (inside) and 260x160x320 mm (outside) for 4 liter tanks; 330x300x200 mm (inside) and 350x320x500 mm (outside) for 18 liter tank. Acoustic energy densities (AED) of 25-40 kHz 100 W (4 liter) and 25 kHz 300 W ultrasonic devices were 0.020 and 0.015 W/cm^3, respectively. The acoustic intensity of ultrasonic devices was also 0.48 W/cm^2 for 4 liter US tanks (25 and 40 kHz) and 0.50 W/cm^2 for 18 liter US tank (25 kHz) (Figure 3.1).

Figure 3.1. Illustration of ultrasonic devices

Digital Micrometer (Mutitoyo, Japan) and analytical balance (with a sensitivity of ±0.0001, Shimadzu, Japan) were used to determine the diameters and weight of chickpea samples, respectively.

Color and texture of samples were measured using Hunter Lab colorimeter (Hunter Lab Colorflex (A60-1010-615, Colorflex, USA) and the Texture Analyzer (Model TA-XT2i, Texture Technologies, Inc., Scarsdale, N.Y., Godalming, Ssurvey, UK), respectively.

Automatic steam distilling unit (UDK 130 A, Velp Scientifica Milano, Italy) was used for digestion of proteins during Kjeldahl procedure. Oven dryer (Nüve, Turkey) and ash oven (Nüve, Turkey) were used to determine moisture and ash content, respectively.

Cooking degree of chickpea was evaluated from a Differential Scanning Calorimeter (DSC) (Perkin-Elmer DSC-6, Nederlands) equipped with a thermal analysis data station (Pyris Manager Program, Perkin-Elmer, Nederlands). 70 µL capacity hermetic aluminum pans (Mettler, ME-27331, USA) were used as sample pans.

Birefringence images of the samples for cooking degree were captured in a PC using a polarized light microscope (OLYMPOUS TX51, Euromex Microscopen, Ed Arnhem, Netherlands) equipped with a video camera (VC 3031, Euromex Microscopen, Ed Arnhem, Netherlands) connected to the PC.

Spectrophotometer (Pharmacia LKB-Novaspec II, UK), conductometer (WTW, LF-330, Germany) were used to measure turbidity and electrical conductivity of soaking and cooking water, respectively.

3.2. Methods

3.2.1. Summary of operations and experimental set-up

Overall operations and experimental set-up used in this study are given in Figure 3.2.

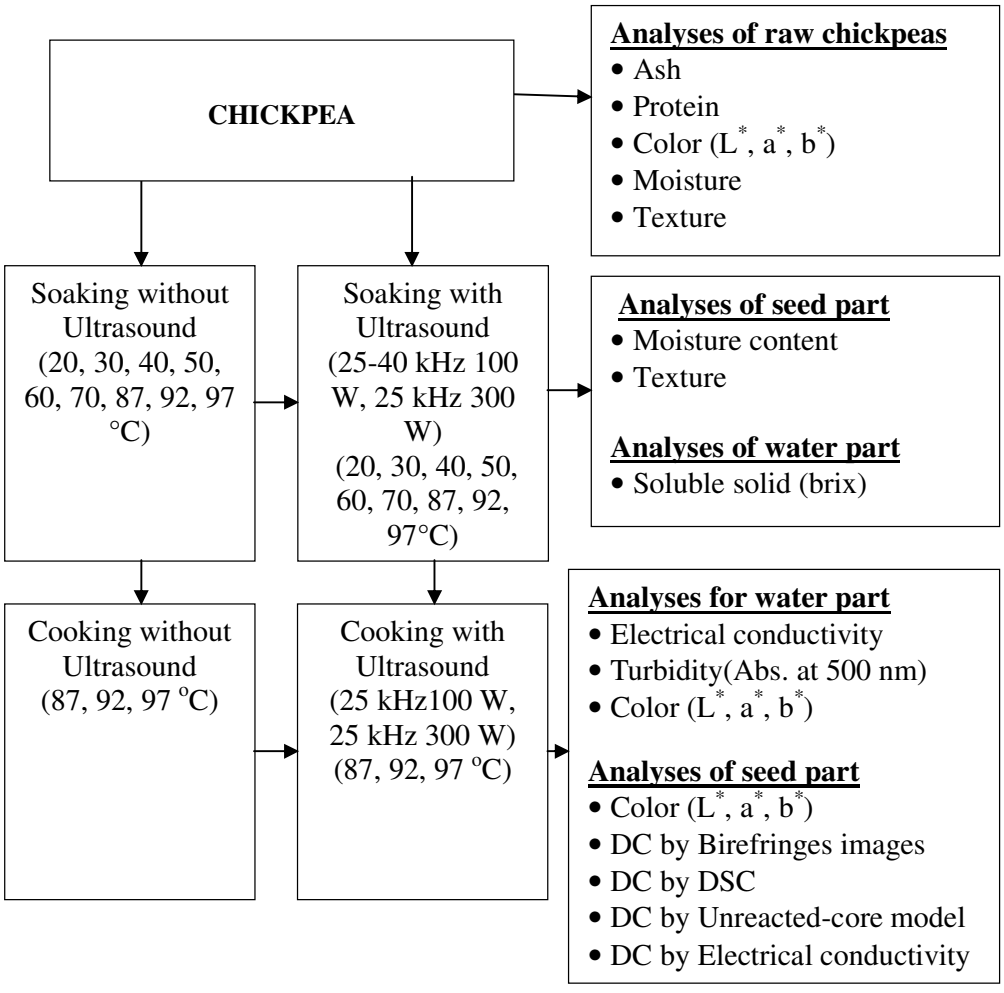


Figure 3.2. Summary of operations and experimental set-up

3.2.2. Soaking operation

Soaking of chickpea was performed at 20, 30, 40, 50, 60, 70, 87, 92 and 97 ^{o}C with and without 25, 40 kHz 100 W and 25 kHz 300 W ultrasounds. Conventional and ultrasonic soaking operations were both performed in the ultrasonic tanks.

One hundred grams of chickpea were immersed in 2000 ml deionized water (1:20) in an ultrasonic tank for the soaking operation at the specified temperatures (20, 30, 40, 50, 60, 70, 87, 92 and 97 ^{o}C). At selected intervals (30 min), 4 g chickpea and 80 ml soaking water (1:20) were quickly removed from the soaking chamber for moisture content, turbidity and conductivity determinations. Soaking water samples were used to determine the turbidity (absorbance at 500 nm) and conductivity measurements at 25 ^{o}C. Chickpea seeds were gently wiped with clean paper towel in order to remove excess water and grinded for the determination of moisture content. The soaking operation was finalized when seeds were fully hydrated. Moisture contents were used for the water absorption and diffusion characteristic of chickpea and modelling.

For the texture determination, 400 grams of chickpea were immersed in 2400 mililiters of deionized water (1:6) in the soaking chamber. At pre-defined time intervals (20 min) for each temperature (20-97 ^{o}C), 10 chickpea seeds were removed from the soaking tank, gently wiped with clean paper towel in order to remove excess water. The seed coats were removed manually. They were lightly pressed between tips of thumb and pointed the finger to separate them into two cotyledons. The cotyledons were placed on a Texture Analyzer to determine hardness as compression force.

3.2.3. Cooking operation

Cooking operation of chickpea was performed at 87, 92, 97 ^{o}C under atmospheric condition without soaking. When the temperature of the cooking water (2400 mL) reached to these specified temperatures, 400 g of chickpea (1:6) were placed in the chamber without and with 25 kHz 100-300 W ultrasounds. Twenty grams of chickpea, 120 mL of cooking water (1:6) samples were collected at 20 minutes intervals during 280 minutes of cooking operations. Twenty grams of chickpea sample was used to determine the diameter of cooked and uncooked parts, degree of cooking and color (L^{*}, a^{*} and b^{*}) measurements. Twenty milliliters of cooking water

was used to determine color (L^*, a^* and b^*), turbidity (absorbance at 500 nm) and conductivity at 25 ^oC. To prepare samples for measuring degree of cooking, cooked chickpea samples were dried in a forced air oven at 45 ^oC, ground by coffee grinder and passed through a 200 mesh screen.

3.2.4. Determination of moisture content

Moisture contents of randomly selected grains (5 g) were determined in dry basis at 105 ^oC for 48 h using oven dry method (AOAC, 2002) and used for Water absorption modelings of water diffusion. The experiments were replicated twice and the measurements were duplicated.

3.2.5. Determination of protein content

The contents of total nitrogen in each raw ten samples were estimated by using the Kjeldahl procedure (AOAC, 2000). The percentage of the crude proteins was calculated by multiplying the percent nitrogen by 6.25 in dry basis.

3.2.6. Determination of ash content

An analytical method was used to determine the ash content of raw chickpea sample at 900 ^oC in dry basis (AOAC, 1990).

3.2.7. Measurement of electrical conductivity of cooking water and chickpea

The electrical conductivity (µS/cm or mS/cm) of the cooking water and chickpea was measured using conductometer (WTW, LF-330, Germany) at 25 ^oC. The electrical conductivity of cooking water was measured by immersing the probe of the conductometer in to the cooking water. For the electrical conductivity measurement of chickpea, EC of a solution of 10 % chickpea/deionized water was measured.

3.2.8. Measurement of turbidity/absorbance of cooking water

The turbidity (absorbance at 500 nm) of the soaking and cooking water samples was measured using spectrophotometer (Pharmacia LKB-Novaspec II, UK) against deionized water as standard at 25 ^oC.

3.2.9. Determination of soluble solids loss during the soaking of chickpeas

Four grams of chickpea and 80 mL of soaking water (1:20 ratio) were removed from the soaking chamber after 3.5 h of soaking operation at 97 ^{o}C. Soluble solids content (Brix, g/g%) of the soaking water was measured at 25 ^{o}C by using Abbe-refractometer (Opton-F.G. Bode and Co., Germany).

3.2.10. Measurement of colors of cooking water and chickpeas

Color (L^*, a^* and b^*) of raw chickpea, cooked chickpea and cooking water samples at 87, 92 and 97 ^{o}C without and with 25 kHz 100 and 300 W power ultrasounds were measured using a Hunter Lab colorimeter (Colorflex, USA). The instrument was calibrated with a white standard tile (L_o^*=93.01, a_o^*= -1.11 and b_o^*= 1.30). The color measurement was performed on the samples at room temperature (25 ^{o}C).

The opponent-color scales give measurements of color in units of approximate visual uniformity through out the color solid. The L*, a* and b*, or CIELab, color space is an international Standard for color measurements, adopted by the Commission Internationale d'Eclairage (CIE) in 1976. L* is the luminance or lightness component, which ranges from 0 to 100, and parameters a* (from green (-) to red (+)) and b* (from blue (-) to yellow (4)) are the two chromatic components, which range from -120 to 120.

3.2.11. Measurement of textural properties of chickpeas

The texture properties (F_{max}) of chickpeas were measured by use of a TA-XT2i Texture Analyzer (Texture Technologies Corp, Scarsdale, NY/Stable Micro Systems, Godalming, UK) with penetration (stainless needle) tests. Penetration test was used to predict the force required to push a needle probe into the sample and related with structural properties inside the sample and space between the cells. Graphical results were examined as F_{max} (maximum force, N) with respect to time. F_{max} was used to explain the hardness of chickpea samples (Figure 3.3). Texture Analyser Project (pre-test, test, post test, distance, load cell and temperature) parameters for chickpea were also given in Table 3.1. The needle was applied on the kernel along y-axis side. The texture values (F_{max}) of chickpeas at each temperature (20-97 ^{o}C) related to soaking and cooking times were used for texture modeling.

Table 3.1. TA-XT2i and needle probe settings for chickpea

Pre-test speed	2 mm/s
Test speed	1 mm/s
Post test speed	2 mm/s
Distance	4 mm
Load cell	0.04903 N (5 kg)
Temperature	25 ^{o}C
Needle probe length	60 mm
Needle probe diameter	0.2 mm

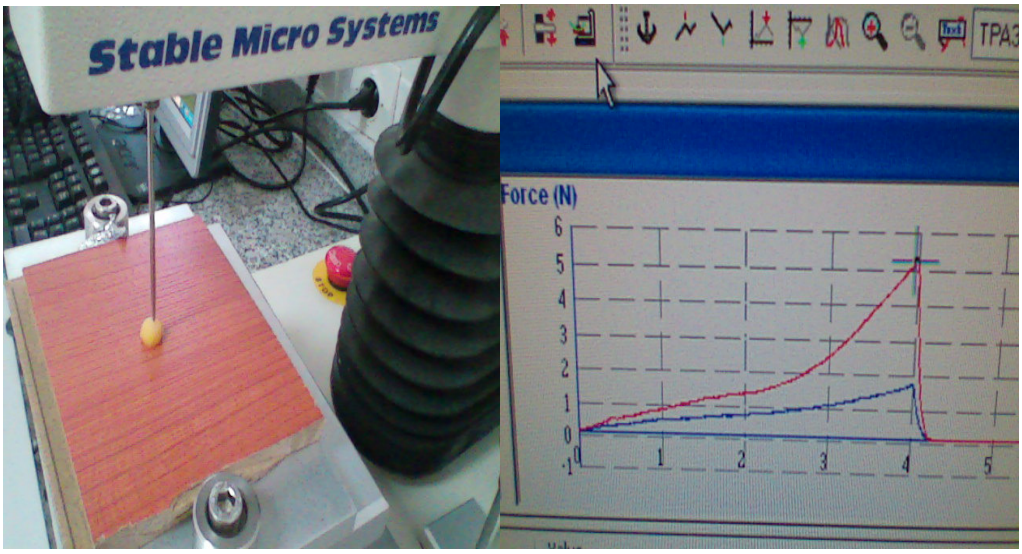


Figure 3.3. Illustration of Texture Analyser device with needle and a typical graph obtained

3.2.12. Determination of cooking degree and temperature of chickpea

Four hundred gram chickpea seeds were cooked in 2400 ml deionized water at 87, 92 and 97 ^{o}C without and with ultrasounds (25 kHz 100 W and 25 kHz 300 W) in a time intervals of 20 minutes until 280 min. For the determination of degree of cooking and temperature of cooking, Birefringes images, Unreacted-core model, Differential Scanning Calorimetric (DSC) and Electrical conductivity methods were used. During the cooking, 20 g chickpea seeds were removed and cooked seeds were put in ice water immediately to prevet further gelatinization. Cooked, dried and grinded samples were analyzed for the degree of cooking.

3.2.12.1. Determination of cooking degree and temperature of chickpea using birefringence images

Birefringence images of the samples were captured in a PC using a polarized light microscope (OLYMPOUS TX51, Euromex Microscopen, Ed Arnhem, Netherlands) equipped with a video camera (VC 3031, Euromex Microscopen, Ed Arnhem, Netherlands) connected to the PC. A solution of 1 % (flour/water) cooked, dried, grinded and screened chickpea samples was prepared and mixed for 30 min. After mixing, 20 μL of suspensions were spread on lamella, and the birefringence was observed through the microscope for capturing the images.

Birefringence images of the chickpea samples at soaking temperatures of 40, 50, 60 and 70 ^{o}C were used for determination of cooking temperature of chickpea. The cooking temperature of the grains is defined as the temperature at which the birefringence of starch start to diminish (Hoseney, 1994). The number of crosses at 40, 50, 60 and 70 ^{o}C was observed and temperature at which disappearance of crosses of starch was taken as cooking temperature.

For determination of cooking degree of chickpea at 87, 92 and 97 ^{o}C without and with US (25 kHz 100 and 300 W), # of crosses were counted. Degree of cooking was calculated using $(N_o-N_t)/N_o*100$ where N_o and N_t are initial (raw) numbers of crosses and numbers of crosses at any cooking time.

3.2.12.2. Determination of degree of cooking using unreacted-core model

Four hundred grams of chickpea grains were cooked in 2400 ml deionized water (Chickpea seed/deionized water=1/6) at 87, 92 and 97 ^{o}C without and with ultrasound of 25 kHz 100 and 300 W in a temperature controlled ultrasonic tank, 10 seeds were periodically (20 min) removed from the cooking chamber and immediately immersed in ice-cold water in order to prevent further gelatinization. Seed coats were removed manually and seeds were lightly pressed between tips of thumb and pointing finger to separate them into two cotyledons. Diameters of cotyledons (D) and white cores (D_c, unreacted part) were measured in mm by a digital micrometer. Degree of cooking was evaluated using volume of unreacted core and whole seed volume by Equation 3.1. Also, the cooking time from unreacted core model was calculated by Equation 3.2 (Levenspiel. 1972).

$$DC(\%) = \frac{(4/3)\pi * r^3 - (4/3)\pi * r_C^3}{(4/3)\pi * r^3} = \frac{r^3 - r_C^3}{r^3} * 100 \quad (3.1)$$

$$\frac{t}{\tau} = 1 - \left(\frac{r_C}{r}\right) \quad (3.2)$$

where, DC (%), r_c, r, t and τ are the degree of cooking, average radius of unreacted core, whole chickpeas in m, any cooking and complete cooking times in min, respectively.

3.2.12.3. Determination of degree of cooking and temperature using Differential Scanning Calorimetric (DSC) method

Cooked, dried, grinded and sieved chickpea samples at 92 ^oC for 20 min time intervals (0-280 min) were stored in refrigerator. These samples was studied by using Differential Scanning Calorimeter (Perkin-Elmer, Pyris-6 DSC, Netherlands) equipped with a thermal analysis data station (Pyris Manager Program) in order to find enthalpy of gelatinization and starch cooking temperature. Chickpea flour samples (10 µg, dry weight) was loaded into a 70 µL capacity aluminum pan (Mettler, ME-27331) and deionized water was added with the help of microsyringe to achieve a flour-water suspension containing 70% water. Samples was hermetically sealed and allowed to stand for 24 h at refrigerator temperature before heating in DSC. The DSC analyzer was calibrated using indium. An empty aluminum pan was used as a reference. Sealed and allowed to stand for 24 h sample pans were heated at a rate of 10 °C/min from 20 to 100 °C. Onset temperature (T_o), and enthalpy of gelatinization (ΔH_{gel}) was calculated automatically. Degree of cooking for each sample was calculated from ΔH_{gel} using Equation 3.3.

$$(DC\ (\%) = [1-(\Delta H_{heat\text{-}treated} / \Delta H_{Raw})*100) \quad (3.3)$$

3.2.12.4. Determination of degree of cooking using electrical conductivity of cooking water and chickpeas

Four hundred grams chickpea grains were cooked in 2400 ml deionized water (Chickpea seed/deionized water=1/6) at 87, 92 and 97 ^oC in a temperature controlled water bath. For each sample 65 chickpea seeds (20 g) and 120 ml soaking water was removed for every 20 min time intervals up to 180 min. Electrical conductivity of

cooking water (EC) and seed part samples removed periodicaly (every 20 min) were measured.

For chickpea seed part, cooked, dried and grinded samples (chickpea flour) were used for determining degree of cooking using electrical conductivity. A standard calibration curve was prepared for degree of cooking to be used with seed part. Standard cooked (gelatinized) chickpea was prepared by autoclaving at 15 psig for 1.5 h, grinded, and dried in a tunel dryer at 45 ^{o}C. Grinded raw (uncooked) chickpea was also used as standard. For standardization, 1 g of total chickpea flour (raw + cooked) were added to 50 ml of water and mixed for 30 minutes. Electrical conductivities (EC) of different mixed suspensions (raw chickpea + cooked chickpea + water) was measured by conductometer in µS/cm at 25 ^{o}C (Table 3.2). Percent cooking versus electrical conductivity was plotted in Table 3.2. A strait line Eq.3.4. was obtained from the regression of plot (Figure 3.4). Degree of cooking of cooked chickpeas at different times was found from the calibration curve Eq.3.3 (Tables 3.2 and 3.3).

$$DC(\%) = 144.2363-0.2471*EC) \quad (3.3)$$

Table 3.2. Experimental values of conductivity standard curve related to degree of cooking (DC) of cooked chickpea

Cooked Chickpea (g)	Raw Chickpea (g)	DC (%)	ml of Water	Conductivity (µS/cm)
0.0	1.0	0	50	580(±3.54)
0.1	0.9	10	50	545(±1.41)
0.2	0.8	20	50	506(±2.05)
0.3	0.7	30	50	467(±1.77)
0.4	0.6	40	50	422(±2.83)
0.5	0.5	50	50	382(±2.33)
0.6	0.4	60	50	335(±1.06)
0.7	0.3	70	50	296(±1.41)
0.8	0.2	80	50	256(±2.69)
0.9	0.1	90	50	217(±1.41)
1.0	0.0	100	50	189(±1.41)

EC of cooking water method must be coupled with another method. In order to find the relationship between DC with EC of cooking water, other methods (DSC, Electrical conductivity of chickpea, Birefringes images and Unreacted-core model) were compared. EC at fully gelatinized (%100) from these methods were assumed as

the maximum electrical conductivity of cooking water. Then, EC of cooking water at any cooking time was converted to percentage. Percentage electrical conductivity (%) of cooking water of chickpeas was evaluated by Equation 3.4.

$$EC\ (\%) = (EC_t/EC_{max})*100 \quad (3.4)$$

where, EC_t, and EC_{max} are electrical conductivity at any time and at 100% electrical conductivity.

Table 3.3. Predicted DC values from calibration curve of DC (%) by EC of chickpea

Time(min)	DC (%)
0	0.00
20	41.45
40	55.04
60	70.11
80	75.55
100	81.48
120	86.42
140	89.14
160	92.10
180	95.07
200	97.04
220	99.02
240	100.00

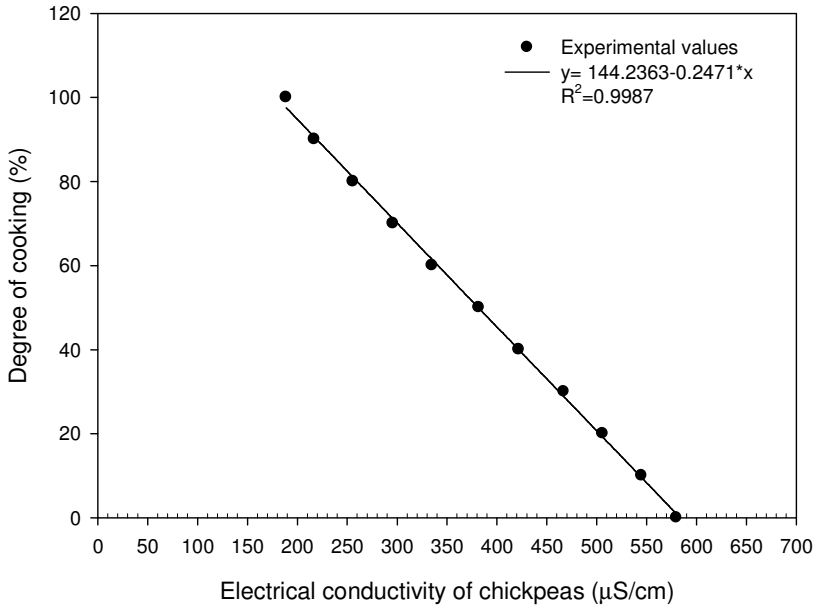


Figure 3.4. Regression of experimental electrical conductivity and degree of cooking values for calibration curve of DC (%) by EC of chickpea

3.3. Statistical Analysis

Calculated parameters for modeling and plots were compared using Statgraphics 10 (SIGMAPLOT 10 software, Jandel Scientific, San Francisco, USA) and Excel 2003 (Microsoft, USA) software.

A general linear model of SPSS version 16 statistical software (SPSS Inc., USA) was also used with data to determine significant differences ($P<0.05$) and the effect of parameters on responses. ANOVA and Duncan's multiple-range tests at $P < 0.05$ were performed to predict optimum process conditions.

Models validation was performed by R^2, $P<0.05$ and RMSE (%) = Root mean square error: $100 * \sqrt{\frac{1}{n}\sum_{1}^{n}\left[(M_{exp} - M_{pre}) / M_{exp}\right]^2}$.

All measurements were made with a minimum of duplicate replications.

CHAPTER IV

RESULTS AND DISCUSSIONS

Processing steps such as soaking, cooking and thermosonication of chickpea were studied. All processes were made at atmospheric conditions. Soaking operations were studied at 20, 30, 40, 50, 60, 70, 87, 92 and 97 ^{o}C temperatures without (w/o) and with (w/) ultrasound. Cooking operation was made at 87, 92 and 97 ^{o}C temperatures without and with ultrasound. Three different ultrasound frequency and power combinations, 25 kHz 100 W, 40 kHz 100 W and 25 kHz 300 W, were used in the study.

The initial moisture content of chickpea was found as 11.58 (±0.25) (% g/g, d.b.) which is similar to m.c found as 11.92 % by Gowen et al. (2007). The protein content of raw chickpea was found as 24.31 (±0.041) (% g/g, d.b.) which were also reported as in the range of 21.30-27.00 % by Jambunathan and Singh (1979), Almeida Costa et al. (2006), Maheri-Sis et al. (2008), and Saleh and El-Adawy (2006). Ash content (% g/g, d.b.) of raw chickpea was determined as 2.61 (±0.054). Ash value of raw chickpea was found in the range of 2.10-2.80 by study of Kaur et al. (2005); Coşkuner and Karababa (2004). The texture (hardness, maximum force in N) of raw chickpea was measured as 67.73 N (±1.10). This value is similar to the values found (39.20-75.50) by Kaur et al. (2005). The Hunter L^{*}, a^{*} and b^{*}color values of raw chickpea were found as 55.43, 9.30 and 22.58, respectively. L* and a* value for different chickpea cultivars reported by Kaur et al. (2005) is between 66.15 to 76.78 and 0.34 to 2.08, respectively. The b* value for chickpea cultivars is between 19.39 and 22.34 (Kaur et al., 2005).

4.1. Soaking of Chickpea

Soaking of chickpea was carried out at 20, 30, 40, 50, 60, 70, 87, 92 and 97 ^{o}C in order to analyse the effect of temperature on water absorption, texture and cooking.

Soaking operation was ended until seeds were fully hydrated at each temperature with and without ultrasound (US).

Moisture content and texture (F_{max}) values were determined in every 30 min and 20 minutes during soaking, respectively. Different models were fit to water absorption and texture data of chickpea in order to find optimum soaking and cooking parameters such as equlibrium soaking and cooking times, rate of soaking, cooking temperatures.

4.1.1. Water absorption/diffusion characteristics of chickpea during soaking

Soaking to hasten the gelatinization of starch in the seed, is the first step during processing of edible seeds and grains. Seeds are usually soaked before cooking. The most important property for soaking of chickpea is the moisture content to achieve the proper cooking operation. It can be achieved either through conditioning below the cooking temperature and then cooking above the cooking temperature, or through direct cooking above the cooking temperature. Understanding water absorption in legumes during soaking is of practical importance since it affects subsequent processing operations and the quality of the final product.

The water absorption characteristics of chickpea were analyzed using moisture content (% g/g, d.b.) values. Summary of multiple range analysis (Duncan test) on moisture contents (% g/g, d.b.) of soaked chickpeas at 20, 30, 40, 50, 60, 70, 87, 92 and 97 ^{o}C without and with ultrasounds were given in Tables A1-A4. The relation of moisture content with temperature, time and ultrasounds were illustrated in Figures 4.1-4.10.

The moisture content (% g/g, d.b.) of chickpea during soaking were significantly ($P<0.05$) increased as the temperature, time and power of ultrasounds increased. Rate of increase in m.c. was higher during the early times of soaking whereas lower in the late soaking periods.

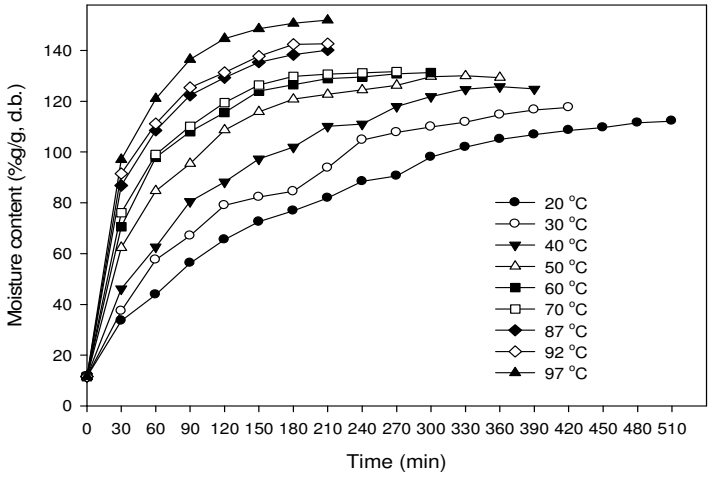


Figure 4.1. Effects of soaking temperature on water absorption of chickpea

Chickpea water absorption curves, illustrated in Figures 4.1-4.10 are characterised by an initial phase of rapid water pickup followed by an equilibrium phase, during which the chickpea approaches its full soaking capacity. Results indicated that increasing soaking temperature enhanced water pickup in the initial phase, increasing the slope of the water absorption curve, thereby leading to faster attainment of the equilibrium phase, and this was in agreement with previously published data (Turhan et al., 2002). The rate of water absorption increased with increasing temperature (Figures 4.1-4.10). The behavior of material during moisture absorption depends on the heat and mass transfer characteristics of the product (Fasina et al., 1993).

4.1.1.1. Primary modelling of chickpea water absorption as a function of time

Many theoretical, empirical, and semi-empirical models have been employed for modeling the water absorption behaviour of agricultural products during soaking. Theoretical models allow us to relate the experimental results with physical laws. The theoretical mechanisms for the kinetics of the diffusion process have been proposed, from the simplest, Fickian diffusion (Bello et al., 2004; Kashaninejad et al., 2007) to other, more complex ones, of the non-Fickian diffusion (Nussinovitch and Peleg, 1990; Singh and Kulshrestra, 1987).

Several other models are utilized in modeling the hydration and rehydration process. These include: Peleg's model (Abu-Ghannam and McKenna, 1997; Bilbao-Sainz et

al., 2005; Hung et al., 1993; Machado et al., 1998; Maskan, 2002; Peleg, 1988; Sacchetti et al., 2003; Sopade et al., 1992; Turhan et al., 2002), Asymptotic first order model (Chhinnan, 1984; Krokida and Marinos-Kouris, 2003; Machado et al., 1998; Maskan, 2001; Pappas et al., 1999); and Normalized Weibull distribution function (Marabi and Saguy, 2004a,b; Marabi et al., 2003).

Moisture diffusivity is an important transport property necessary for the design and optimization of all the processes that involve internal moisture movement. Diffusion coefficient is the factor of proportionality representing the amount of substance diffusing across a unit area through a unit concentration gradient in unit time. Total amount of diffusing substance entered into a spherical grain of radius r can be obtained from the following Fick's series type equation (Equation 4.1) and Normalized Weibull distribution function (Equation 4.2):

$$\frac{M_t - M_e}{M_o - M_e} = \sum_{n=1}^{\infty} \frac{6}{n^2 \pi^2} exp\left[- \frac{D_{eff} \pi^2}{r^2} n^2 t \right] \quad (4.1)$$

$$M_t = M_e + (M_o - M_e) * exp[-(\frac{t * D_{eff} * R_g}{r^2})^{\beta}] \quad (4.2)$$

where M_t, M_e, M_o are moisture contents (g/g %, d.b.) at any time, equilibrium and initial, respectively. D_{eff} and r are effective diffusion constant (m^2, s^{-1}) and average radius of chickpea (m). $\alpha = \frac{R^2}{D_{cal}}$, $D_{eff} = D_{cal} / R_g$; R_g was a constant and is a characteristic of the geometry utilized.

A fit of the experimental data for times of soaking leads to the determination of an average diffusion coefficient. D_{eff}, via Equation 4.1 and 4.2 which are Fick's law and Normalized Weibull distribution function of diffusion of water in solids of spherical shape. The chickpea seeds may be approximated as spheres with a mean diameter of 0.0040 m (±0.0001). Fick's laws of diffusion (Equation 4.1) and its derived equations account for the vast majority of the models utilized in food science, as can be observed from publications (Garcia-Pascual et al., 2006; Gowen et al., 2007.

Some of the common assumptions and simplifications often made for solving Fick's second law (Equation 4.1) and Normalized Weibull model (Equation 4.2) include the following:

1) the moisture transfer is one dimensional, unsteady state in the radial direction,
2) chickpea is considered to be an almost spherical object,
3) the initial temperature and moisture distributions are uniform,
4) there is a moisture gradient in the chickpea with respect to time,
5) the thermal properties are constant,
6) chickpea is considered as a homogeneous isotropic solid,
7) moisture transfer to and from the seed is due to concentration gradient,
8) the amount of solid loss in the grains during cooking was neglected,
9) for long soaking times, only the first term of series equation is significant,
10) constant dimensions of chickpea also is assumed

In this study, the effect of loss of soluble solids from chickpea seeds was not taken into account in calculating the moisture content because maximum loss of soluble solids from chickpea at temperatures of 97 ^{o}C for 3.5 h soaking was about 2.06 % of the original mass which in comparison with the water gain was assumed to be negligible. Other researchers have also reported similar assumption for other seeds (Sayar et al., 2001; Sabapathy, 2005). When these assumptions were applied on Fick's second law, the following equation was obtained.

$$M_t = M_e + (M_o - M_e) * \frac{6}{\pi^2} * exp\left[-\left(\frac{\pi^2 * D_{eff}}{r^2} \right) * t \right] \quad (4.3)$$

Both Weibull distribution and Fick's law of diffusion functions are related to diffusion of water and diffusion coefficient (D_{eff}), Diffusion coefficient is the factor of proportionality representing the amount of substance diffusing across a unit area through a unit concentration gradient in unit time. The Weibull distribution function was frequently utilized and lately improved for describing the rehydration of dried foods. This model is able to describe the behavior of systems or events that have some degree of variability, such as water absorption and soluble solids losses during hydration of grains and seeds (Machado et al.,1998, 1999; Marabi et al., 2003).

Table 4.1. Predicted parameters of Fick's model during soaking of chickpeas at different temperatures without and with ultrasound applications

Process	M_e (%, d.b.)	D_{eff} x 10^{10} (m^2 s^{-1})	R^2	RMSE (%)
20 °C	119.82	1.40	0.9960	8.03
20 °C + 25 kHz 100 W	119.48	1.70	0.9907	13.88
20 °C + 40 kHz 100 W	123.10	1.28	0.9943	10.76
20 °C + 25 kHz 300 W	120.94	2.01	0.9925	11.29
30 °C	122.81	1.87	0.9894	9.70
30 °C + 25 kHz 100 W	122.61	2.10	0.9910	10.97
30 °C + 40 kHz 100 W	122.41	1.86	0.9885	12.02
30 °C + 25 kHz 300 W	124.40	2.62	0.9904	8.78
40 °C	128.44	2.39	0.9944	8.93
40 °C + 25 kHz 100 W	129.86	2.98	0.9914	9.88
40 °C + 40 kHz 100 W	127.56	2.46	0.9952	8.01
40 °C + 25 kHz 300 W	130.79	3.79	0.9951	6.59
50 °C	128.64	4.11	0.9942	2.70
50 °C + 25 kHz 100 W	130.72	4.94	0.9988	2.72
50 °C + 40 kHz 100 W	127.30	4.42	0.9981	2.53
50 °C + 25 kHz 300 W	133.56	6.52	0.9944	2.91
60 °C	129.76	5.58	0.9957	4.74
60 °C + 25 kHz 100 W	131.68	5.92	0.9978	3.43
60 °C + 40 kHz 100 W	129.17	5.57	0.9966	4.10
60 °C + 25 kHz 300 W	133.67	7.29	0.9978	1.87
70 °C	130.66	6.01	0.9944	5.85
70 °C + 25 kHz 100 W	131.05	7.11	0.9924	5.45
70 °C + 40 kHz 100 W	130.22	5.78	0.9935	6.19
70 °C + 25 kHz 300 W	134.06	7.96	0.9993	1.29
87 °C	137.47	7.12	0.9938	5.55
87 °C + 25 kHz 100 W	139.06	8.19	0.9944	4.13
87 °C + 40 kHz 100 W	138.78	6.76	0.9942	5.75
87 °C + 25 kHz 300 W	150.63	9.77	0.9937	4.18
92 °C	139.70	7.49	0.9908	6.36
92 °C + 25 kHz 100 W	149.74	8.54	0.9935	5.00
92 °C + 40 kHz 100 W	139.67	7.40	0.9925	5.73
92 °C + 25 kHz 300 W	151.37	11.20	0.9948	9.85
97 °C	150.05	7.72	0.9959	2.51
97 °C + 25 kHz 100 W	157.88	9.23	0.9974	2.02
97 °C + 40 kHz 100 W	150.32	7.53	0.9954	5.29
97 °C + 25 kHz 300 W	159.75	11.90	0.9960	2.55

RMSE (%) = Root mean square error: $100 * \sqrt{\frac{1}{n}\sum_{1}^{n}\left[(M_{exp} - M_{pre}) / M_{exp}\right]^2}$

Typically, Weibull distribution is described by two parameters: the scale parameter, α (s) which is related to the reciprocal of the process rate constant, and the shape parameter, β. The scale parameter defines the rate and represents the time needed to accomplish approximately 63 % of the process. Different values of β lead to very different curves, and therefore could describe various mechanisms (i.e. diffusion,

convection, relaxation). When β =1, the Weibull distribution reduces to 1st order kinetics. The model predicts a lag phase for larger values of β (Machado et al., 1999).

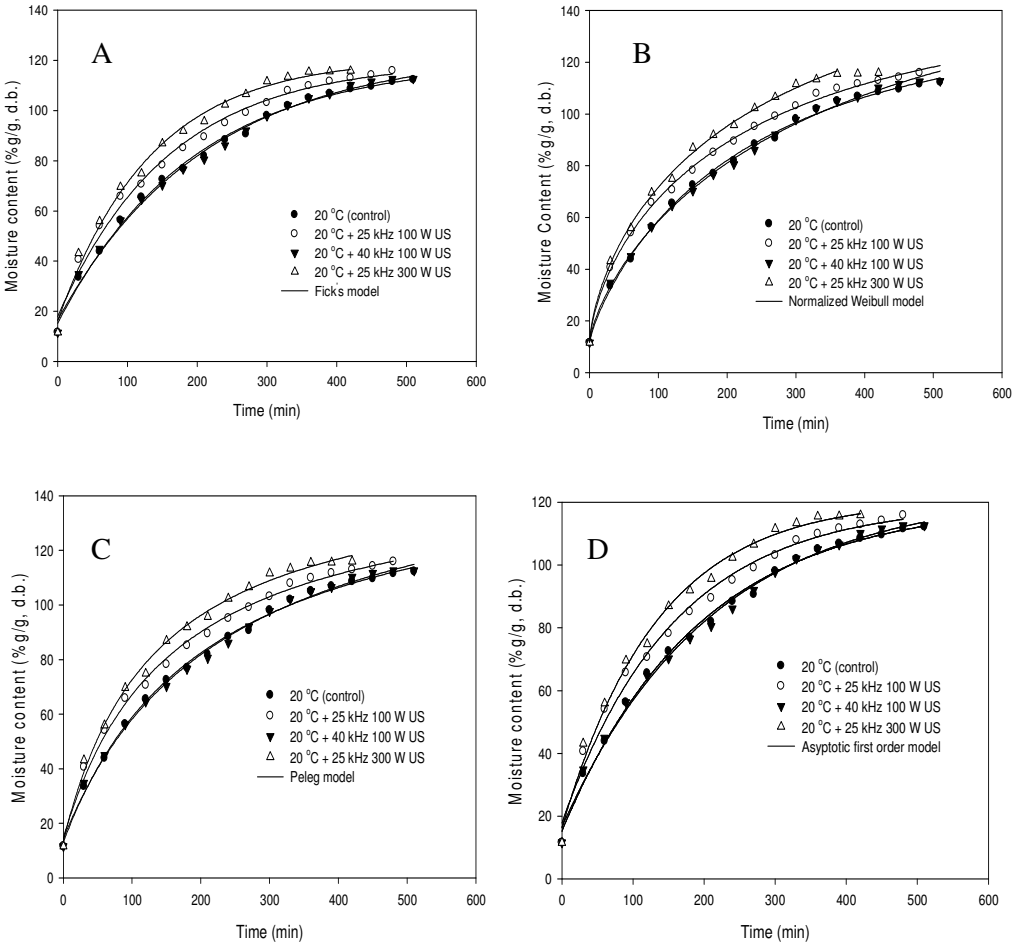


Figure 4.2. Means of experimental and predicted moisture contents (% g/g, d.b.) of chickpeas during soaking at 20 °C temperatures without and with ultrasound treatments for the Fick's (A), Normalized Weibull (B), Peleg (C) and Asymptotic first order (D) models

Recently, many attempts were made in order to utilize the shape parameter of the Weibull distribution function as an indicator of the mechanism (i.e. diffusion. external resistance and matrix relaxation) of liquid uptake during rehydration (Cunha et al., 1998; Marabi et al., 2003). It was also shown that for rehydrating air-dried carrots, the derived β value closely agreed with the value representing diffusion. In contrast, the values of β obtained for freeze-dried carrots did not match any of the modeled values corresponding with the above mechanisms. Thus, it was proposed

that liquid uptake may ocur also by capillary flow, due to the very high porosity of the samples (Marabi et al., 2003).

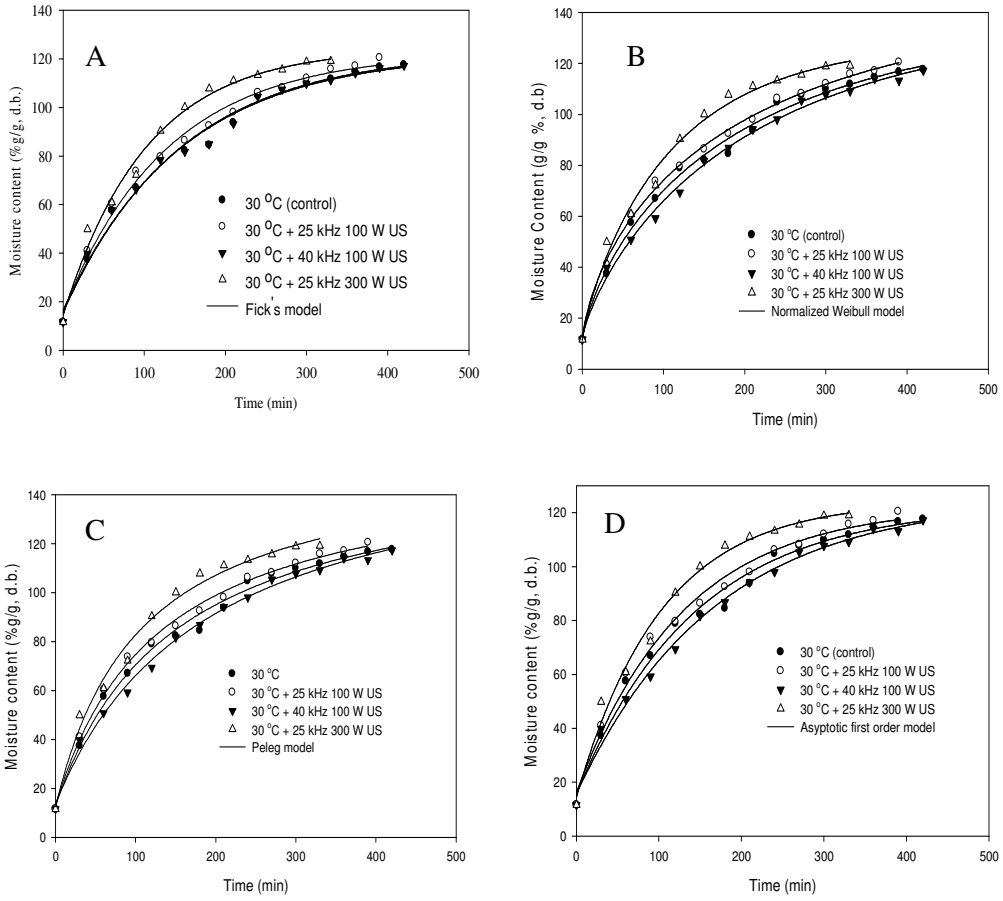


Figure 4.3. Means of experimental and predicted moisture contents (% g/g, d.b.) of chickpeas during soaking at 30 °C temperatures without and with ultrasound treatments for the Fick's (A), Normalized Weibull (B), Peleg (C) and Asymptotic first order (D) models

The most other popular empirical and semi-empirical models which has been used to model the water absorption process of agricultural products are Peleg model (Garcia-Pascual et al., 2006; Gowen et al., 2007; Sayar et al., 2001; Turhan et al., 2002), and Asmptotic first order model (Gowen et al., 2007; Kashaninejad et al., 2007).

Peleg (1988) proposed a two-parameter sorption equation and tested its prediction accuracy during water vapor adsorption of milk powder and whole rice, and soaking of whole rice. This equation has since been known as Peleg model (Equation 4.4)

$$M = Mo \pm \frac{t}{K_1 + K_2 * t} \quad (4.4)$$

Table 4.2. Predicted parameters of Normalized Weibull model during soaking of chickpeas at different temperatures without and with ultrasound applications

	Normalized Weibull model					
Process	M_e (%. d.b.)	D_{eff} x 10^{10} (m^2 s^{-1})	R_g	β	R^2	RMSE (%)
20 °C	131.93	1.40	8.16	0.819	0.9979	1.86
20 °C + 25 kHz 100 W	144.26	1.70	6.45	0.686	0.9984	1.47
20 °C + 40 kHz 100 W	145.09	1.28	6.95	0.767	0.9975	2.26
20 °C + 25 kHz 300 W	135.39	2.01	7.82	0.759	0.9970	2.38
30 °C	139.29	1.87	7.56	0.766	0.9936	3.07
30 °C + 25 kHz 100 W	147.32	2.10	6.43	0.705	0.9980	2.09
30 °C + 40 kHz 100 W	139.39	1.86	7.88	0.819	0.9960	3.92
30 °C + 25 kHz 300 W	129.51	2.62	9.18	0.882	0.9913	5.33
40 °C	139.01	2.39	8.47	0.793	0.9979	1.61
40 °C + 25 kHz 100 W	136.76	2.98	9.08	0.811	0.9945	3.12
40 °C + 40 kHz 100 W	136.88	2.46	8.62	0.804	0.9985	1.28
40 °C + 25 kHz 300 W	134.81	3.79	9.44	0.864	0.9967	2.61
50 °C	133.45	4.11	9.57	0.785	0.9987	1.21
50 °C + 25 kHz 100 W	132.08	4.94	9.86	0.907	0.9996	0.58
50 °C + 40 kHz 100 W	128.86	4.42	9.82	0.900	0.9990	1.34
50 °C + 25 kHz 300 W	136.26	6.52	11.56	0.832	0.9961	2.24
60 °C	133.33	5.58	9.74	0.800	0.9990	1.04
60 °C + 25 kHz 100 W	134.44	5.92	9.77	0.842	0.9996	0.61
60 °C + 40 kHz 100 W	131.92	5.57	9.82	0.831	0.9989	1.02
60 °C + 25 kHz 300 W	135.51	7.29	9.88	0.869	0.9986	1.29
70 °C	135.76	6.01	9.61	0.752	0.9992	0.89
70 °C + 25 kHz 100 W	139.19	7.11	9.31	0.665	0.9992	0.89
70 °C + 40 kHz 100 W	136.76	5.78	9.34	0.730	0.9991	0.92
70 °C + 25 kHz 300 W	135.48	7.96	9.92	0.894	0.9998	0.42
87 °C	148.44	7.12	8.79	0.661	0.9999	0.41
87 °C + 25 kHz 100 W	152.49	8.19	8.48	0.628	0.9994	0.78
87 °C + 40 kHz 100 W	149.12	6.76	8.82	0.689	0.9996	0.66
87 °C + 25 kHz 300 W	181.44	9.77	6.45	0.489	0.9999	0.39
92 °C	155.43	7.49	8.19	0.588	0.9995	0.74
92 °C + 25 kHz 100 W	162.10	8.54	8.99	0.631	0.9989	1.23
92 °C + 40 kHz 100 W	153.01	7.40	8.51	0.621	0.9998	0.43
92 °C + 25 kHz 300 W	165.72	11.20	9.52	0.548	0.9991	1.06
97 °C	156.54	7.72	9.65	0.729	0.9996	0.68
97 °C + 25 kHz 100 W	161.66	9.23	9.94	0.802	0.9985	1.29
97 °C + 40 kHz 100 W	162.29	7.53	8.68	0.624	0.9998	0.40
97 °C + 25 kHz 300 W	173.87	11.90	9.86	0.540	0.9994	0.86

RMSE (%) = Root mean square error: $100 * \sqrt{\frac{1}{n}\sum_{1}^{n}\left[(M_{exp} - M_{pre}) / M_{exp}\right]^2}$

The rate of sorption (R) can be obtained from first derivative of the Peleg equation

$$R = \frac{dM}{dt} = \pm \frac{K_1}{(K_1 + K_2 * t)^2} \tag{4.5}$$

The Peleg rate constant K_1 (s/% m.c (d.b)) relates to sorption rate at the very beginning (R_o), i.e., R at $t = t_o$

$$R_o = \frac{dM}{dt}\Big|_{t_o} = \pm \frac{1}{K_1} \tag{4.6}$$

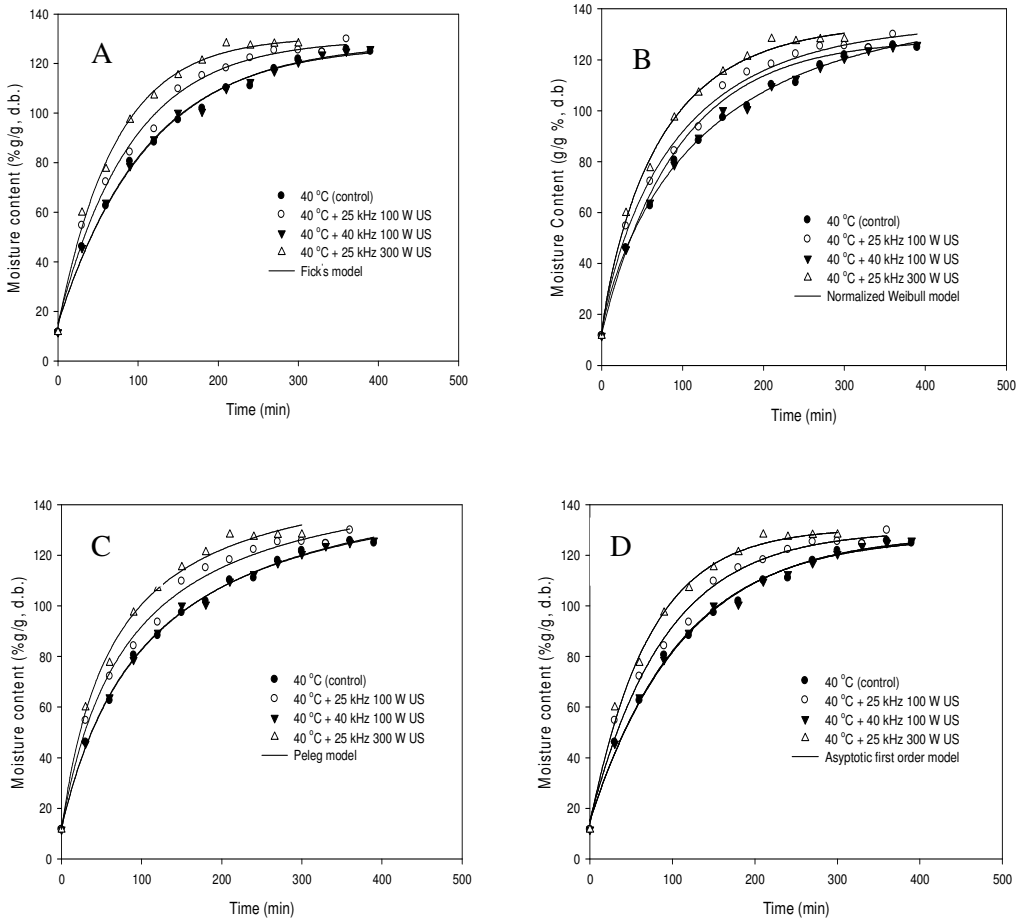


Figure 4.4. Means of experimental and predicted moisture contents (% g/g, d.b.) of chickpeas during soaking at 40 °C temperatures without and with ultrasound treatments for the Fick's (A), Normalized Weibull (B), Peleg (C) and Asymptotic first order (D) models

The Peleg capacity constant K_2 (1/% m.c (d.b)) relates to maximum (or minimum) attainable moisture content. As $t \to \infty$, Eq.4.4 gives the relation between equilibrium moisture content (M_e) and K_2, $M_e=M_o+1/K_2$.

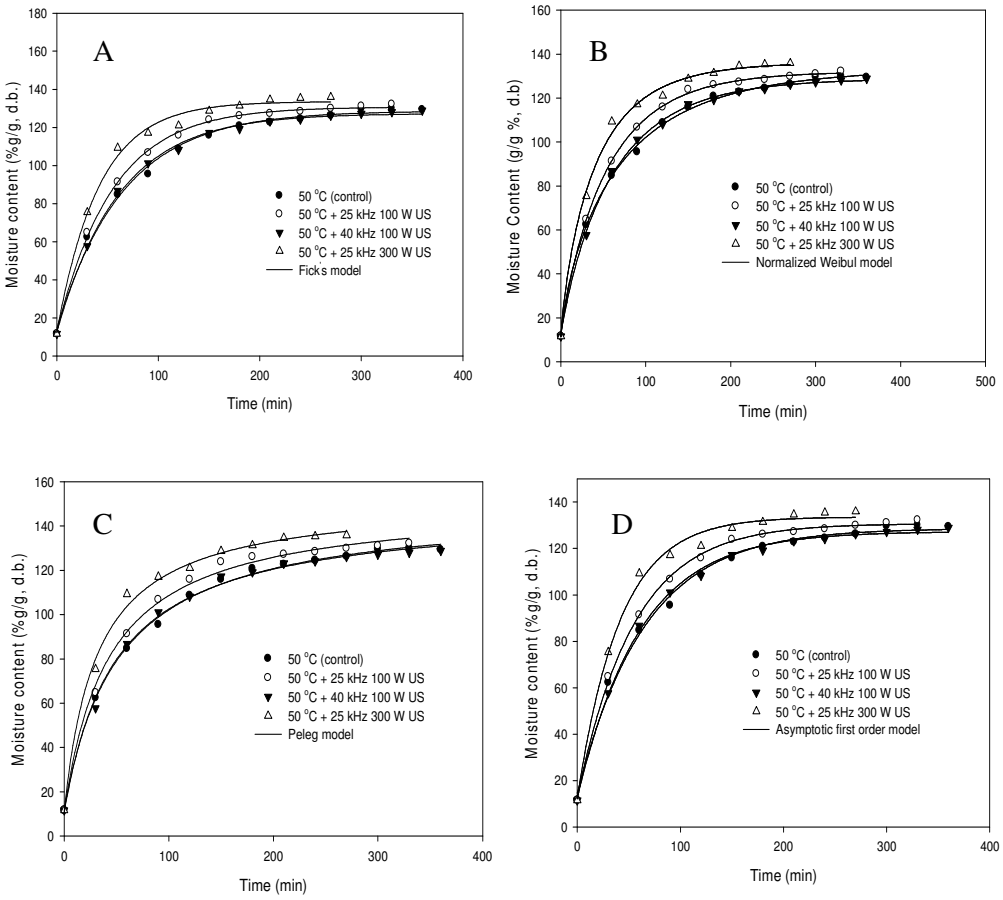


Figure 4.5. Means of experimental and predicted moisture contents (% g/g, d.b.) of chickpeas during soaking at 50 °C temperatures without and with ultrasound treatments for the Fick's (A), Normalized Weibull (B), Peleg (C) and Asymptotic first order (D) models

The Peleg model has been used to describe sorption processes in various foods. Maharaj and Sankat (2000) applied the model for studying water absorption of dasheen leaves. Sopade and Kaimur (1999) used it for describing water desorption of sago starch. Palou et al. (1994) studied simultaneous water desorption and sucrose absorption of papaya using the model. The Peleg model was also exploited to model water absorption of many starchy and oily kernels (Abu-Ghannam and McKenna,

1997; Hung et al., 1993; Lopez et al., 1995; Sopade et al., 1992; Sopade et al., 1994; Sopade and Obekpa. 1990; Turhan et al., 2002).

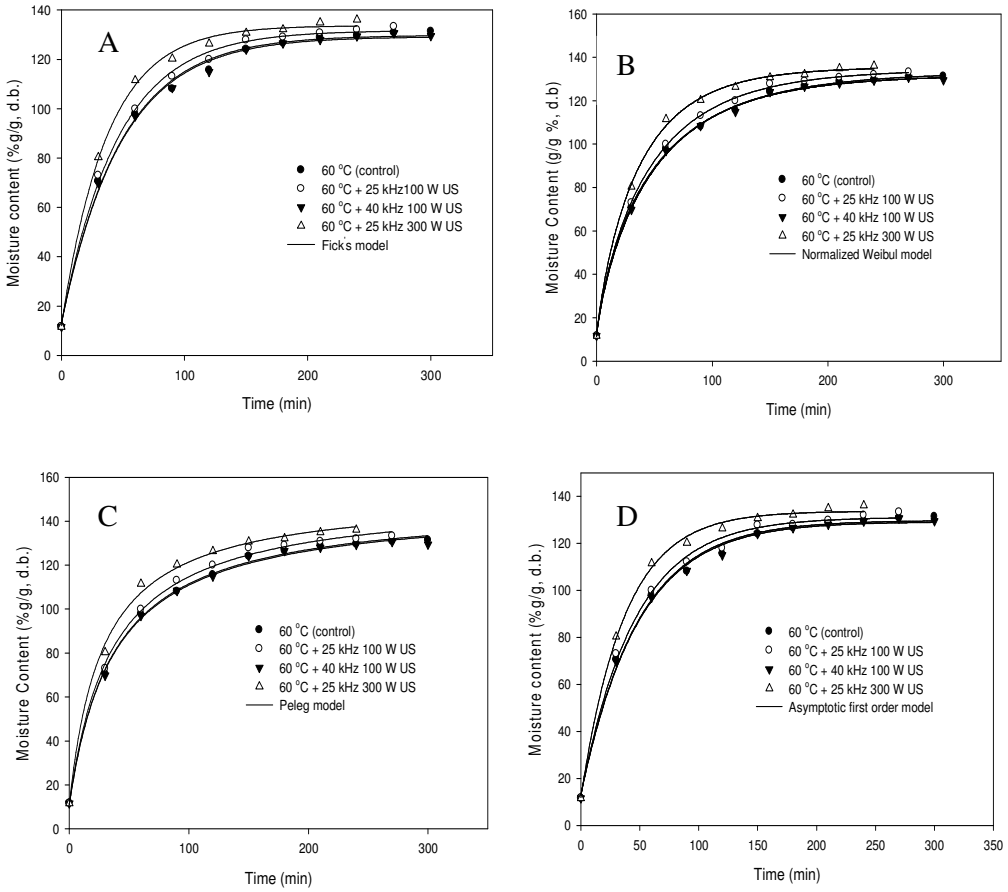


Figure 4.6. Means of experimental and predicted moisture contents (% g/g, d.b.) of chickpeas during soaking at 60 °C temperatures without and with ultrasound treatments for the Fick's (A), Normalized Weibull (B), Peleg (C) and Asymptotic first order (D) models

Chickpea water absorption curves (Figures 4.1-4.10) follow a general pattern of bounded growth characteristic of a Asymptotic first order process. Therefore the following equation can also be applied for primary modelling of the data:

$$M = M_e + (M_o - M_e) * exp(-k_H * t) \quad (4.7)$$

Table 4.3. Predicted parameters of Peleg model during soaking of chickpeas at different temperatures without and with ultrasound applications

	Peleg model				
Process	M_e (%. d.b.)	K_1 s/% m.c.(d.b.)	$K_2 \times 10^3$ 1/% m.c.(d.b.)	R^2	RMSE (%)
20 °C	155.47	88.74	7.02	0.9973	3.87
20 °C + 25 kHz 100 W	148.92	69.57	7.45	0.9954	7.10
20 °C + 40 kHz 100 W	161.23	96.28	6.81	0.9963	6.55
20 °C + 25 kHz 300 W	151.36	58.04	7.25	0.9954	5.32
30 °C	155.77	62.01	6.99	0.9928	4.15
30 °C + 25 kHz 100 W	153.86	54.63	7.10	0.9965	4.10
30 °C + 40 kHz 100 W	164.22	74.69	6.65	0.9948	6.36
30 °C + 25 kHz 300 W	157.14	43.93	6.92	0.9895	5.40
40 °C	159.34	44.53	6.80	0.9976	2.53
40 °C + 25 kHz 100 W	157.44	34.05	6.89	0.9930	3.66
40 °C + 40 kHz 100 W	157.87	43.45	6.85	0.9984	1.73
40 °C + 25 kHz 300 W	157.90	26.37	6.83	0.9955	2.60
50 °C	149.14	22.61	7.27	0.9978	1.45
50 °C + 25 kHz 100 W	150.64	18.39	7.14	0.9960	3.18
50 °C + 40 kHz 100 W	147.42	21.36	7.30	0.9963	3.90
50 °C + 25 kHz 300 W	152.39	13.38	7.07	0.9973	3.03
60 °C	148.47	16.12	7.28	0.9982	1.75
60 °C + 25 kHz 100 W	151.62	15.21	7.12	0.9982	1.91
60 °C + 40 kHz 100 W	147.87	16.24	7.31	0.9973	2.13
60 °C + 25 kHz 300 W	152.18	11.85	7.09	0.9971	2.47
70 °C	149.53	14.81	7.25	0.9984	1.14
70 °C + 25 kHz 100 W	148.93	12.25	7.28	0.9991	0.91
70 °C + 40 kHz 100 W	149.90	15.71	7.23	0.9989	0.98
70 °C + 25 kHz 300 W	152.85	10.80	7.06	0.9977	2.04
87 °C	158.66	12.05	6.80	0.9996	0.82
87 °C + 25 kHz 100 W	160.66	10.38	6.71	0.9994	0.79
87 °C + 40 kHz 100 W	161.35	12.80	6.68	0.9993	1.00
87 °C + 25 kHz 300 W	172.96	7.73	6.20	0.9991	1.21
92 °C	160.01	11.02	6.75	0.9988	1.43
92 °C + 25 kHz 100 W	171.48	8.89	6.26	0.9985	1.51
92 °C + 40 kHz 100 W	160.43	11.27	6.72	0.9995	0.89
92 °C + 25 kHz 300 W	170.05	6.21	6.31	0.9988	1.28
97 °C	171.45	9.82	6.25	0.9992	0.90
97 °C + 25 kHz 100 W	179.72	7.68	5.94	0.9982	1.66
97 °C + 40 kHz 100 W	170.64	10.27	6.29	0.9995	0.95
97 °C + 25 kHz 300 W	178.49	5.43	5.99	0.9994	0.83

RMSE (%) = Root mean square error: $100 * \sqrt{\frac{1}{n}\sum_{1}^{n}\left[(M_{exp} - M_{pre}) / M_{exp}\right]^2}$

This is a three-parameter asymptotic model, where k_H (s^{-1}), the hydration rate constant and is representative of the rate of moisture intake. M_e and M_o are equilibrium moisture content in % d.b. and initial moisture content in % d.b. of Asymptotic first order model, respectively. This model was also applied to chickpeas

for soaking by Gowen et al., (2007). Such asymptotic model have been previously employed to describe the soaking process in kidneybeans (Abu-Ghannam and McKenna, 1997) and faba beans (Haladjian et al., 2003).

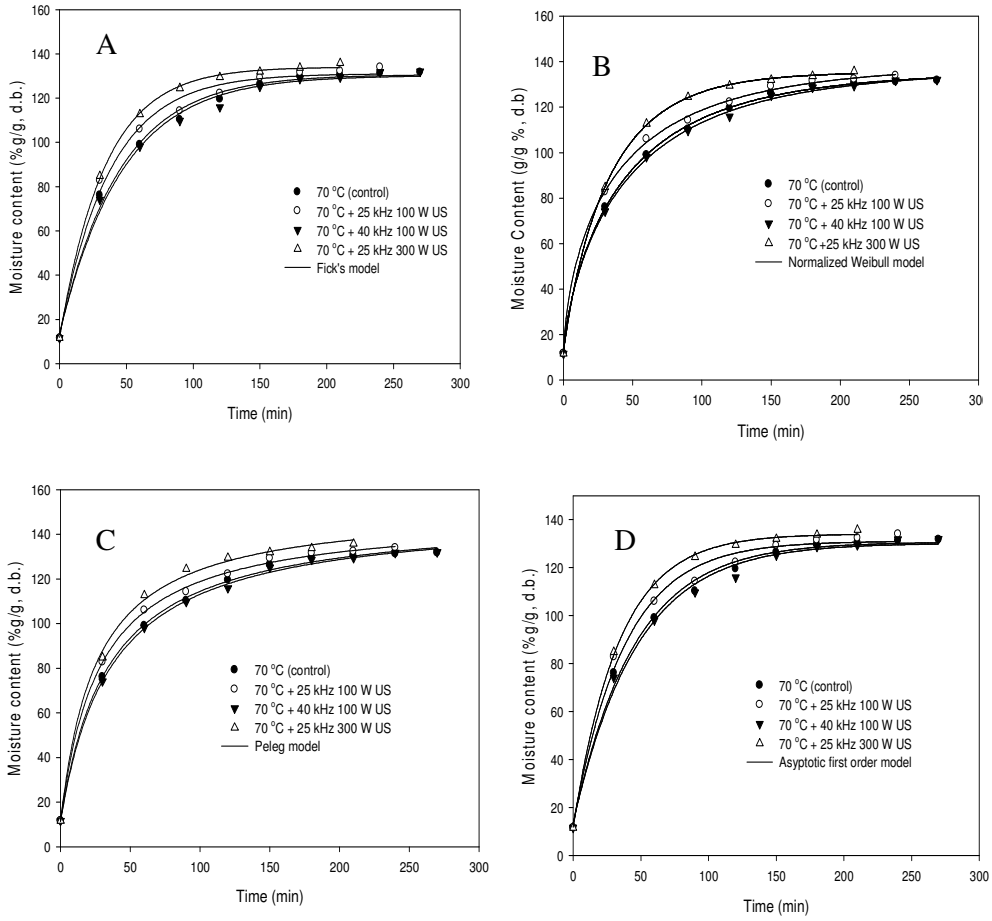


Figure 4.7. Means of experimental and predicted moisture contents (% g/g, d.b.) of chickpeas during soaking at 70 ^{o}C temperatures without and with ultrasound treatments for the Fick's (A), Normalized Weibull (B), Peleg (C) and Asymptotic first order (D) models

For mathematical modeling of variation of moisture content of chickpea during soaking at each temperature without and with ultrasound, Fick's law, Normalized Weibull distribution function, Peleg and Asymptotic first order models were tested. The parameters in these models such as $D_{eff,}$ M_e, β, K_1, K_2, R_g and k_H were estimated by using the non-linear regression analysis of equations (4.1-4.10) (Tables 4.1-4.4). The performances of the models were compared according to their coefficient of

determination (R^2), residuals of either moisture content and percentage of root mean square error (% RMSE (Tables 4.1-4.4 and A1-A4).

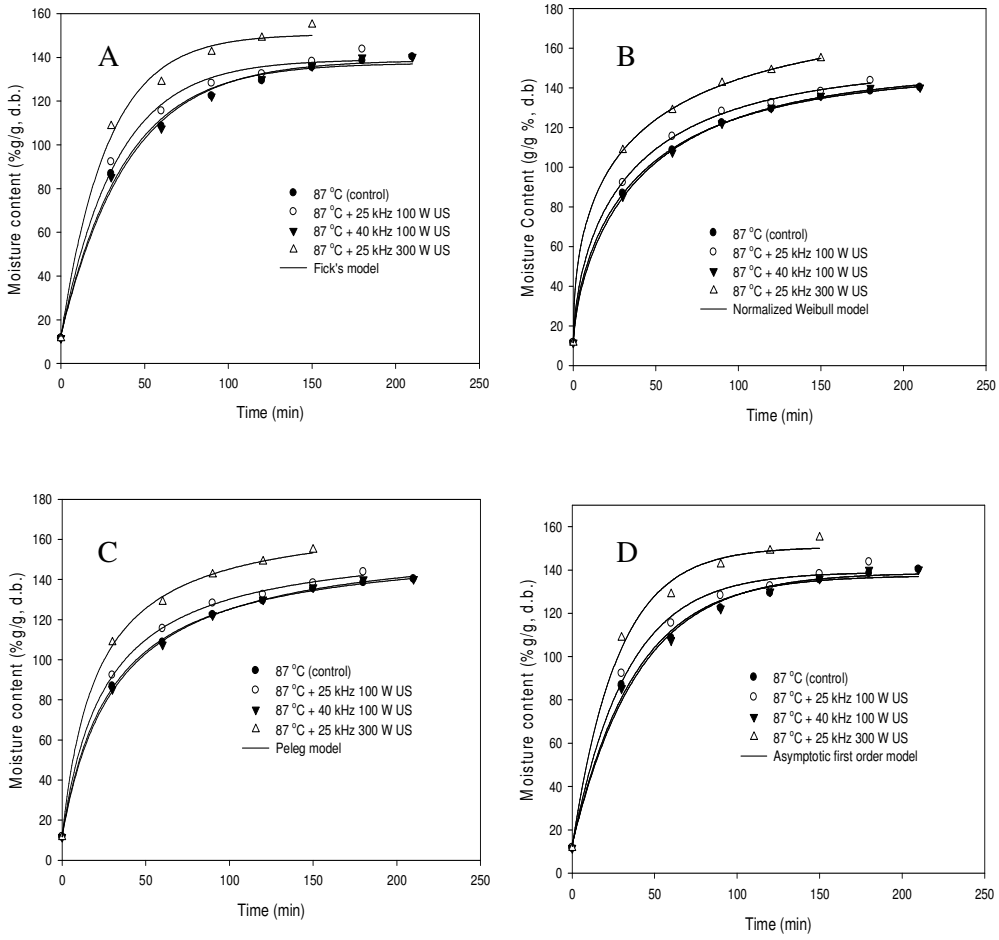


Figure 4.8. Means of experimental and predicted moisture contents (% g/g, d.b.) of chickpeas during soaking at 87 ^{o}C temperatures without and with ultrasound treatments for the Fick's (A), Normalized Weibull (B), Peleg (C) and Asymptotic first order (D) models

Data on the amount of water absorbed (moisture content) during soaking are illustrated in Figures 4.2-4.10 for all models. The course of the hydration, adequately fitted by four nonlinear equations with coefficients, shows that the seed water content increases with soaking time at all temperatures and treatments such as ultrasounds. With the process continuing, water absorption decreases until it ceases when the seed attained the equilibrium water content (Sayar et al., 2001).

Tables 4.1-4.4, Tables A1-A4 and Figures 4.2-4.10 shows that the diffusion, calculated by the Fick's law, the Normalized Weibul, the Peleg and the Asymptotic first order models was a thermally activated process and was sensitive to temperature, time and ultrasound.

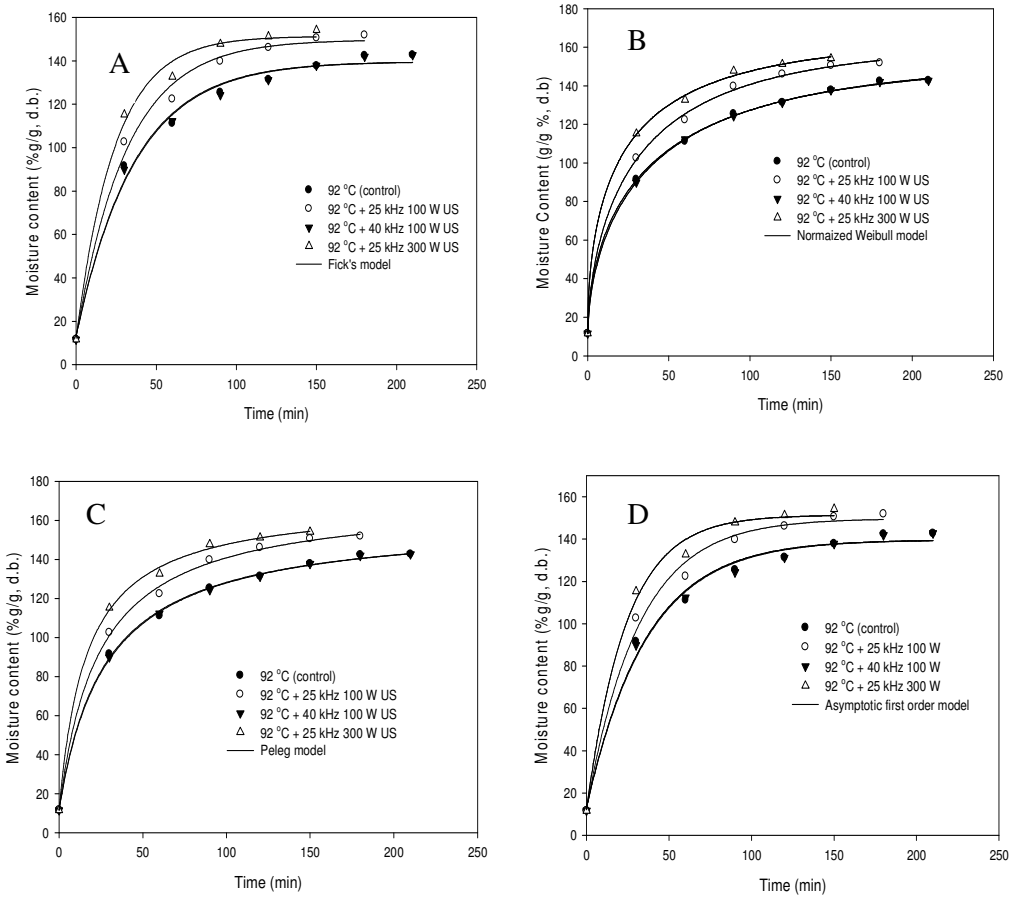


Figure 4.9. Means of experimental and predicted moisture contents (% g/g, d.b.) of chickpeas during soaking at 92 °C temperatures without and with ultrasound treatments for the Fick's (A), Normalized Weibull (B), Peleg (C) and Asymptotic first order (D) models

Temperature had an increasing effect on diffusion coefficient, e.g., when the temperature was raised from 20 to 97 °C, D_{eff} values were increased from $1.40x10^{-10}$ to $7.72x10^{-10}$ ($m^2.s^{-1}$) for both the Fick's and the Normalized Weibull models (Tables 4.1-4.2). The diffusion coefficient (D_{eff}) values for both Fick's and the Normalized Weibull models were found as the same values. Also, increasing in temperature from 20 to 97 °C significantly ($P<0.05$) increased in equilibrium moisture content (M_e)

from 119.82 to 155.05 (% g/g, d.b.) for Fick's model (Table 4.1). Furthermore, M_e values from Normalized Weibull model were found between 131.93 and 156.54 (%g/g, d.b.) as temperature was changed from 20 to 97 °C (Table 4.2). R^2 and % RMSE values were found in range as 0.9894-0.9960 and 2.51-9.70 for the Fick's model, respectively. R^2 and % RMSE for the Normalized Weibull model were found in the range of 0.9936-0.9999 and 0.41-3.07, respectively.

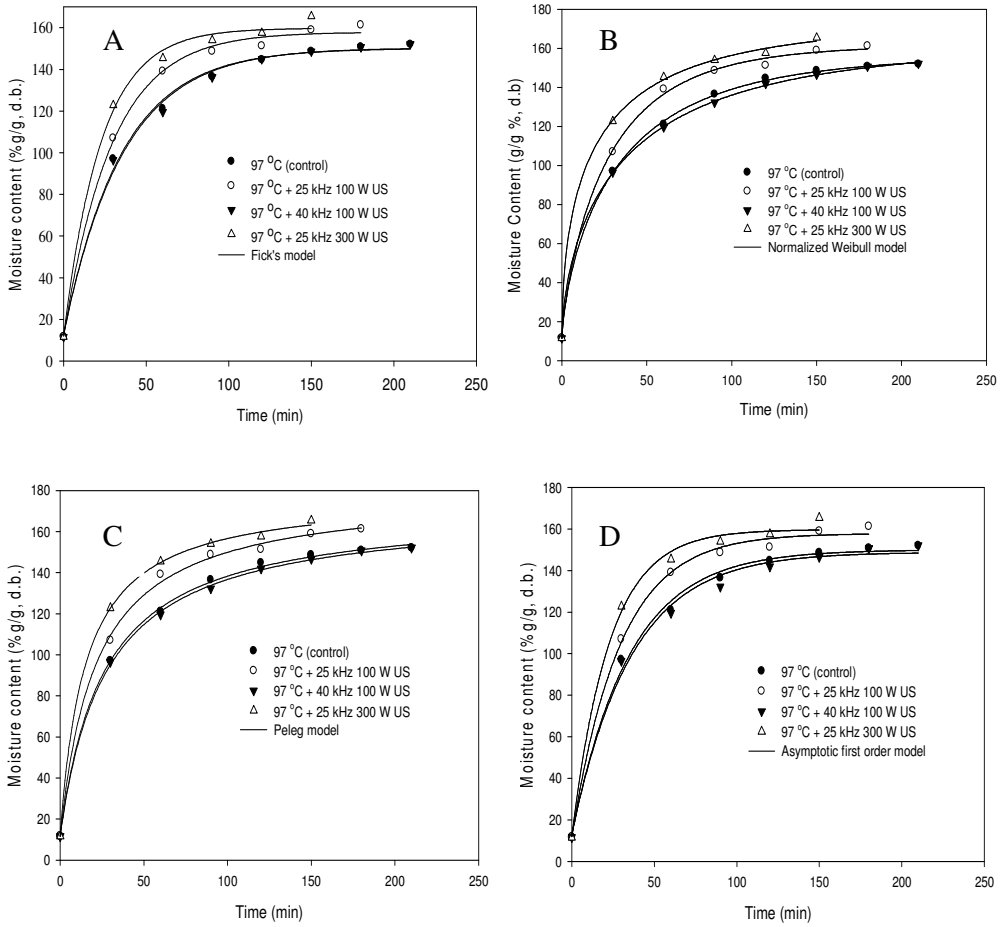


Figure 4.10. Means of experimental and predicted moisture contents (% g/g, d.b.) of chickpeas during soaking at 97 °C temperatures without and with ultrasound treatments for the Fick's (A), Normalized Weibull (B), Peleg (C) and Asymptotic first order (D) models

The magnitude of diffusion coefficient reported by (Sayar et al., 2001) for temperatures ranging from 20 to 100 °C were varied between 2.43 and 39.16×10^{-10} $m^2.s^{-1}$ for spring chickpea and 1.99 to 36.94×10^{-10} $m^2.s^{-1}$ for winter chickpea. The

water diffusion coefficient of chickpea ranged from $9.71x10^{-11}$ to $5.98x10^{-10}$ $m^2.s^{-1}$ (Seyhan-Gürtaş et al., 2001). The diffusion coefficients of chickpeas for temperature range of 45.0-98.7 ^oC were found in another study as $0.14x10^{-10}$-$5.51x10^{-10}$ ($m^2.s$) (Sababathy et al., 2005). Diffusivity values reported in this study were quite similar to the published literature results for different grains such as soybean ($2.15x10^{-11}$ $m^2.s$ at room temperature) (Deshpande et al., 1994) and white rice ($5.20x10^{-11}$ $m^2.s$ at 30 °C) (Engels et al., 1986).

When the experimental values of moisture contents were fitted to the Normalized Weibull distribution equation, the shape parameter (β) and geometric factor (R_g) values were also found. When the soaking temperature was increased from 20 to 97 ^oC, β and R_g values also increased from 0.588 to 0.819 and 7.56 to 9.74, respectively. The mean of β value was found as 0.745. This value is relativelly close to that found for the diffusion in spherical bodies in the study of Marabi et al. (2003) which was 0.670. Furthermore, the value of R_g was similar to values of Marabi et al. (2003) (8.50-18.60). The β values for sesame seeds at temperatures between 27 and 60 ^oC were found as 0.780 to 0.361 in a another study from Khazaei and Mohammadi (2009).

A change in temperature varies the rate of diffusion, thus changing the overall absorption behaviour. Additionally, moisture absorption at elevated temperatures may induce irreversible changes of the seeds, such as chemical and structural degradation. These damages to food material will also change the weight gain behavior of the material correspondingly.

It was reported that the rate of water absorption by legumes increased with increase in the temperature during soaking (Quast and de Silva, 1977; Tang et al., 1994; Sopade and Obekpa, 1990; Abu-ghannam and McKenna, 1997; Hung et al., 1993 and Hsu et al., 1983).

The term of $1/K_1$ is called the initial rate of absorption thus, at a given temperature, as K_1 decreases, the amount of water absorbed becomes greater. Evaluation of the K_1 values of the Peleg's model showed that the values of this parameter decreased from

88.74 to 9.82 s/% m.c. with increasing temperature from 20 to 97 °C (Table 4.3 and Figures 4.2-4.10).

Table 4.4. Predicted parameters of Asymptotic first order model during soaking of chickpeas at different temperatures without and with ultrasound applications

	Asymptotic first order model			
Process	M_e (%. d.b.)	$k_H x 10^5$ (s^{-1})	R^2	RMSE (%)
20 °C	119.82	8.64	0.9960	8.03
20 °C + 25 kHz 100 W	119.48	10.51	0.9907	13.88
20 °C + 40 kHz 100 W	123.10	7.92	0.9943	10.76
20 °C + 25 kHz 300 W	120.94	12.40	0.9925	11.29
30 °C	122.81	11.60	0.9894	9.70
30 °C + 25 kHz 100 W	122.61	12.90	0.9910	10.97
30 °C + 40 kHz 100 W	125.18	10.00	0.9941	10.04
30 °C + 25 kHz 300 W	124.40	16.20	0.9904	8.78
40 °C	128.44	14.80	0.9944	8.93
40 °C + 25 kHz 100 W	129.86	18.40	0.9914	9.88
40 °C + 40 kHz 100 W	127.56	15.20	0.9952	8.01
40 °C + 25 kHz 300 W	130.79	23.40	0.9951	6.59
50 °C	128.64	25.40	0.9942	7.82
50 °C + 25 kHz 100 W	130.72	30.50	0.9988	2.72
50 °C + 40 kHz 100 W	127.30	27.30	0.9981	2.53
50 °C + 25 kHz 300 W	133.56	40.20	0.9944	2.91
60 °C	129.76	34.40	0.9957	4.74
60 °C + 25 kHz 100 W	131.68	36.50	0.9978	3.43
60 °C + 40 kHz 100 W	129.17	34.40	0.9966	4.10
60 °C + 25 kHz 300 W	133.67	45.00	0.9978	1.87
70 °C	130.66	37.10	0.9944	5.85
70 °C + 25 kHz 100 W	131.05	43.90	0.9924	5.45
70 °C + 40 kHz 100 W	130.22	35.60	0.9935	6.19
70 °C + 25 kHz 300 W	134.06	49.10	0.9993	1.29
87 °C	137.47	43.90	0.9938	5.55
87 °C + 25 kHz 100 W	139.06	50.50	0.9944	4.13
87 °C + 40 kHz 100 W	138.78	41.70	0.9942	5.89
87 °C + 25 kHz 300 W	150.63	60.30	0.9937	4.18
92 °C	139.70	46.20	0.9908	6.36
92 °C + 25 kHz 100 W	149.74	52.70	0.9935	5.00
92 °C + 40 kHz 100 W	139.67	45.60	0.9925	5.73
92 °C + 25 kHz 300 W	151.37	69.20	0.9948	3.38
97 °C	150.05	47.60	0.9959	4.50
97 °C + 25 kHz 100 W	157.88	56.90	0.9974	2.02
97 °C + 40 kHz 100 W	148.84	46.30	0.9926	6.02
97 °C + 25 kHz 300 W	159.75	73.20	0.9960	2.55

RMSE (%) = Root mean square error: $100 * \sqrt{\frac{1}{n}\sum_{1}^{n}\left[(M_{exp} - M_{pre}) / M_{exp}\right]^2}$

The order of magnitude of K_1 values found in this work is in agreement with those of other chickpeas in the literature. Several investigators have reported similar results for other seeds and grains (Hung et al., 1993; Cunningham et al., 2007; Turhan et al., 2002). In the study of Turhan et al. (2002), the values of K_1 for spring chickpeas were found as between 61.56 and 3.42 (s/% m.c.) for a 20-100 ^oC temperature range. However, Lopez et al. (1995) concluded that for hazelnut kernels, K_1 showed a linearly increasing trend with increasing temperature in the range of 15 to 30 ^oC. Hung et al. (1993) have also reported that the mean value of K_1 for three varieties of chickpeas at temperatures of 25 and 42 ^oC were 39.6 and 28.8 s/% m.c. (d.b.), respectively. These values were similar to those obtained in this study for chickpeas.

According to Table 4.3., the capacity constant K_2 of the Peleg's model showed a significant ($P<0.05$) decrease with temperature. This is due to increasing water absorption capacity of chickpea with increasing temperature. The constant K_2 of the Peleg's model is inversely related to the absorption ability of foods, i.e., the lower the K_2, the higher the water absorption capacity. Water absorbing capacity depends upon the cell wall structure, composition of seeds and compactness of the cells in seeds (Sabapathy, 2005). For some food products, K_2 was reported to decrease with increasing temperature (Cunningham et al., 2007; Lopez et al., 1995; Maskan, 2002; Sopade et al., 1994). But for some other ones, no effect of temperature was reported (Hung et al., 1993; Sopade and Obekpa, 1990; Sopade et al., 1994).

In Peleg's model, the saturation moisture contents (M_e) of chickpea at different temperatures were determined and are given in Figure 4.3. Furthermore, the saturation moisture contents of chickpea at different temperatures were predicted by use of Peleg's equation. When $M_e=M_o+1/K_2$ relation was applied to M_o and K_2 values for different soaking temperatures, M_e (% g/g, d.b.) values were predicted. It was found that as the temperature increased from 20 to 97 ^oC, the saturation or equilibrium moisture content values (M_e) also increased from 155.47 to 171.45. Additionally, R^2 and RMSE values for Peleg model were changed from 0.9928 to 0.9996 and 0.82 to 4.15 (%) for the temperature range of 20-97 ^oC, respectively.

Chickpea water absorption curves (Figures 4.2-4.10) obey characteristic of a first order process. Therefore, the equation 4.7 can be applied for primary modelling of

the data. Such asymptotic model have been previously employed to describe the soaking process in kidneybeans (Abu-Ghannam & McKenna, 1997) and faba beans (Haladjian et al., 2003).

The predicted parameters, M_e, k_H values, from this model are given in Table 4.4. M_e (% g/g, d.b.) increased (119.82 to 150.05) with increasing soak temperature (20 to 97 ^oC) for chickpeas ($P<0.05$) (Table 4.4). Similar temperature dependence was found in the literature for both kidneybeans (Abu-Ghannam and McKenna, 1997) and chickpeas (Turhan et al., 2002). It has been postulated that increasing soak temperature promotes leaching of water-soluble components, resulting in lower asymptotic moisture content (Abu-Ghannam and McKenna, 1997).

Representative of the rate of water intake during soaking, k_H increased from 8.64 x 10^{-5} to 4.76 x 10^{-4} s^{-1} with temperature increased from 20 to 97 ^oC, as was expected from visual inspection of the water absorption curves in this study (Table 4.4 and Figures 4.2-4.10). The k_H values for Red kidney beans had been found between 4.03 x 10^{-5} s^{-1} and 7.93 x 10^{-4} s^{-1} for 20-60 ^oC temperature range in a previous study (Abu-Ghannam and McKenna. 1997). Thus, hydration rate constants for that study were similar to those found in the present study. The R^2 and RMSE for the Asymptotic first order model were found in the range of 0.9894-0.9960 and 4.50-9.70 for temperature of 20-97 ^oC, respectively.

As the process continued, water absorption rate decreased steadily due to water filling into the free capillary and intermicellar spaces, and increasing the extraction rates of soluble solids from grains (Abu-Ghannam and McKenna, 1997). As the driving force in the water movement decreases, the extraction of soluble solids in the reverse direction to the water movement offers additional resistance to water transfer (Sayar et al., 2001).

Water absorption ceased when the grains attained the equilibrium water content. The rate of water absorption increased with increasing temperature as suggested by the slopes of the absorption curves getting steeper with increased temperature. Earlier studies reported that the water absorption rate by whole beans is influenced by seed size (Hung et al., 1993), initial water content (Smith and Nash. 1961), thickness and

structure of seed coat (Abu-Ghannam and McKenna, 1997; Singh and Kulsherstha, 1987).

When the models used in this research were compared with respect to their goodness of fit, the mean values of RMSE (%) was 6.12, 1.46, 2.54 and 6.14 for Fick's, Normalized Weibull, Peleg and Asymptotic first order models, respectively. The means R^2 values of Fick's, Normalized Weibull, Peleg and Asymptotic first order models were found as 0.9944, 0.9983, 0.9973 and 0.9944, respectively. As a result, the goodness of fit of Normalized Weibull model was higher than other models (RMSE (%): 1.46).

4.1.1.2. A general model to describe water absorption as a function of soaking time and temperature

Previous studies showed that temperature is one of the most important factors affecting the water diffusivity and water absorption of agricultural products (Kashaninejad et al., 2007; Turhan et al., 2002). In order to find the cooking temperature of chickpeas and effect of temperature, an Arrhenius type equation was applied to soaking temperatures for diffusion constant (D_{eff}), Peleg rate constant (K_1) and hydration rate constant (k_H) found from both Fick's and Normalized Weiubull models, Peleg and Asymptotic first order models.

The dependence of diffusion coefficient (D_{eff}) for the Fick's and the Normalized Weibull models, Peleg capacity constant (K_2) and k_H of the Asymptotic first order model on temperature were modelled using the Arrhenius equation (Equations 4.8-4.10), which had been used previously to describe the temperature dependent hydration kinetics of legumes (Abu-Ghannam and McKenna, 1997; Turhan et al., 2002):

$$ln(D_{eff}) = ln(D_{ref}) - (\frac{E_a}{R}) * (\frac{1}{T}) \quad (4.8)$$

$$ln(1 / K_1) = ln(K_{ref}) - (\frac{E_a}{R}) * (\frac{1}{T}) \quad (4.9)$$

$$ln(k_H) = ln(k_{ref}) - \left(\frac{E_a}{R}\right) * \left(\frac{1}{T}\right) \quad (4.10)$$

where D_{eff}, K_1, k_H and T are effective diffusion coefficient of the Fick's and the Normalized Weibull models, Peleg capacity constant and hydration rate constant, the soaking temperature (in Kelvin), respectively. E_a is the activation energy for the hydration process and R is the ideal gas constant (8.314 $x10^{-3}$ kJ/mol ^oK). D_{ref}, K_{ref} and k_{ref} are reference hydration rate constants for the Fick's, the Normalized Weibull, the Peleg and the Asymptotic first order models, respectively.

The rate of water transfer and/or starch gelatinization in whole cereal and legume grains during soaking were investigated in a number of studies (Bakshi and Singh, 1980; Lin, 1993; Sayar et al., 2001; Turhan et al., 2002; Sağol et al., 2006). In these studies a coefficient for water transfer rate and/or starch gelatinization rate changed linearly versus temperature and every curve brakes at a spesific temperature which is close to cooking temperature.

Arrhenius plots (natural logarithm of rate constants versus the inverse of T (in Kelvin)) for chickpeas are superposed in Figures 4.11-4.13. The activation energy, E_a, is related to the slope of these graphs, and is indicative of the temperature dependence of D_{eff}, K_1 and k_H. For soaked chickpeas, a break seemed to occur at a certain soak temperature in the Arrhenius curve.

To locate the temperature at which the break in the Arrhenius curve for soaked chickpeas occurred, the estimated natural log of rate constants (D_{eff}, K_1 and k_H) were fitted to a linear model with break point (Muggeo, 2003), and the break temperature were estimated to be 61.47, 59.96 and 61.47 ^oC for Fick's, Normalized Weibull and Asymptotic first order models, respectively. To confirm the validity of applying a linear model with a break to the soaked chickpea data, the following approach was taken. A linear model with a break at 61.47, 59.96 and 61.47 ^oC for Fick's, Normalized Weibull and Asymptotic first order models was applied (R^2 = 0.9349-0.9954).

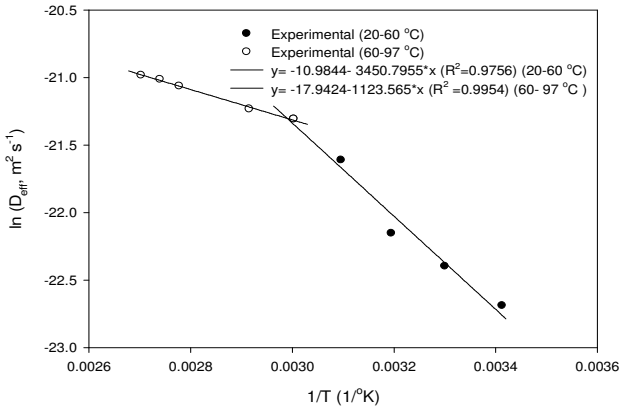


Figure 4.11. Arrhenius plot of Fick's law and Normalized Weibull models of diffusion constant, $D_{eff,}$ of chickpea over the soaking temperature range of 20-97 ^{o}C

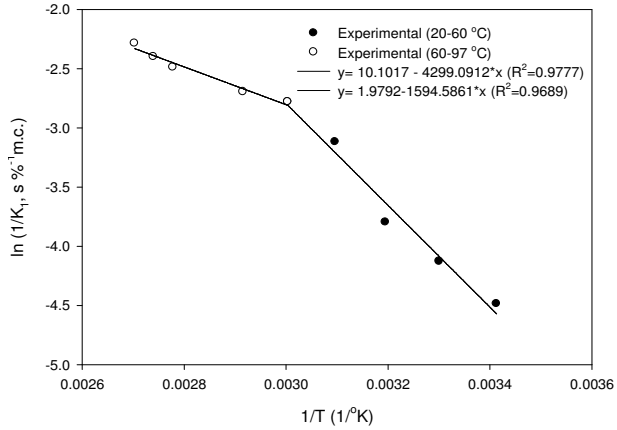


Figure 4.12. Arrhenius plot of Peleg model of $K_{1,}$ of chickpea over the soaking temperature range of 20-97 ^{o}C

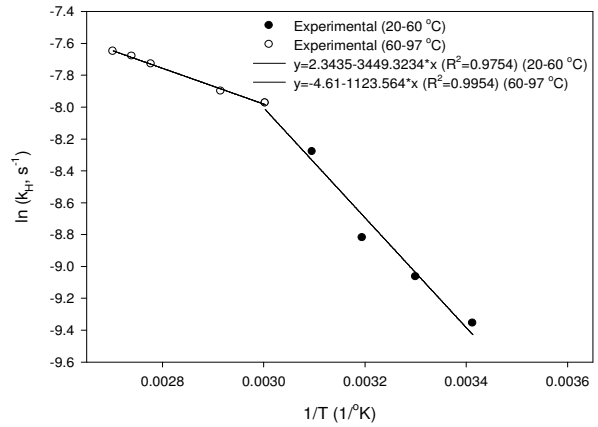


Figure 4.13. Arrhenius plot for Asymptotic first order model of water absorption rate constant, k_H, over the soaking temperature range 20-97 ^{o}C

The models were compared by the correlation coefficient, and inclusion of the break was shown to significantly improve the model ($P < 0.05$). Such a discontinuity in the Arrhenius curve had been observed during the soaking of rice (Bakshi and Singh, 1980) and chickpeas (Sayar et al., 2001; Turhan et al., 2002), and it has been suggested that the break is linked to the early onset of starch gelatinization. However, it has been suggested (Sayar et al., 2001; Turhan et al., 2002) that chickpea gelatinization may actually commence between the lower temperatures of 55 and 60 ^{o}C. Starch granules of the chickpeas used in this study kept the integrity of Maltase crosses till 61 ^{o}C (Figure 4.44). They noticeably started to decrease in number and distort in shape between 60 and 70 ^{o}C (Figure 4.44) pointing that cooking temperature of chickpeas starts between 60 and 70 ^{o}C. Also, onset temperature was found as 61.13 ^{o}C with DSC method (Table 4.8). This observed temperature range is fairly close to the reported cooking temperature of 63-70 ^{o}C for chickpea (Fernandez & Berry, 1989). It is possible that the break in the Arrhenius curve for soaked chickpeas was due to partial gelatinization and/or structural changes, promoted soaking at temperatures above 60 ^{o}C. From the results of four models, the mean value of break temperature was found to be approximately 61±0.75 ^{o}C. So, the cooking temperature of chickpeas studied in the present study was 61 ^{o}C. The cooking temperature was around 60 °C for whole soybean (Kubota, 1979). This implies a significant change in chickpeas affecting the water absorptivity and reactivity of starch. This observed cooking temperature is fairly close to the reported cooking temperature of 55-70 ^{o}C for chickpea (Fernandez and Berry, 1989; Sayar et al., 2001).

To estimate the model parameters such as M_o (initial m.c), M_e (equilibrium m.c), T (temperature in Kelvin) and t (time in second), a generalized non-linear regression of Equations of 4.11–4.18 can be performed on the entire dataset. It may be interesting to compare the activation energy resulting from the variation of the values of D_{eff}, K_1 and k_H with temperature, with the value obtained from the diffusive process. The dependence of constants (D_{eff}, K_1 and k_H) on temperature was modeled using the Arrhenius equation, which has been used previously to describe the temperature dependent hydration kinetics of other grains and seeds (Maskan, 2002; Turhan et al., 2002).

Incorporating temperature break at 61.47, 59.96 and 61.47 ^{o}C for Fick's, Normalized Weibull, Peleg and Asymptotic first order models, time and temperature dependence of moisture content for soaked chickpeas, and dependence of initial and equilibrium moisture contents, the following general models were derived to describe the water absorption kinetics of chickpeas:

For Fick's model;

$$M = M_e + (M_o - M_e)(6/\pi^2)exp\left[-(\pi^2/r^2)1\cdot 696\times 10^{-5} exp(-3450.79/T)t\right] \quad (\leq 60^{o}C) \quad (4.11)$$

$$M = M_e + (M_o - M_e)(6/\pi^2)exp\left[-(\pi^2/r^2)*1.613\times 10^{-8} exp(-1123.56/T)t\right] \quad (>60^{o}C) \quad (4.12)$$

For Normalized Weibull model;

$$M = M_e + (M_o - M_e)exp\left[-\left(\frac{R_g}{r^2}1.696\times 10^{-5} exp(-3450.79/T)t\right)^{\beta}\right] \quad (\leq 60\ ^{o}C) \quad (4.13)$$

$$M = M_e + (M_o - M_e)exp\left[-\left(\frac{R_g}{r^2}1.613\times 10^{-8} exp(-1123.56/T)t\right)^{\beta}\right] \quad (>60\ ^{o}C) \quad (4.14)$$

For Peleg model;

$$M = M_o + \left[t/4.08\,x\,10^{-5} exp(4299.10/T) + t/(M_e - M_o)\right] \quad (6\leq 0\ ^{o}C) \quad (4.15)$$

$$M = M_o + \left[t/(0.14exp(1594.59/T) + t/(M_e - M_o)\right] \quad (>60\ ^{o}C) \quad (4.16)$$

For Asymptotic first model;

$$M = M_e + (M_o - M_e)exp\left[-10.42exp(-3449.32/T)t\right] \quad (\leq 60\ ^{o}C) \quad (4.17)$$

$$M = M_e + (M_o - M_e)exp\left[-0.00995exp(-1123.56/T)t\right] \quad (>60\ ^{o}C) \quad (4.18)$$

The D_{eff}, K_1 and k_H values decreased as temperature increased suggesting a corresponding increase in the initial water absorption rate. When Arrhenius equations (4.8-4.10) were applied to the D_{eff}, K_1 and k_H values for temperatures bellow and

above break points (61.47 and 59.96), the activation energy values were predicted. The activation energy values of soaked chickpeas bellow 60 ^{o}C for Fick's, Normalized Weibull, Peleg and Asymptotic first order models were found as 28.69 (R^2=0.9756), 35.74 (R^2=0.9777) and 28.68 (R^2=0.9754) kJ/mol, respectively. The activation energy for all models at soaking temperatures above 60 ^{o}C was also predicted and found as 9.34 (R^2=0.9954), 13.26 (R^2=0.9689) and 9.34 (R^2=0.9349) kJ/mol, respectively. This value agrees well with the literature value of 19.50 kJ mol^{-1} for the activation energy of osmotic hydration of chickpeas at 5-50 ^{o}C (Pinto and Esin, 2004). The activation energies of chickpea were found as 41.79 kJ mol^{-1} and 8 kJ mol^{-1} for 25-37 ^{o}C and 37-60 ^{o}C temperature ranges by Goven et al. (2007). In another study, the activation energy for chickpea was 48 and 18 kJ mol^{-1} for temperature bellow and above 55 ^{o}C, respectively (Sayar et al., 2001).

When the activation energy of chickpea found in present study was compared with respect to bellow and above the cooking temperatures it can be seen that a 60-70% decrease was obtained after cooking temperature. Therefore, the lower activation energy for the rate of water transfer above the cooking temperature implies that it travels faster in cooked chickpea than in uncooked chickpea.

4.1.1.3. Effect of ultrasounds on water absorption during soaking of chickpeas

One emergent application of power ultrasound in food industry is the enhancement of mass transfer in processes where diffusion takes place. The application of ultrasounds on drying has been studied before in some researches (Gallego-Juarez, 1998). Power ultrasound introduces pressure variations at solid/liquid interfaces, and therefore increases the moisture absorption rate. Acoustic energy also causes oscillating velocities and microstreaming at the interfaces which may affect the diffusion boundary layer (Gallego-Juarez et al., 1999). Furthermore, ultrasonic waves also produce rapid series of alternative contractions and expansions (sponge effect) of the material in which they are travelling (Gallego-Juarez, 1998; Mulet et al., 2003); this alternating stress creates microscopic channels which may make the moisture gain easier. In addition, acoustic waves may produce cavitation of water molecules inside the solid matrix, which may be beneficial for the gain of strongly attached moisture (Mulet et al., 2003). Therefore, external and internal resistance

may be seriously affected during drying by the effects associated to acoustic energy. thus increasing mass transfer.

Ultrasound has been used to enhance mass transfer in solid/liquid systems like meat (Carcel et al., 2007a), cheese (Sanchez et al., 1999) brining and osmotic dehydration of apple (Simal et al., 1998a; Carcel et al., 2007b). Different applications in conventional extraction processes (Romdhane and Gourdon, 2002) and solid/supercritical fluid systems, mass transfer have also been found in the literature (Fuente et al., 2004; Riera et al., 2004). Han and Baik (2006) reported the effect of ulrasounds in reduction soaking and cooking time of legumes. Wambura et al. (2008) has reported that use of ultrasound made to reduce in cooking time of rice by 70%. These studies show that thermosonication can be used to icrease the water absorption during soking operation.

The effects of ultrasounds are illustrated in Figures 4.2-4.10. The moisture contents at each temperature without US were used as control. The moisture contents of chickpea during soaking are given in Tables A2-A4. The statistical analysis (multiple range analysis, Duncan test) of moisture contents are also tabulated in Tables A2-A4. Aplication of 25 kHz ultrasounds significantly ($P<0.05$) increased the water absorption of chickpea for all temperatures (20-97 ^{o}C). The moisture content (% g/g, d.b.) values of chickpea increased from 76.91 to 85.14 (% g/g, d.b.) with 25 kHz 100 W US application for 20 ^{o}C and 180 min soaking. A similar increase was observed for other soaking times at constant temperatures. Increase in power of US (from 100 to 300 W) significantly ($P<0.05$) increased the moisture content (from 85.14 to 91.89) of chickpea during soaking at 20 ^{o}C. When the higher US powers such as 300 W at 20 ^{o}C and 180 min was compared with control, moisture content of chickpea was found to increase from 76.91 to 91.89 (% g/g, d.b.). Similarly, 25 kHz US and increase in power (100 to 300 W) increased the moisture content of soaked chickpea at all other temperatures. However, increase of US frequency from 25 to 40 kHz decreased (from 85.14 to 76.55 %) in water absorption of chickpea for constant 180 min and 20 ^{o}C. 40 kHz US application did not significantly effect the moisture content (76.55) of chickpea at constant 180 min soaking when compared with conventional soaking (76.91% g/g, d.b.). Increase in ultrasound frequency from 25 to 40 kHz nonsignificantly ($P>0.05$) affected on moisture content from at 20 ^{o}C soaking

temperature and 180 min time (Tables 4.1-4.4 and Figures 4.2-4.10). 40 kHz 100 W US application did not effect or/and decreased in moisture content values for the same soaking temperatures (Tables A2-A4 and Figures 4.2-4.10). Ultrasound applications except 40 kHz affected the water absorption capacity of chickpea during soaking at different temperatures and times due to create a more effective cavitation that cause the chickpea grain as porous or sponge.

D_{eff}, K_1, k_H values found from the Fick's, Normalized Weibull, Peleg and Asymptotic first order models were main parameters for the ultrasonic assisted process of diffusion which were compared with the conventional soaking at different temperatures (Tables 4.1-4.4). Ultrasound application changed D_{eff}, K_1, k_H values that means the water absorption of chickpea was effected during soaking. When the ultrasound such as 25 kHz 100 W was applied to chickpeas during soaking at 20 ^oC, D_{eff}, K_1 and k_H values changed from $1.40x10^{-10}$ to $1.70\ x10^{-10}$ $m^2.s^{-1}$, 88.74 to 69.57 s/% m.c and $8.64x10^{-5}$ to $10.51\ x10^{-5}$ s^{-1}, respectively. Also, increase in power of ultrasound (from 100 to 300 W) changed D_{eff}, K_1 and k_H values from $1.40x10^{-10}$ to $1.70\ x10^{-10}$ $m^2.s^{-1}$, 88.74 to 58.04 s/% m.c and $8.64x10^{-5}$ to $12.40x10^{-5}$ s^{-1} at the same soaking temperature (20 ^oC) (Tables 4.1-4.4), respectively. Similarly, for 60 ^oC without US, with 25 kHz 100 W and 25 kHz 300 W US applied chickpea the values of D_{eff}, K_1 and k_H from different models were changed from $5.58x10^{-10}$ to $5.92x10^{-10}$ and $7.29x10^{-10}$ $m^2.s^{-1}$, 16.12 to 15.21 and 11.85 s/% m.c, $34.40x10^{-5}$ to $36.50x10^{-5}$ and $45.00x10^{-5}$ s^{-1}, respectively. A significant ($P<0.05$) change in D_{eff}, K_1 and k_H values was observed for other soaking temperatures (20-97 ^oC) when ultrasound was applied to chickpeas during soaking. The ultrasound increased the water absorption of chickpea during soaking due to increasing of mass diffusion rate (Fuente et al., 2004). However, application of high frequency ultrasonic (40 kHz) for all soaking temperatures did not significantly ($P>0.05$) affect or/and decreased the water absorption rate and the diffusion coefficient of chickpea (Tables 4.1-4.4 and Figures 4.2-4.10). Change of ultrasound frequency from 25 to 40 kHz decrease D_{eff} value from $1.40x10^{-10}$ to $1.28\ x10^{-10}$ $m^2.\ s^{-1}$ (20 ^oC soaking).

It could not be confirmed that the ultrasound soaking leads to a lowering of the energy requirement. It needs to be determined whether the chickpea quality resulting from ultrasound applied soaking treatment can justify its use for chickpea soaking.

Further studies are needed to improve the processing equipment in conjunction with industrial requirements in order to apply this technology in the food industry. Finally, the ultrasound enhanced soaking described in this study will facilitate the advancement in the study of the mechanisms involved for the aim of extending the application of this technology.

4.1.2. Change in texture of chickpea during soaking

Texture is a quality attribute that is closely related to the structural and mechanical properties of a food. Foods come from biological origins, they, whether raw or processed, constantly change with time due to chemical reactions, microbial actions, and physical interactions with the environment such as temperature, humidity, air compression and pressure, and the supply and consumption of energy (Kilcast, 2004).

Force/deformation methods are widely used for objective measurement of the textural properties of solid foods. There are two approaches to force/deformation measurement of food texture : *destructive* versus *non-destructive*. Destructive force/deformation methods are considered by many to be a preferred means of measuring the texture of food because they are usually related to the sensory evaluation than are non-destructive methods (Bourne, 2002). Destructive methods are useful for providing information about the average quality for a bach of food items (Kilcast, 2004).

Many earlier researchers employed instrumental texture measurement (also known as the hardness) to quantify product quality. Hardness is often defined as the peak force corresponding to the first compression of the sample (Lee et al., 1979; Vu et al., 2004; Sila et al., 2004, 2005; Anthon and Barrett, 2002, 2006).

Texture of the chickpea was analysed using F_{max} (maximum force in N) values. F_{max} values were used to determine the degree of hardness of chickpea during soaking. F_{max} values of chickpea at 20-97 ^{o}C temperature without and with US were given in Tables A5-A9 and relations with time, temperature and US were illustrated in Figures 4.14-4.17. The statistical results (ANOVA) of texture values with respect to time, temperature and US were also given in Table A6. From Section 3.1, 40 kHz

100 W ultrasound application did not effect or adverse effect on water absorption of chickpea during soaking. Therefore, 25 kHz 100 W and 25 kHz 300 W US were used in texture experiments.

Curves of chickpea hardness (F_{max}) versus time, over the set of soak temperatures (20-97 ^{o}C) and ultrasounds (25 kHz 100 and 300 W) studied, were shown in Figures 4.15-4.17 and Tables A5-A9. Chickpea was soaked until the water was at the center of chickpea seed.

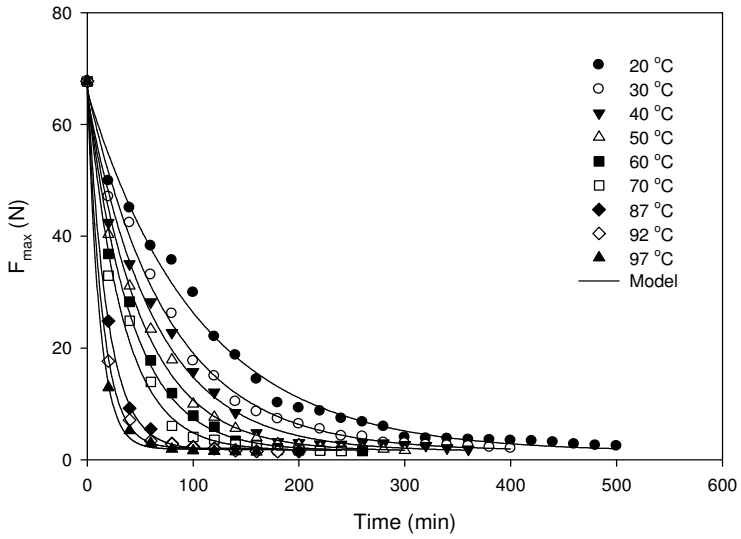


Figure 4.14. Average experimental and predicted F_{max} values from texture model relations to time for soaked chickpeas at 20-97 ^{o}C

As the soaking temperature increased time needed to reach the water at the center of chickpea decreased. It took 500 min at 20 ^{o}C while 200 min at 97 ^{o}C soaking. Chickpea hardness decreased from an initial dry value (67.73 N) towards an average equilibrium value 2.09 ±0.43 N for all temperatures after a certain amount of soaking time (Tables A5-A9 and Table 4.5). Increase in soaking time signifficantly ($P < 0.05$) decreased in F_{max} values (Tables A5-A9). Also, increase in soaking temperature and US application decreased F_{max} values. The graphs (Figures 4.14-4.17) and texture data (Tables A5-A9) show two phases, a rapid softening phase, which may be associated with the high rate of water absorption followed by a saturation phase where texture degradation rate slows down until an equilibrium texture property is achieved.

Variability of chickpea hardness was large among samples, especially at early stages of hydration. This reflects the natural variability inherent in the dry chickpea. As soaking proceeds, water is absorbed, resulting in a more uniform texture, and intra-bean variability consequently decreases. Such a pattern of decreasing variability with soak time was observed for all soaking temperatures studied.

4.1.2.1. Modelling of chickpea hardness as a function of soaking time

In the powder and granular food materials, researchers have paid attention on granular compression stres (Peleg, 1977). Compression tests have been used in pharmaceutical, ceramic, Metallurgical, civil engineering and food industries (Alvarado and Aguilera, 2001).

Chickpea hardness decreased towards an asmptotic equilibrium state during soaking, and the general shape of the textural degradation curves (Figures 4.14-4.17) resembled the inverse shape of the water absorption curves in section 4.1.1 (Figures 4.2-4.10). Furthermore, Kim et al. (1984a), Sacchetti et al.(2003), Liu and Scanlon (2007), Sajeev et al.(2008), Cunningham et al. (2008) and Goven et al.(2007) showed that the changes in hardness of foods during processings such as soaking has been followed as a asymptotic first order model. Therefore, for symmetry and simplicity, the following primary model was chosen for application to the data to describe the decrease of chickpea hardness over time:

$$F = F_e + (F_o - F_e)\exp(-k_F t) \tag{4.19}$$

Where, F, F_o, F_e and k_F are forces at any time (t), initial and equilibrium, the rate constant of chickpea softening in s^{-1}, respectively. The experimental chickpea texture data for each sample replication at each soaking temperature was fitted by non-linear regression to Equation 4.19. From the Equation 4.19 the soaking time required to any particular value of hardness could be predicted. Predicted time (t_e) in min taken to reach equilibrium texture level for soaked chickpea was calculated from the model Equation (4.19).

Table 4.5. Predicted parameters (F_o, F_e, k_F and t_e), R^2 and RMSE values from non-linear regression analysis of texture model for soaking of chickpeas at different temperatures without and with US

Process	F_o (N)	F_e (N)	$k_F x10^4$ (s^{-1})	t_e (min)	R^2	RMSE (%)
20	66.25	2.11	1.68	941	0.9945	9.10
20 °C + 25 kHz 100 W	64.90	2.07	1.89	836	0.9924	9.38
20 °C + 25 kHz 300 W	65.19	2.37	2.36	670	0.9935	7.14
30	64.83	1.78	2.37	667	0.9914	9.81
30 °C + 25 kHz 100 W	65.82	2.51	3.29	480	0.9957	16.64
30 °C + 25 kHz 300 W	66.32	2.92	4.26	371	0.9956	24.35
40	65.22	1.79	3.16	500	0.9928	12.54
40 °C + 25 kHz 100 W	66.35	2.64	4.53	349	0.9953	23.19
40 °C + 25 kHz 300 W	67.17	2.48	5.85	270	0.9968	24.83
50	66.94	2.73	4.72	335	0.9979	19.19
50 °C + 25 kHz 100 W	66.33	2.52	5.77	274	0.9986	17.16
50 °C + 25 kHz 300 W	67.61	2.75	9.10	174	0.9986	23.14
60	67.72	2.57	6.09	260	0.9998	5.88
60 °C + 25 kHz 100 W	67.74	2.59	8.56	185	0.9999	4.76
60 °C + 25 kHz 300 W	67.73	2.70	13.30	119	0.9999	5.78
70	67.64	2.61	6.84	231	0.9999	2.86
70 °C + 25 kHz 100 W	67.77	2.62	9.33	169	0.9999	5.26
70 °C + 25 kHz 300 W	67.69	2.73	14.20	111	0.9993	16.13
87	67.57	1.91	7.82	202	0.9995	10.59
87 °C + 25 kHz 100 W	67.67	1.92	10.90	145	0.9996	16.15
87 °C + 25 kHz 300 W	67.72	1.82	15.10	105	0.9999	21.66
92	67.65	1.72	8.28	191	0.9999	4.33
92 °C + 25 kHz 100 W	67.70	1.89	11.70	135	0.9996	11.62
92 °C + 25 kHz 300 W	67.72	1.80	17.50	90	0.9999	7.89
97	67.71	1.61	8.78	180	0.9999	5.82
97 °C + 25 kHz 100 W	67.76	1.62	12.60	125	0.9998	9.99
97 °C + 25 kHz 300 W	67.72	1.75	19.20	82	0.9998	12.52

RMSE (%) = Root mean square error: $100 * \sqrt{\frac{1}{n}\sum_{1}^{n}\left[(M_{exp} - M_{pre}) / M_{exp}\right]^2}$

With the aim of building a general model to describe chickpea hardness as a function of time and temperature, the estimated model parameters (F_o, F_e and k_F) were investigated (Table 4.5). Fitted curves for different soking temperatures (20-97 °C) are illustrated in Figure 4.14. The predicted values for both the initial hardness, F_o, and the equilibrium hardness, F_e, were in the ranges of 64.83-67.71 and 1.61-2.73 N for chickpeas over the range of 20-97 °C temperatures studied, respectively. In average, F_o and F_e values were 66.84(±1.14) and 2.09(±0.43) N for the same temperature range studied (20-97 °C). The experimental hardness (texture) of dry chickpea samples was measured as 67.73 N which is close to the predicted value (66.84 N).

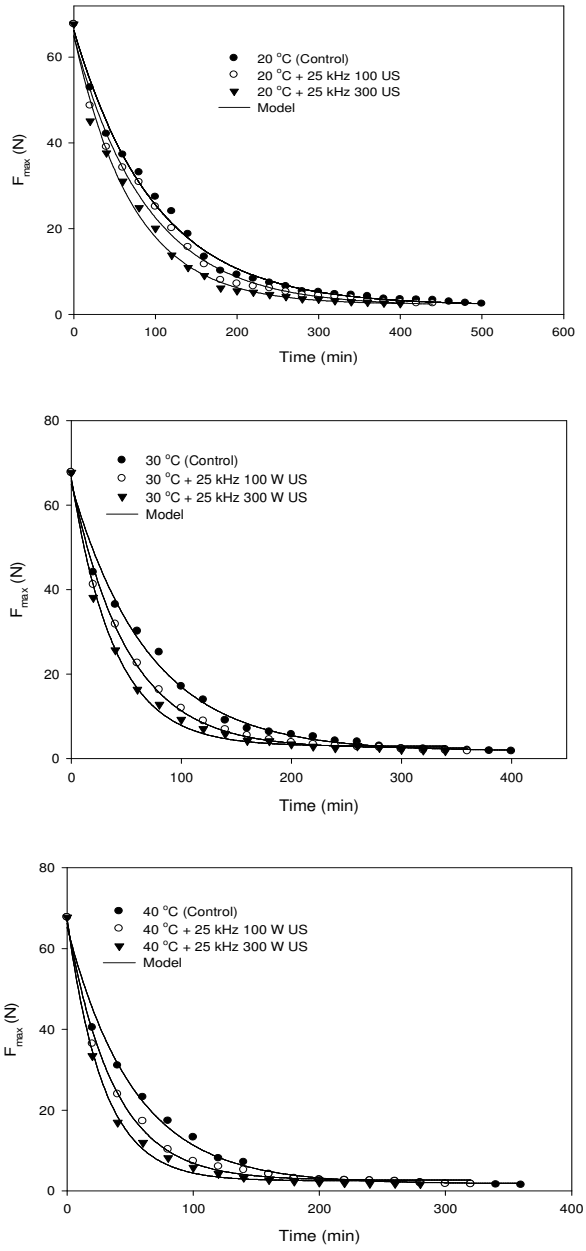


Figure 4.15. Average experimental and predicted F_{max} values from texture model relations to US and time for soaked chickpeas at 20, 30 and 40 ^{o}C

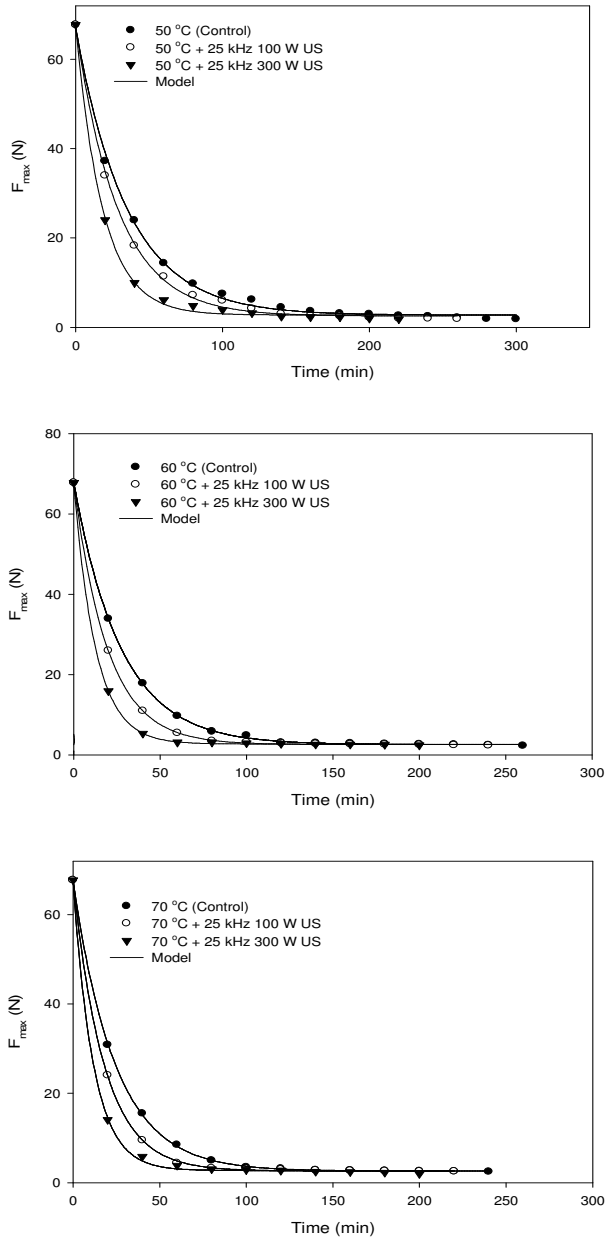


Figure 4.16. Average experimental and predicted F_{max} values from texture model relations to US and time for soaked chickpeas at 50, 60 and 70 ^{o}C

Increasing the soaking temperature caused an increase in k_F (s^{-1}). Increase in temperature from 20 to 97 ^{o}C increased in k_F value from $1.68x10^{-4}$ to $8.78x10^{-4}$ s^{-1} (Table 4.5 and Figure 4.14). Softening time of chickpea decreased as the soaking temperature was increased due to increase in k_F resulting more softening. Predicted time (t_e) values of chickpea taken to reach equilibrium texture level was decreased from 941 to 180 min when the soaking temperature was increased from 20 to 97 ^{o}C.

Increase in soaking temperature of chickpea from 20 to 60 ^{o}C decreased in t_e value from 941 to 260 min (681 min decrease). On the other hand, when soaking temperature was increased from 60 to 97 ^{o}C, t_e value decreased from 260 to 180 min (80 min decrease). So, soaking temperatures below gelatinization affected more than that of above gelatinization of chickpea. R^2 and RMSE (%) values were found as in a range of 0.9914-0.9999 and 2.86-19.19 (%) for chickpea soaked at 20-97 ^{o}C temperature range (Table 4.5).

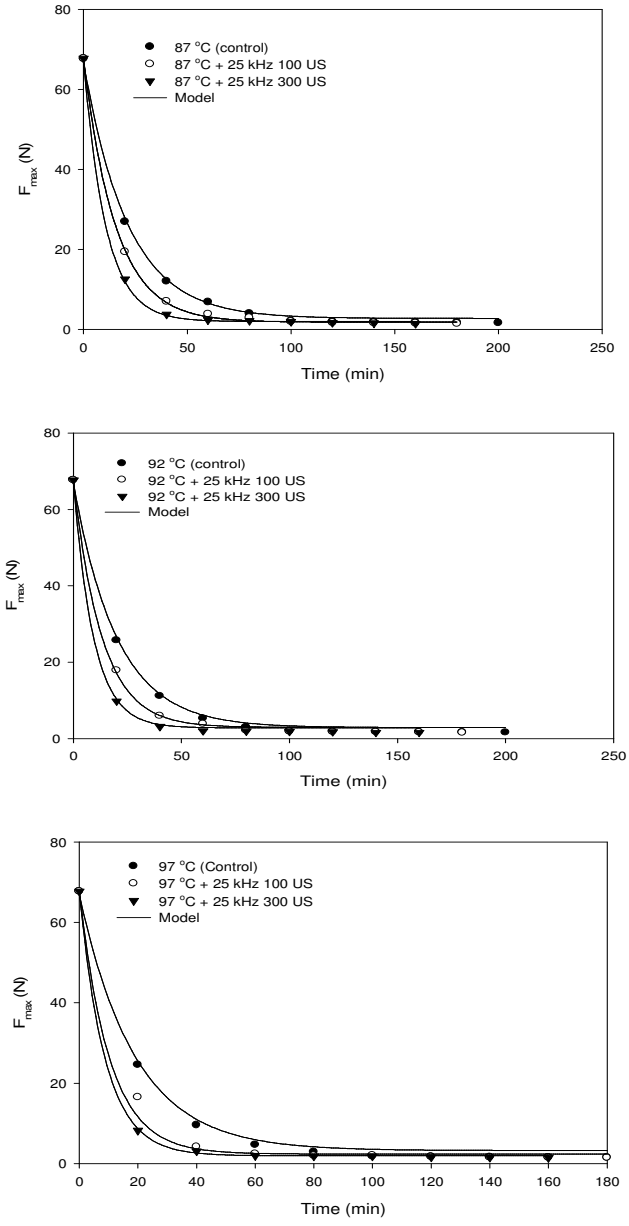


Figure 4.17. Average experimental and predicted F_{max} values from texture model relations to US and time for soaked chickpeas at 87, 92 and 97 ^{o}C

4.1.2.2. Modelling of chickpea hardness as a function of soaking time and temperature

The effect of temperature on texture of soaked chickpeas is illustrated in Figures 4.14, 4.18 and 4.19. As the soaking temperature was increased, the shape of curves was changed. Additionaly, in order to describe the dependence of chickpea hardness on temperature the Arrhenius equation can be proposed.

$$ln(k_F) = ln(k_{Fo}) - \frac{E_a}{R}\left(\frac{1}{T}\right) \quad (4.20)$$

Arrhenius plots of natural logarithm of the estimated value of k_F versus 1/T for chickpeas were shown in Figure 4.18. The slope of curve is related to the activation energy E_{a-F}, for the process of chickpea softening. For chickpeas, a break in the Arrhenius curve was apparent, after which the slope or activation energy changed. The regression analysis was performed and the equation of $\ln(k_F)$=2.1680-3186.3394*(1/T) was predicted for temperatures range of 20-60 ^oC with the coefficient of determination of 0.9963. Also, the equation for 60-97 ^oC temperature range was found as $\ln(k_F)$= -3.8856-1170.7331*(1/T) with R^2=0.9938. These equations were related to k_F and temperature. From the regression of these equations, the activation energies (E_a) for 20-60 and 60-97 ^oC temperature ranges were calculated as 26.49 and 9.73 kJ/mol, respectively.

In order to find where the break occurred, the natural log of k_F was fitted to a linear model with break point (Muggeo, 2003), and the break temperature (cooking temperature) was estimated to be 60 ± 1 ^oC ($R^2 \geq 0.9938$). This is in agreement with the break temperature estimated (61±0.75) for the water absorption models in section 4.1.1. Therefore, the change in chickpea water absorption was related to a change in the texture, as has been suggested in previously published data (Sayar et al., 2001; Goven et al., 2007).

When the texture model (Equation 4.19) was combined with Equation 4.20, the texture, time and temperature relation was derived:

For 20 -60 ^{o}C temperature range;

$$F = F_e + (F_o - F_e)exp\left[-\left(8.740exp\left(-3186.34 / T\right)t\right)\right] \quad (4.21)$$

and for 60-97 ^{o}C temperature range;

$$F = F_e + (F_o - F_e)exp\left[-\left(0.205exp\left(-1170.73 / T\right)t\right)\right] \quad (4.22)$$

These general models, incorporating constant F_o and F_e were proposed to describe the dependence of chickpea hardness on time and temperature. At any soaking temperature and time, the texture of chickpea during soaking can be found by these equations.

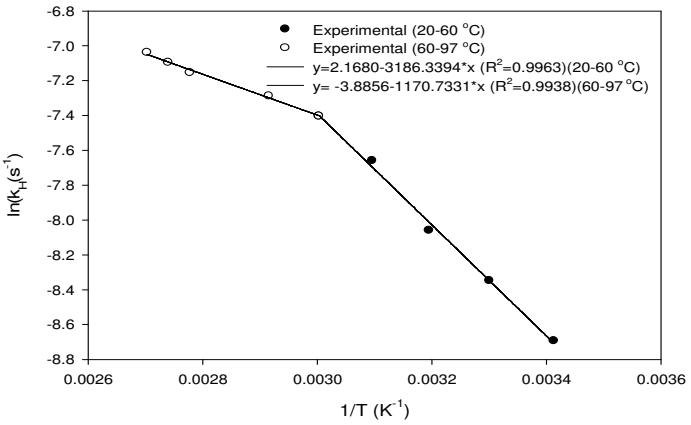


Figure 4.18. Arrhenius plot for texture degradation rate constant, k_F, over the temperature range 20–97 ^{o}C for chickpea soaking

4.1.2.3. Effect of ultrasounds on texture of chickpeas during soaking

In order to see the effect of ultrasound on chickpea softening, 25 kHz 100 W and 25 kHz 300 W ultrasounds were used for a temperature range of 20-97 ^{o}C. From the Tables A5-A9 and Figures 4.15-4.17 and 4.19, the application of US to chickpea during soaking significantly ($P<0.05$) decreased texture values (F_{max}, N) at all studied temperatures (20-97 ^{o}C). F_{max} (N) value at 20 ^{o}C and 120 min soaking of chickpea was found as 24.05 N. It's value decreased to 20.49 and 17.81 N with 25 kHz 100 W and 25 kHz 300 W US at the same temperature and time. A similar decrease in F_{max} (N) was observed for other temperatures and times. Ultrasound applied chickpeas also affect $F_{o,}$ F_e, k_F and t_e values. k_F value of chickpea increased from 1.68 x 10^{-4} to

1.89 x 10^{-4} (s^{-1}) with the application of 25 kHz 100 W US at 20 ^{o}C. When 25 kHz 300 W US was applied to chickpea during soaking, k_F values was changed from 1.68 x 10^{-4} to 2.36 x10^{-4} (s^{-1}) at the same soaking temperature (20 ^{o}C).

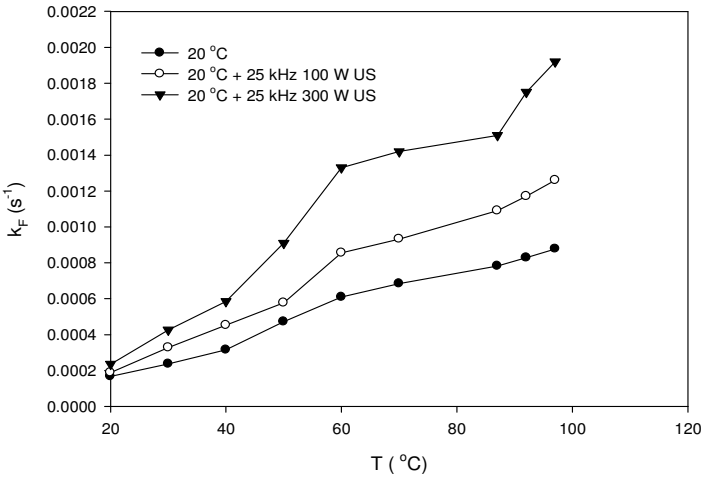


Figure 4.19. The effect of temperature (^{o}C) and ultrasound on texture rate constant k_F (s^{-1}) for chickpea soaking

The benefit of ultrasounds is evident from Tables A5-A9, Table 4.5 and Figures 4.15-4.17. For example, when 25 kHz 100 W US was applied to chickpea at 20 ^{o}C, time to reach the equilibrium texture (t_e) was 836 min, compared to 941 min for without US. This represents 105 min benefit for 25 kHz 100 W US application to chickpea soaking. At the same temperature (20 ^{o}C), when 25 kHz 300 W ultrasound was applied for soaking of chickpea, time (t_e) required to equilibrium texture value decreased from 941 to 670 min which represents 271 min benefit of soaking. The time required to equilibrium texture (t_e) of chickpea also decreased for other temperatures when US applied during soaking. 25 kHz 100 W and 25 kHz 300 W US applied chickpea during soaking at 30 ^{o}C represented 187 and 296 min benefits. t_e value at 87, 92 and 97 ^{o}C without US was found as 202, 191 and 180 min, respectively. When 25 kHz 100 W US was applied, time required to reach equilibrium texture (t_e) decreased to 145 (57 min decrease), 135 (56 min decrease) and 125 (55 min decrease) min at the same soaking temperature (87, 92 and 97 ^{o}C), respectively. t_e value for 25 kHz 100 W was applicated chickpea during soaking at 87, 92 and 97 ^{o}C decreased from 202 to 105 min, 191 to 90 min and 180 to 82 min. As a result, application of ultrasounds increased in k_F values and decreased in F_{max}

and t_e values. The effect of US at low temperatures was higher than at high temeratures. Furthermore, high power US such as 300 W affected texture more than low power (100 W) US.

4.2. Cooking of Chickpea

Cooking is usually done before the use of legumes in human diet. This improves the protein quality by destruction or inactivation of the heat labile antinutritional factors. However, cooking causes considerable losses in soluble solids, especially vitamins and minerals. Cooking time and temperature are the main parameters that affect the penetration of water into kernel. Determination of the cooking mechanism and the prediction of the dimensional changes of kernal are essential for the control of the operation. Long cooking times use more fuel and cause losses of nutrient, limiting the use of the dry grain as a food in developing countries (Barampama and Simard, 1995; Uzogara et al., 1992). Food legumes are usually cooked either by simple boiling or in a pressure cooker. The literature is replete with reports that simple boiling improves the nutritional quality of food legumes due to reduction in antinutrients. In fact, cooking of food legumes is related to heating temperature and time, initial moisture and amount of water added during the cooking process. Like other pulses, chickpeas contain several antinutritional factors (α-galactosides, trypsin inhibitors, tannins, etc.) which may limit their consumption and the nutritive utilization of their protein. These antinutritional factors can be eliminated or reduced by cooking or with other simple technologies. These changes differ widely depending on the technology and conditions involved (Nestares et al., 1993a).

Cooking operation in this study was made without presoaking process. The effect of ultrasonics (25 kHz 100 W and 25 kHz 300 W) on cooking operation was searched at different times and temperatures (87, 92 and 97 ^{o}C). The leaching characteristics of chickpea during cooking was analysed by turbidity (absorbance at 500 nm), electrical conductivity (mS/cm) and color values (L^*, a^* and b^*). Also, the degree of cooking of chickpea starch was investigated using DSC, unreacted-core, electrical conductivity and birefringes images methods.

4.2.1. Effect of cooking on leaching characteristics of chickpea

4.2.1.1. Effect of time, temperature and ultrasounds on electrical conductivity of cooking water of chickpeas

Electrical conductivity in water is affected by the presence of inorganic dissolved solids (electrolytes) such as chloride, nitrate, sulphate, and phosphate anions (ions that carry a negative charge) or sodium, magnesium, calcium, iron, and aluminium cations (ions that carry a positive charge). Organic compounds like oil, phenol, alcohol, and sugar do not conduct electrical current very well and therefore have a low electrical conductivity in water. The major mineral components of chickpea are potassium, sodium, calcium, magnesium, sulphur, phosphorus, iron, cupper and zinc (Synder and Kwon, 1987; Singh et al., 1991).

The electrical conductivity of cooking water of chickpea at temperatures of 87, 92 and 97 ^{o}C without (w/o) and with (w/) 25 kHz 100 - 300 W ultrasounds are given in Tables A10-A11 and Figure 4.20. It was measured in mS/cm (millisiemens/cm). For electrical conductivity measurement, the deionized water was used as a reference. The electrical conductivity of deionized water was 1.6 µS/cm. The statistical results (Duncan test) of electrical conductivity values were also given in Tables A10-11. Cooking time, temperature and US application significantly ($P<0.05$) affected the electrical conductivity of chickpea during cooking (Tables A10-11 and Figure 4.20).

Increase in cooking temperature (87 to 97 ^{o}C) of chickpea significantly ($P<0.05$) increased electrical conductivity due to dissolved solids and electrolytes. As the cooking temperature was increased from 87 to 97 ^{o}C for 20 min cooking, the electrical conductivity of cooking water was increased from 1.66 (±0.06) to 2.78 (±0.04) mS/cm which provided a % 67.5 increase (Table A10 and Figure 4.20). When the cooking temperature was increased from 87 to 97 ^{o}C for 120 min of cooking, the electrical conductivity of cooking water increased from 3.97 (±0.06) to 4.32 (±0.08). Increase EC (mS/cm) at this temperature range was % 9. Similarly, increase in temperature increased EC for other cooking times. Furthermore, increase in cooking time increased electrical conductivity of chickpea due to dissolving leaching materials to cooking water. When the cooking time of chickpea increased from 20 to 280 min, the electrical conductivity value increased from 1.66 (±0.06) to 4.82 (±0.05) mS/cm at 87 ^{o}C. Similarly, EC of chickpea at 92 and 97 ^{o}C was

increased from 1.98 (±0.04) to 5.09 (±0.06) and from 2.78 (±0.04) to 5.46 (±0.07) mS/cm as cooking time was increased from 20 to 260 min, respectively. Increase in soaking times decreased % change of electrical conductivity values. When cooking time increased from 20 to 260 min for a temperature range of 87-97 ^{o}C, % change in electrical conductivity decreased from 67.50 to 9.00. But, it increased at a higher rate up to 100 minutes of cooking. The rate of increase in electrical conductivity at higher cooking times was lower than that of low ones (Figure 4.20).

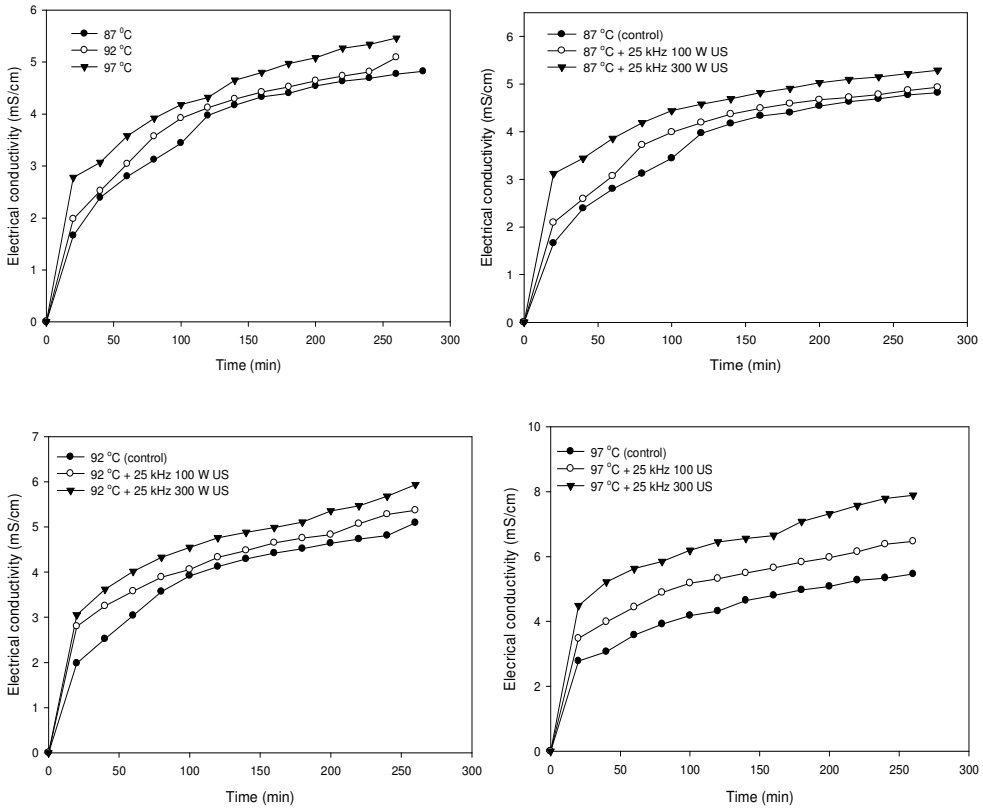


Figure 4.20. Change in electrical conductivity values (mS/cm) of cooking water of chickpea at 87, 92 and 97 ^{o}C without and with US

When ultrasounds was applied to chickpeas during cooking, the electrical conductivity (mS/cm) increased significantly ($P<0.05$) (Table A11 and Figure 4.20). At constant temperature (87 ^{o}C) and 80 min, electrical conductivity of cooking water was increased from 3.12 to 3.72 mS/cm (%19.23 increase) when 25 kHz 100 W ultrasound applied. At the same temperature and cooking time of chickpeas, 25 kHz 300 W ultrasound application increased electrical conductivity of cooking water from 3.12 to 4.19 mS/cm (%34.30 increase) (Table A11 and Figure 4.20). Increase in

power of ultrasound (from 100 to 300 W) also increased the electrical conductivity of cooking water of chickpea (i.e. 3.72 to 4.19 mS/cm (% 12.63 increase) at 80 min cooking). A similar increase was observed for 300 W ultrasounds application at 92 and 97 ^{o}C. So, the application of ultrasound and increase in power of ultrasound increased electrical conductivity of cooking water due to leaching of the electrolytes (potassium, sodium, calcium, magnesium, sulphur, phosphorus, iron, cupper and zinc). Because, ultrasound is of great help in the pre-treatment of solid samples, as it facilitates and accelerates operations such as the extraction of organic and inorganic compounds due to cavitation effect on chickpea (Luque-Garcia and Luque de Castro, 2003).

4.2.1.2. Effect of time, temperature and ultrasounds on turbidity (absorbance at 500 nm) of cooking water of chickpeas

Turbidity of the water is an important parameter for cooking operation. Measured absorbances at 500 nm were used to determine the turbidity level. Turbidity can be caused by compounds (e.g. organic compounds, pigments, protein, sugars, starch, vitamins etc.) leaching into the water during cooking. The turbidity of blank (deionized water) used in cooking operation was 0.019 (absorbance at 500 nm). The turbidity results of cooking water at 87, 92 and 97 ^{o}C without and with ultrasounds of 25 kHz 100 and 300 W as a function of cooking time are given in Tables A10-11 and Figure 4.21. Tables A10-A11 and Figure 4.21 showed that cooking time, temperature, ultrasounds and power of ultrasounds significantly ($P<0.05$) effect and increased the turbidity of cooking water.

The change in absorbance at low temperature (87 ^{o}C) was less than at high temperatures due to the lower temperature effect on leaching. Increase in turbidity of cooking water of chickpeas increased the leached materials (minerals and organic compounds) due to cooking operation.

Figure 4.21 shows the effect of ultrasounds on turbidity of cooking water of chickpeas. As the cooking time was increased, the turbidity of cooking water was increased for 87-97 ^{o}C temperatures. The power of ultrasounds (100-300 W) was also increased the turbidity of cooking water for all temperatures and times (Figure 4.21). According to these results, inorganic dissolved solids such as chloride, nitrate,

sulphate, phosphate, sodium, magnesium etc. could have leached into the cooking water. Ultrasounds increased the turbidity of cooked chickpea water due to effect of cavitation of US.

The increase in turbidity value of cooking water of chickpea resulted from gelatinised starch may be attributed to leaching of amylose and amylopectin chains for functional zones (Perera and Hoover, 1999), also starch. Legume starch contains varying amount of phosphate monoester derivatives, which result in increased turbidity (Jane et al., 1996).

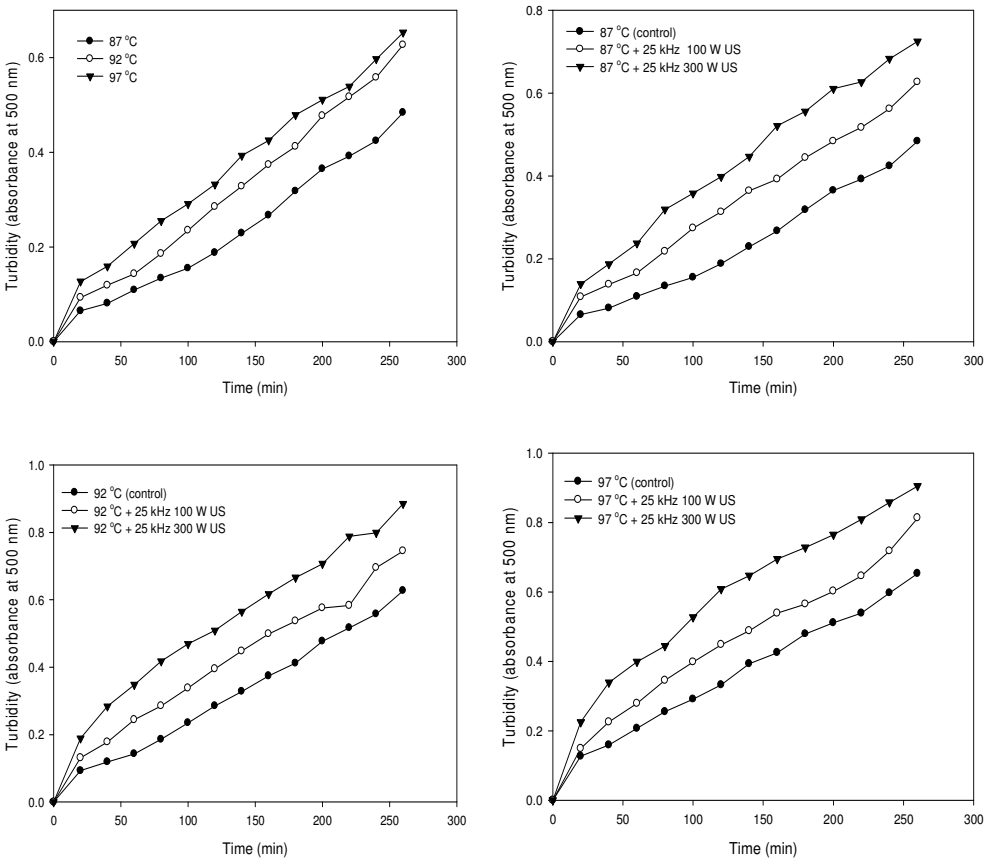


Figure 4.21. Change in turbidity values (Absorbance at 500 nm) of cooking water of chickpea at 87, 92 and 97 °C without and with US

4.2.1.3. Effect of time and temperature on colour values (L^*, a^* and b^*) of cooking water and chickpea seeds during cooking

Processing steps affect the color of chickpea. In order to examine the color of the cooking water and chickpea seeds, and also effect of the temperature, time and US,

colors of soaking water and chickpea were measured during cooking operation in present study.

Periodicaly (20 min) 120 ml of cooking water was removed, cooled to room temperature (25 ^{o}C), and measured the color values (L^{*}, a^{*} and b^{*}) at each cooking temperature. The results and relations to cooking time at each cooking temperature are given in Table A12 and Figure 4.22.

Increase in cooking temperature and time significantly ($P<0.05$) increased in L^{*}(lightness) value of cooking water due to leached materials especially chickpea starch. Starch content of Kabuli and Desi cultivars of chickpea has been reported to be 42.1 and 45.2 %, respectively (Meares et al., 2004). Starch content of chickpea reported in the study of Chavan et al. (1986) was 55.3–58.1% of the dehulled seed and in study of Jood et al. (1998) was 48-53% for Kabuli and 55-58% for Desi cultivar. L^{*}-value of 0.1%, 1% and 2% of extracted both raw and cooked chickpea suspensions in this study were measured as 14.67, 46.14, 61.16 and 8.17, 42.44, 55.48, respectively. Therefore, during cooking of chickpea starch might be leached to cooking water and enhanced to increase in L^{*}-value.

Increase in cooking temperature from 87 to 97 ^{o}C at constant 120 min increased in L^{*} values (Lightness) of cooking water from 4.97 to 6.48 (Table A12 and Figure 4.22). The L^{*} value at 87 ^{o}C increased from 2.06 to 10.44 during 260 min cooking. Same trend was observed for 92 and 97 ^{o}C that it reached to 10.70 and 10.85 during 260 min cooking. But, increase in cooking time (0 to 260 min) and temperature (87 to 97 ^{o}C) decreased ($P<0.05$) L^{*}-value of chickpea seeds in contrast to L^{*} value of cooking water (Table A12 and Figure 4.22). Increase in cooking time from 0 to 260 min decreased lightness (L^{*}) of chickpea from 55.43 (L^{*}-value of uncooked chickpea) to 46.72 at 97 ^{o}C.

The change in a^{*}-value of cooking water and chickpea seeds for different time and temperatures are illustrated in Figure 4.22. The summary of multiple range analysis of time and temperature (Duncan test) for a^{*}-value is also given in Table A12. Increase in cooking time and temperature affected a^{*}-value of cooking water and chickpea seeds. Increase in cooking time of chickpea from 20 to 260 min at 87 ^{o}C

changed a^*-value from -0.40 to 0.71. This means that color of cooking water was changed from green to red color. Green color of water resulted from disolving of chlorophyll from chickpea seed to water phase. After 220 min cooking at 87 ^oC, the color of cooking water was changed from green to red (-0.40 to 0.71) due to propably more carotenoids destruction. Similarly, the values of a^* were changed from -0.36 to 0.08 in 160 min at 92 ^oC and from -0.52 to 0.15 in 140 min at 97 ^oC, respectively (Table A12). The color of cooking water was green ($-a^*$) due to leaching of chlorophyll pigments at the beginning of cooking operation while it changed to red ($+a^*$) at the end of cooking due to destruction of carotenoids (Table A12). Increase in cooking time (20 to 260 min) and temperature (87 to 97 ^oC) also increased a^*-value from 10.23 to 11.85 and from 10.06 to 12.89 of chickpea seed due to browning and caramelization reactions ocured in chickpea (Table A12 and Figure 4.22).

b^*-value of cooking water of chickpea was also changed during cooking at different time and temperatures. From Table A12 and Figure 4.22, increase in cooking time significantly ($P<0.05$) increased b^*-value of cooking water of chickpea. The b^*-value of cooking water increased from 1.19 to 2.02 as the cooking time was increased from 20 to 260 min at 87 ^oC. Similarly, at 92 and 97 ^oC cooking temperatures, increase of cooking time increased the b^*-value of cooking water of chickpea. Additionaly, increase in cooking temperature from 87 to 97 ^oC increased b^*-value of cooking water. When the temperature was increased from 87 to 97 ^oC for 160 min cooking, b^*-value of cooking water increased from 3.30 to 6.37. A similar increase was observed for other cooking times.

Increase of time and temperature of cooking also increased b^*-value of chickpea seed. The b^*-value (yellowness) of chickpea increased slightly during cooking and was affected by cooking time and temperature, significantly ($P<0.05$) (Table A12 and Figure 4.22). Increase in b^*-value might be explained as the degradation of red pigments into yellow color and yellowish pigments and vitamins participate in chickpea. b^*-value of chickpea seed had a maximum value at 97 ^oC (31.03). This can be explained as the effect of temperature on the gelation of the protein at 87, 92 and 97 ^oC and it might affect the appearance and firmness or existence of the degradation of yellowish pigments at this temperature, proportionally.

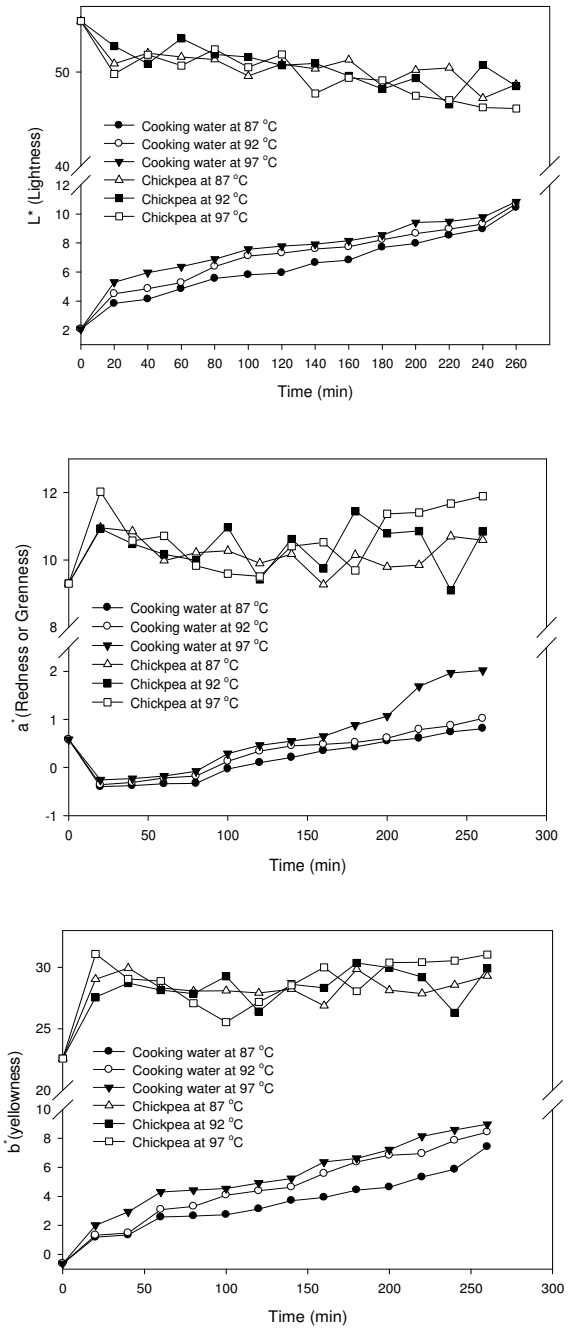


Figure 4.22. Change in L^*, a^* and b^* values of cooking water and chickpea at 87, 92 and 97 ^oC for different cooking times

The b-values were determined as positive which means that yellowness was present in chickpea and cooking water (Table A12). At the end of the cooking, yellowness (b^*) of cooking water was 7.42, 8.13 and 8.27 at 87, 92 and 97 ^oC, respectively. At

high temperatures (97 ^{o}C), high yellowness was observed. Increase in yellowness can be explained as the leaching of yellow color pigments and vitamins by the effect of temperature during cooking. Increase in yellowness correlated with the leaching of other coloring compounds and loss of the greenness in soaking water (Table A12).

Additionally, carotenoids (nearly red pigment, nonpolar water-insoluble) that are found in chickpeas were not solubilized in cooking water at the early cooking times (e.g., 220 min at 87 ^{o}C) to water-solubilized green pigments and their derivatives. Pigment decomposition and loss of this color degree were also correlated with the decreasing redness level in chickpea during cooking.

Somiari and Balogh (1993), Akinyele and Akinlosotu (1991) and Han and Baik (2006) reported that change in color value (L^*, a^* and b^*) of chickpea during soaking and cooking was due to dissolved solids and oligosaccharides such as verbascose, raffinose and stachyose. All color values of cooking water and chickpea (L^*, a^* and b^* values) were affected by time and temperature. Leaching and water absorption occurred simultanously where leaching and cooking increased with increase in time and temperature. So, water transferred through the chickpea dissolves the solute carries it into the bulk solution.

4.2.1.4. Effect of ultrasounds on colour values (L^*, a^* and b^*) of cooking water and chickpea seeds during cooking

The summary of multiple range analysis (Duncan test) of color values (L^*, a^* and b^*) of cooking water and chickpea seeds relation to time and ultrasounds are given in Tables A13-A15. The color values (L^*, a^* and b^*) without US for each cooking temperatures were used as control values. The change of color values both for cooking water and chickpea seeds with respect to time and ultrasounds are also illustrated in Figures 4.23-4.25. The color values (L^*, a^* and b^*) of ultrasound (25 kHz 100 and 300 W) applied chickpea seeds and cooking water were changed as the time and temperature were increased. Increase of the power of ultrasounds (100 to 300 W) also changed the color values (Tables A13-A15 and Figures 4.23-4.25).

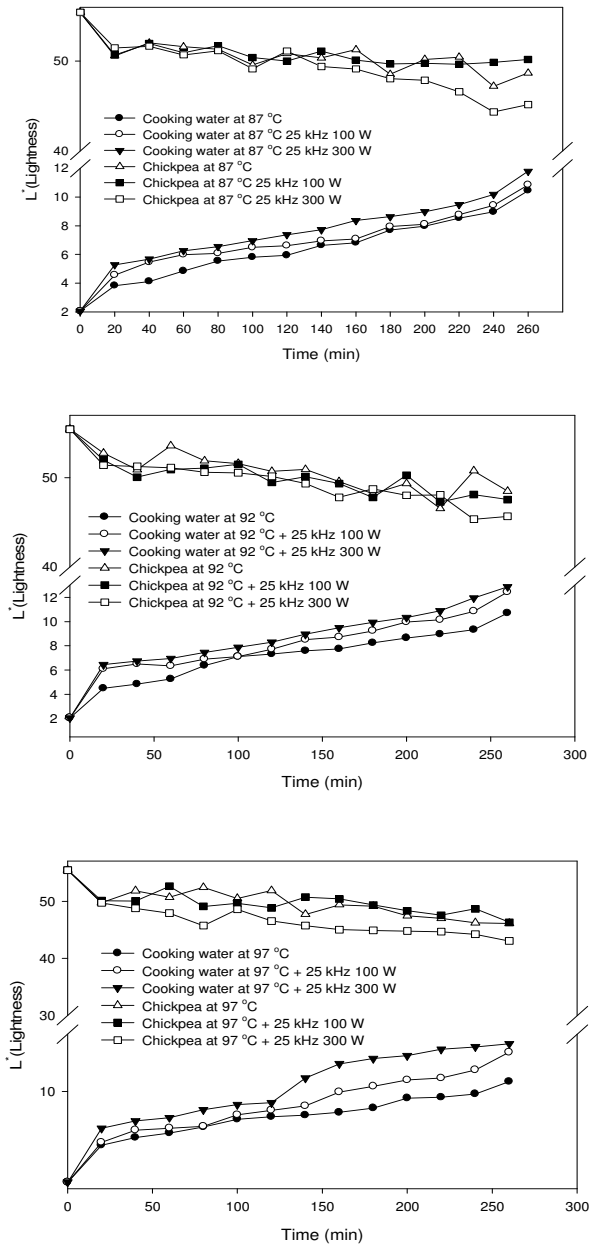


Figure 4.23. Change in L^* (Lightness) values of cooking water and chickpea at 87, 92 and 97 °C without and with US for different cooking times

L^* (lightness) value of cooking water between 0 and 260 min at 87 °C without US was changed from 2.06 to 10.44. The values increased to 10.84 for 25 kHz 100 W and 11.79 for 25 kHz 300 W (Table A13 and Figure 4.23). Similar increase in L^* value was observed at 92 and 97 °C tempearures with US (Table A13 and Figure 4.23). Also, L^* value of chickpea seed was effected by US. At 87 °C and 260 min

cooking, the lightness (L^*) of chickpea without and with 25 kHz 100-300 W ultrasounds was found as 48.67, 50.17 and 45.15, respectively (Table A13 and Figure 4.23). For other temperatures (92 and 97 ^oC) similar change was found when ultrasounds were applied to cooking chickpeas (Table A13 and Figure 4.23).

When 25 kHz 100 W and 25 kHz 300 W US were applied to cooking chickpea at 87, 92 and 97 ^oC, a^*-value of both cooking water and chickpea seeds were also changed (Table A14 and Figures 4.24). Increase in cooking time significantly ($P<0.05$) increased a^*-value of cooking water and chickpea seed. a^*-value of cooking water of chickpea without, with 25 kHz 100 W and 25 kHz 300 W US was changed from -0.40 to 0.61, -0.29 to 0.70 and -0.73 to 1.99 for a cooking time range of 20-260 min at 87 ^oC. After 220 min of cooking with 25 kHz 100 W US at 87 ^oC, the color of cooking water changed from green to red (-0.29 to 0.70) due to leaching of carotenoids. Furthermore, application of 25 kHz 300 W US at 87 ^oC cooking, the color of cooking water changed to red ($+a^*$, 0.37) after 80 min while 200 min for control (without US). Similarly, at 92 and 97 ^oC cooking with 25 kHz 100 W and 25 kHz 300 W, at the begining of cooking period, the color of cooking water was green ($-a^*$). It changed to red ($+a^*$) at 120 and 100 min cooking for 25 kHz 100 W and 25 kHz 300 W US at 92 ^oC, respectively. The green color value ($-a^*$) change of cooking water was found as 100 and 40 min for 25 kHz 100 W and 25 kHz 300 W US at 97 ^oC, respectively. Also, a^*-value of US applicated chickpea similar to controls (without US) during cooking was red ($+a^*$) and increased as the cooking time was increased at all cooking temperatures due to browning reactions and starch gelatinization.

As a conclusion, a^*-value of cooking water and chickpea for each cooking time changed significantly ($P<0.05$) when 25 kHz 100 W and 25 kHz 300 W US was applied to chickpea at cooking temperatures studied (87, 92 and 97 ^oC) (Table A14 and Figur 4.24).

Thermosonication significantly ($P<0.05$) affected b^*-value of cooking water and chickpea seeds (Table A15 and Tables 4.25). Increase in soaking time range of 0-260 min increased b^*-value (yellowness) of cooking water from -0.63 (blueness) to 6.58 and 9.97 for both 25 kHz 100 W and 25 kHz 300 W US treated samples, respectively (Figure 4.25). Similarly,

b^*-value of cooking water for different US powers at 92 and 97 ^oC increased as the cooking time increased (0 to 260 min) (Figure 4.25).

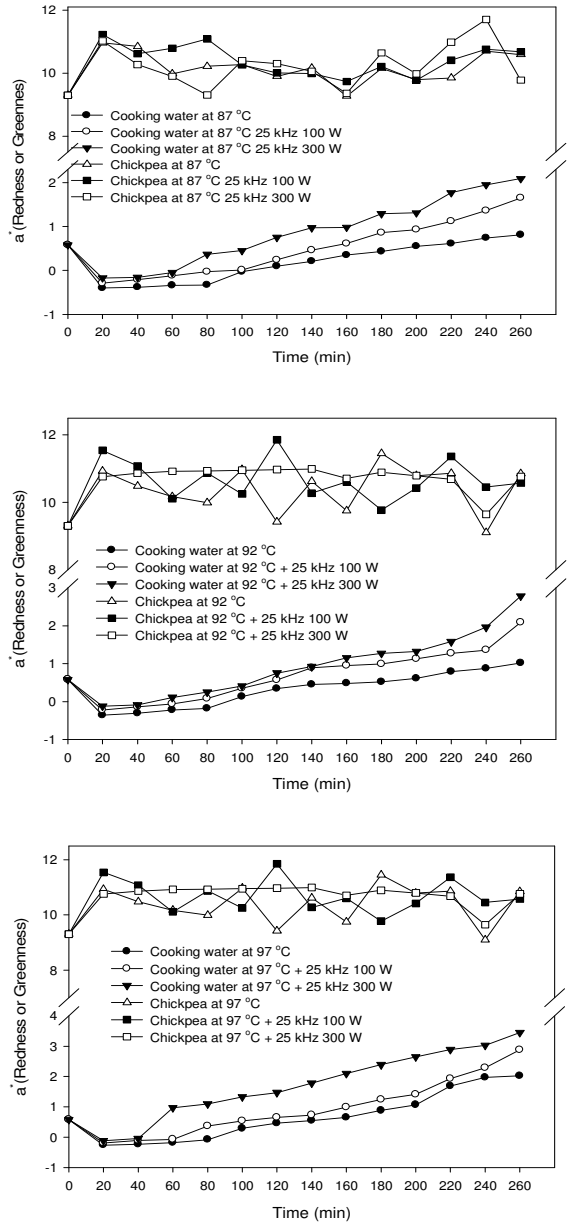


Figure 4.24. Change in a^* (redness, greenness) values of cooking water and chickpea at 87, 92 and 97 ^oC without and with US for different cooking times

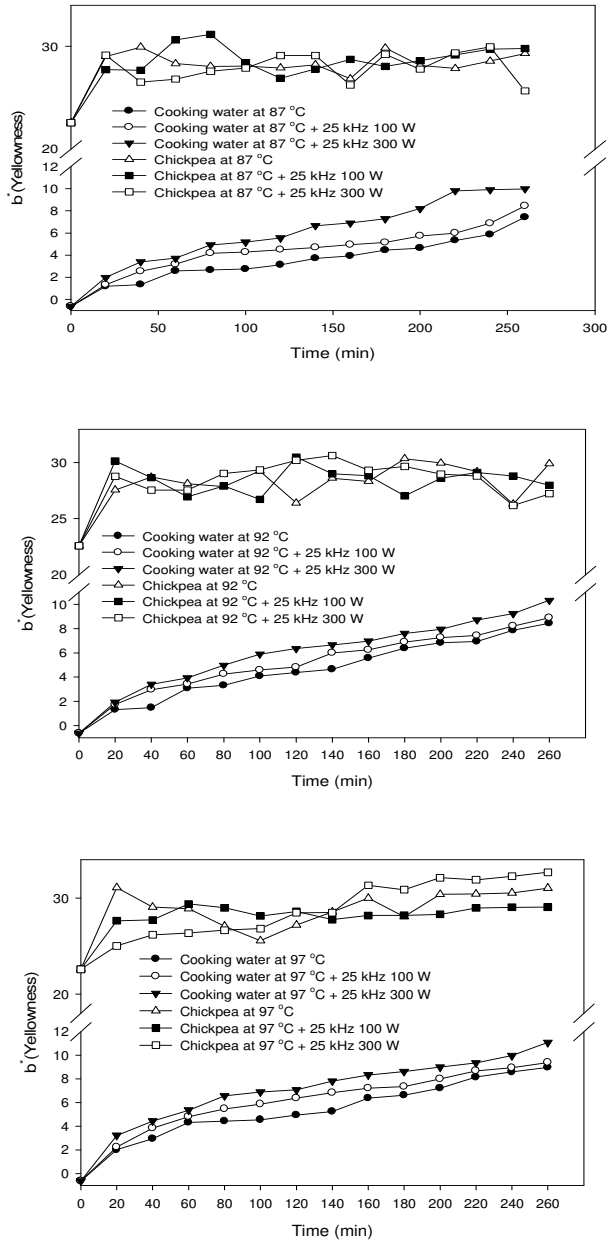


Figure 4.25. Change in b^* (yellowness) values of cooking water and chickpea at 87, 92 and 97 °C without and with US for different cooking times

Both 25 kHz 100 W and 25 kHz 300 W US application increased yellowness (b^*) value of cooking water at 87, 92 and 97 °C. For example, for 140 min cooking at 87 °C, b^*-value of cooking water increased from 3.21 to 4.69 and 6.65 when the values without US was compared with 25 kHz 100 W and 25 kHz 300 W US applications (Table A15 and Figure 4.25). A similar increase was observed for 92 and 97 °C with

US applications (25 kHz 100-300 W) (Table A15 and Figure 4.25). The application of 25 kHz 100 and 25 kHz 300 W US also increased b^*-value of chickpea seeds as the cooking time increased. So, both 25 kHz 100 W and 25 kHz 300 W US applications affected the b^*-value of chickpea seeds as irregularly.

Ultrasound application and increase in power of ultrasounds both affected the color values of chickpea and cooking water. Change of color values might be due to mass transfer (leaching) (Carcel et al., 2007a; Sanchez et al., 1999; Simal et al., 1998a; Carcel et al., 2007b; Romdhane and Gourdon, 2002; Fuente et al., 2004; Riera et al., 2004; Han and Baik, 2006; Wambura et al., 2008) and some reactions such as browning reactions. Also, Cheng et al. (2004) reported that lightness of seed color (L* value) of pea seeds exhibited increasing during soaking/cooking. Yellowness (b*) value of the seeds also increased at higher rates in wet conditions. These results indicated that the presence of water increase lightness and the yellow color of seeds and decreases greenness and chlorophyll content.

4.2.2. Change in degree of cooking of chickpeas

Legume seeds require a relatively long cooking time. Chickpea without pre-soaking operation has a cooking time of 300 min at 98 ^oC (Sabapathy, 2005). The cooking time of legumes depends primarily on the softness of the cooked seeds. Gelatinization (cooking) can be achieved in water or steam above gelatinization (cooking) temperature (T_{gel}) and a certain water content (M_{gel}) whose values vary depending on the source of the starch (Hoseney, 1994). Gelatinization (cooking) can be described as a sequence of changes in starch granules upon heating: starch granules first absorb large amounts of water, then swell many times their original size, and finally, their starch components are leached (Lund, 1984; Mc Williams, 1989; Zallie 1988).

Cooking (gelatinization) of starch is the disruption of molecular order within granules (BeMiller and Whistler, 1996; Holm et al.,1988). Extensive heating in excess water causes swelling and then rupture of starch granules, loss of crystallinity and release of soluble material from the granules (Chinachoti et al., 1990). Several methods can be used to follow the cooking process, for instance granule swelling, water holding capacity (Pinnavaia and Pizzirani, 1998), solubility, viscosity

(Sandstedt et al., 1960), birefringence (Leach, 1965), nuclear magnetic resonance (NMR) (Mendes da Silva et al., 1996), X-ray diffraction patterns (Collison, 1968), Differential Scanning Calorimetry (DSC) (Holm et al., 1988; Marshall et al., 1993), electrical conductivity, enzymatic susceptibility (Sullivan and Johnson, 1964; Chaiwanichsiri et al., 2001), amylose/iodine method (Birch and Priestly, 1973) and unreacted-core model (Sayar et al., 2003 and Suzuki et al., 1977).

In order to analyse the degree of cooking of chickpea during cooking, birefringes images, DSC, unreacted-core model, electrical conductivity of chickpea seed (a new method) and electrical conductivity of cooking water methods were used. Also, electrical conductivity of cooking water method (like ohmic heating) was compared with other methods.

4.2.2.1. Degree of cooking using birefringes images (BI) method

Starch is a semi-crystalline material. When it was viewed in polarized light microscope, starch granules show birefringes or typical maltase crosses. Some researchers used birefringence images method to find the degree of cooking and cooking times of foods (Sayar et al., 2001; Sayar et al., 2003; Sağol et al., 2006; Baks et al., 2007). Degree of cooking was found using birefringence images and maltase crosses of starch in chickpea with Polarized-light microscope at 87, 92 and 97 ^{o}C for without and with US by evaluating with Eq.4.23 (Table A16 and Figures 4.26-4.28).

Degree of cooking could be evaluated by the following equation;

$$DC(\ \%\ ) = \frac{(N_o - N_t)}{N_o} * 100 \qquad (4.23)$$

where, N_o and N_t are numbers of maltase crosses at initial (Uncooked chickpea) and any cooking time. Typical behavior of maltase crosses for different times at 92 ^{o}C are shown in Figure 4.27. As expected, all the starch granules of the raw chickpea sample displayed a clear maltase cross under polarized light due to the ordering in the granule on the length scale of the wavelength of light (approximately 500 nm) (Lelievre, 1974; Waigh et al., 2000). The average numbers of maltase crosses of raw chickpeas (N_o) was found as 146 (±18.84). The average experimental numbers of maltase crosses (N_t) at different cooking times for 87, 92 and 97 ^{o}C are given in

Table A16. Increase in cooking time decreased the numbers of maltase crosses and increased the cooking percentage (%). The all of the starch granules (100 %) of the cooked chickpea sample retained their birefringence properties at 280, 240 and 200 min cooking at 87, 92 and 97 ^{o}C, respectively (Tables A16, 4.6 and Figure 4.26). The relation of τ (cooking time) and cooking temperature was found as $\tau = -8T + 976$ (R^2=1).

The cooking time of chickpea in this study by use of birefringes images were found as 280, 240 and 200 min at 87, 92 and 97 ^{o}C (Table 4.6). Sayar et al. (2003) reported that the cooking times of chickpea were found as 235, 175 and 125 min at 80, 90 and 100 ^{o}C, respectively. Also, Sabapathy (2005) have found a cooking time of 300 min for pre-unsoaked chickpea at 98 ^{o}C. So, the cooking times in previous studies confirm the values of present study.

The effect of US on degree of cooking is illustrated in Figure 4.28. When the numbers of maltase crosses and the degree of cooking of control (without US) at each temperature was compared with 25 kHz 100 W and 25 kHz 300 W, it can be seen that the degree of cooking at each cooking time increased while the numbers of maltase crosses decreased (Table A16 and Figure 4.28).

Table 4.6. Cooking times of chickpea found using birefringes images at different temperatures without and with US

Process	**Cooking time, τ (min)**
87 ^{o}C	280
87 ^{o}C 25 kHz 100 W	240
87 ^{o}C 25 kHz 300 W	200
92 ^{o}C	240
92 ^{o}C 25 kHz 100 W	200
92 ^{o}C 25 kHz 300 W	160
97 ^{o}C	200
97 ^{o}C 25 kHz 100 W	160
97 ^{o}C 25 kHz 300 W	120

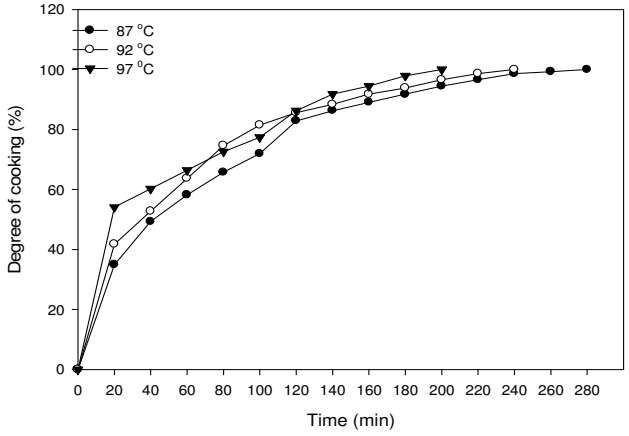


Figure 4.26. Degree of cooking (DC, %) by birefringes images of cooked chickpeas at 87, 92 and 97 ^{o}C

When 25 kHz 100 W and 25 kHz 300 W US was applied to chickpea during 20 min cooking at 87 ^{o}C, the numbers of maltase crosses was decreased from 95±4.75 (control) to 83±7.85 and 54±12.27, respectively. The degree of cooking of US applications for the same cooking time and temperature found from Equation 4.23 was 34.93 (control), 43.15 and 63.01 %, respectively. A similar decrease in numbers of maltase crosses and increase in DC (%) were found for other cooking times with US. Application of US (25 kHz) and increase in power of US (100 to 300 W) of cooked chickpea both increased DC (%) values.

The application of 25 kHz 100 W US to chickpea at 87, 92 and 97 ^{o}C decreased cooking times from 280 to 240 min, 240 to 200 min and 200 to 160 min, respectively. Similarly, the cooking time of chickpea decreased to 200, 160 and 120 min with the application of high power US (25 kHz 300 W) for 3 cooking temperatures, respectively. At all temperatures without and with US, the degree of cooking and cooking time relationship was similar to sigmoidal (Figures 4.26 and 4.28). The cooking time (τ) of chickpea decreased with US application (Table 4.6).

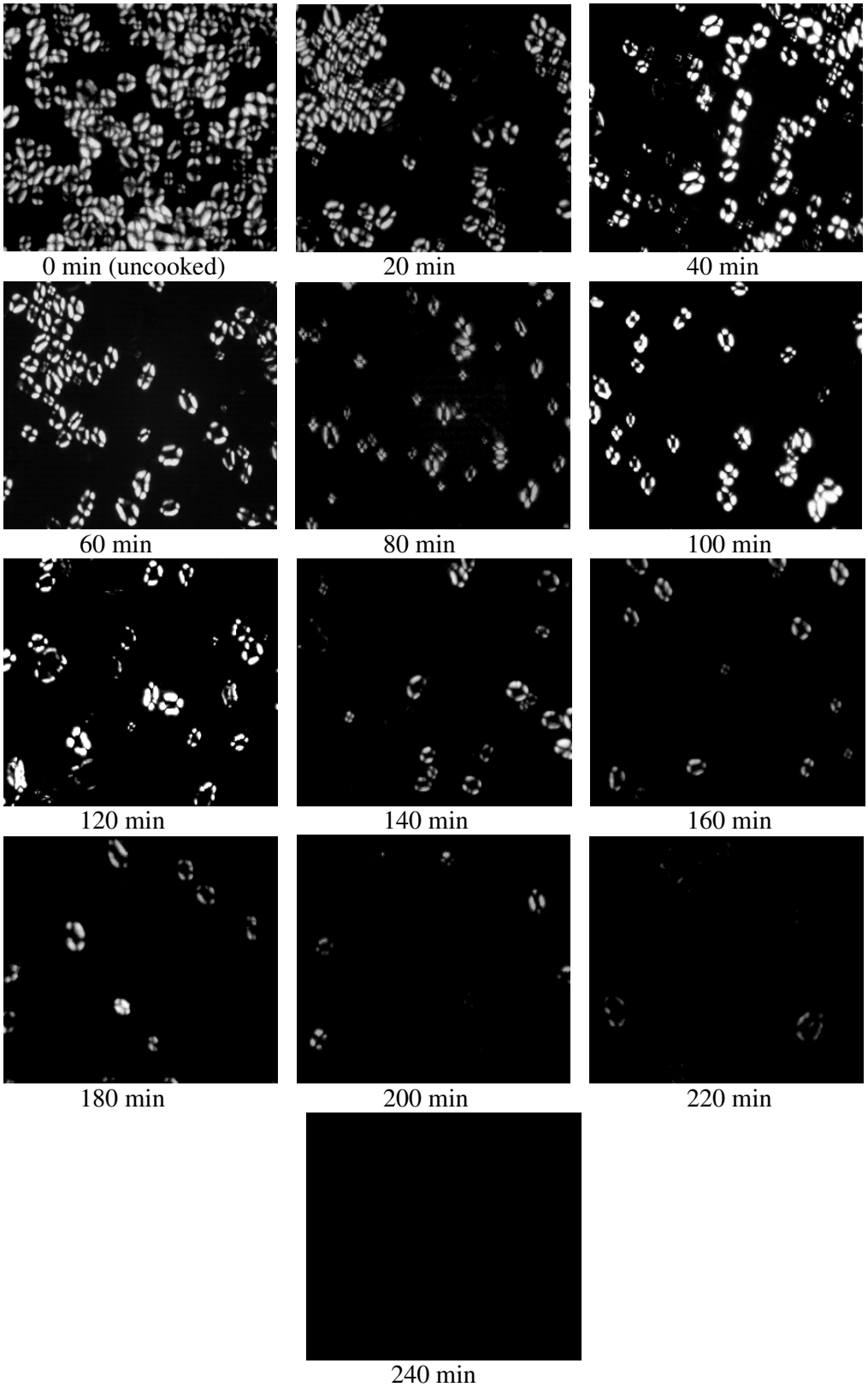


Figure 4.27. Typical behavior of maltase crosses (Polarized-light micrographs) with time in chickpea during cooking in water at 92 ^{o}C

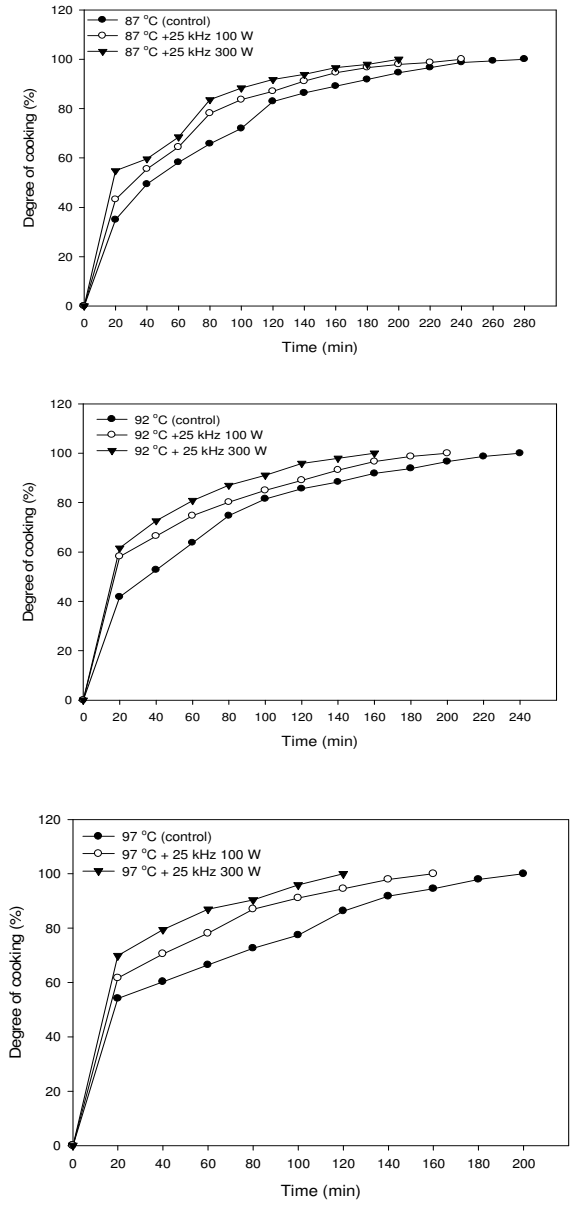


Figure 4.28. Degree of cooking (DC, %) by Birefringes images of cooked chickpeas without and with US at 87, 92 and 97 ^{o}C

4.2.2.2. Degree of cooking using unreacted-core (UC) model

Mathematical expressions for cooking of whole grains have been the major concern for understanding kinetics of the starch gelatinization. Modeling efforts for the gelatinization of chickpea starch are quite scarce compared to other starchy grains especially rice, though it is one of the most consumed legumes in the world (Chavan et al., 1986). The gelatinization of chickpea starch phenomenon during cooking in

water can be considered to mainly consist of heat transfer, water transfer, and gelatinization processes. It can be portrayed by

a) diffusion of water through the film surrounding the grain,
b) diffusion of water in the seed coat covering the cotyledons,
c) diffusion of water in the gelatinized zone,
d) reaction of water with starch granules at the boundary between the gelatinized and ungelatinized zones,
e) heat transfer from the cooking medium to the grain.

Processes (a) and (b) take place successively off the protein matrix, and processes (c) and (d) occur simultaneously in the matrix. The latters are successive to the formers. At the same time the process (e) is simultaneous to all other processes. Sayar et al. (2001) modeled the gelatinization of starch in whole chickpea cooked in water as a simultaneous diffusion and first-order reaction phenomenon. A chickpea grain can be envisaged to comprise of starch granules embedded in a protein matrix covered by a seed coat. During cooking, water molecules ingressing the grain initially gelatinize starch granules in the peripheral zone adjacent to the seed coat if the T_{gel} (Cooking temperature) and M_{gel} (Gelatinization moisture content) conditions are satisfied. The gelatinization appears as a color change in the peripheral zone surrounding an ungelatinized core zone in the grain. The gelatinized zone enlarges toward the center of the grain while the core shrinks with the progress of the cooking. Based on the given scheme, cooking of whole chickpea is analogous to the reaction of particles shrinking in size while leaving a flaking ash. The unreacted-core model developed for such fluid–particle heterogeneous reaction systems (Levenspiel, 1972) can be used for gelatinization of chickpea starch as well as gelatinization of other starches (Figures 4.29 and 4.30). Sayar et al. (2003) (Figure 4.29) and Suzuki et al. (1977) applied the unreacted core approach for cooking of chickpea and some rice varieties, respectively. Unreacted-core approach is relatively simple to work considering the experimentation, data collection, evaluation, and the form of the model equation. Besides, it is especially suitable for chickpea because of the clear separation of the ungelatinized core and the gelatinized zone, and its spherical geometry and size. The thickness of the seed coat of the chickpea samples used in the work was measured around 0.03 mm using a digital micrometer. The average radius of chickpea grains

was approximately 133.3 times greater than the thickness of the seed coat. The seed coat quickly undergoes to plasticization during cooking (Abu-Ghannam and McKenna. 1997; Sayar et al.. 2001). The thin seed coat compared to the cotyledons presents low resistance, and the plasticization gives more permeability to the water molecules. By ignoring the seed coat, the chickpea body can be assumed to form of starch granules immobilized in the protein matrix. The gelatinization of various starches was reported as reaction-controlled (Sayar et al., 2001; Suzuki et al., 1977). It implies that the diffusion of water through the film surface and the gelatinized zone are much faster than the rate of the gelatinization in the boundary and the effect of the diffusion can be neglected.

Sphere is the best possible geometry that can be used for a chickpea grain considering its shape and high sphericity value of 88 % as determined by Konak et al., (2002). The reaction of starch gelatinization is recognized by the following scheme (Lund and Wirakartaksumah, 1984):

aA(Water) + bB(starch) $\rightarrow$ Product (gelatinized starch) $\quad M \geq M_{gel} \quad$ (4.23)

where M is water content, b stoichiometric coefficient, T temperature. Since the gelatinization is assumed as the governing process, the quantity of the starch reacting at the boundary is proportional to the available surface area of the ungelatinized core. Based on the unit surface of the core, the rate of the gelatinization can be given by

$$-\frac{1}{4\pi * r_C}\frac{dN_B}{dt} = -\frac{b}{4\pi * r_C}\frac{dN_A}{dt} = bk_S C_A \quad (4.24)$$

where N_B and N_A are number of moles of starch and water reacting, respectively (kg mol). r_C is radius of ungelatinized zone, t is time (s), k_S is gelatinization rate constant based on unit surface (m s^{-1}). C_A is water concentration (kg mol m^{-3}).

The decrease in the radius of the ungelatinized core together with the disappearance of dN_B moles of starch or bdN_A moles of water can be obtained by

$$dN_B = -bdN_A = -\rho_B d(\frac{4}{3}\pi * r_C^3) = -4\pi\rho_B r_C^2 dr_C \quad (4.25)$$

where $\frac{4}{3}\pi * r_c^3$ is volume (m^3), ρ_B is molar density of starch (kg mol m^{-3}).
Inserting Equation (4.24) into Equation (4.25) and integrating from radius of the chickpea (r) to r_c results in

$$t = \frac{\rho_B}{bk_S C_A}(r - r_C) \quad (4.26)$$

The time required for complete gelatinization (τ) is obtained when $r_c = 0$:

$$\tau = \frac{\rho_B * r}{bk_S C_A} \quad (4.27)$$

The decrease in the radius of the ungelatinized core or increase in the fractional gelatinization of the starch in terms of τ is found by combining Equations 4.26 and 4.27:

$$\frac{t}{\tau} = 1 - \left(\frac{r_C}{r}\right) \quad (4.28)$$

Equation (4.28) allows estimating the cooking time and the kinetics of the reaction-controlled in gelatinization of chickpea starch. Details for the derivation of the model equations for the film-, diffusion-, and reactioncontrolled systems in a sphere were provided by Levenspiel (1972) and Sayar et al. (2003). Their behaviors are presented in Figure 4.29 and 4.30.

Two concentric zones were observed on the flat sides of the cotyledons during cooking of chickpea samples between 87 and 97 ^{o}C without and with US application. The inner zone was in original white color of the intact cotyledon while the outer zone surrounding the inner zone was opaque yellow in color. The two zones were clear to the naked eye with a distinctive boundary between them. With increasing cooking time, the outer yellow zone expanded towards the center of the grain at the expense of the inner white zone.

The typical progress of the process as observed on the chickpea cotyledons during cooking at 92 ^{o}C is illustrated in Figure 4.31. The average radius of unreacted-core (r_c) and cotyledon (r) for without and with different US at 87, 92 and 97 ^{o}C are given in Tables A17-A19, respectively. Increase in cooking time decreased r_c and increased r values. Increase in cooking temperature of chickpea also decreased r_c and increased r values. Furthermore, application of US and increase in power of US decreased r_c and increased r values, respectively. The birefringence study of the cooked samples in Section 4.2.2.1 revealed that in the inner zone maltase crosses kept the original appearance as before the cooking and in the outer zone almost no maltase crosses

existed (Figure 4.32). These images showed that while gelatinization took place in the outer zone, no gelatinization occurred in the inner zone yet. The color conversion from the original white into the opaque yellow in the outer zone was interpreted as the manifestation of the starch gelatinization.

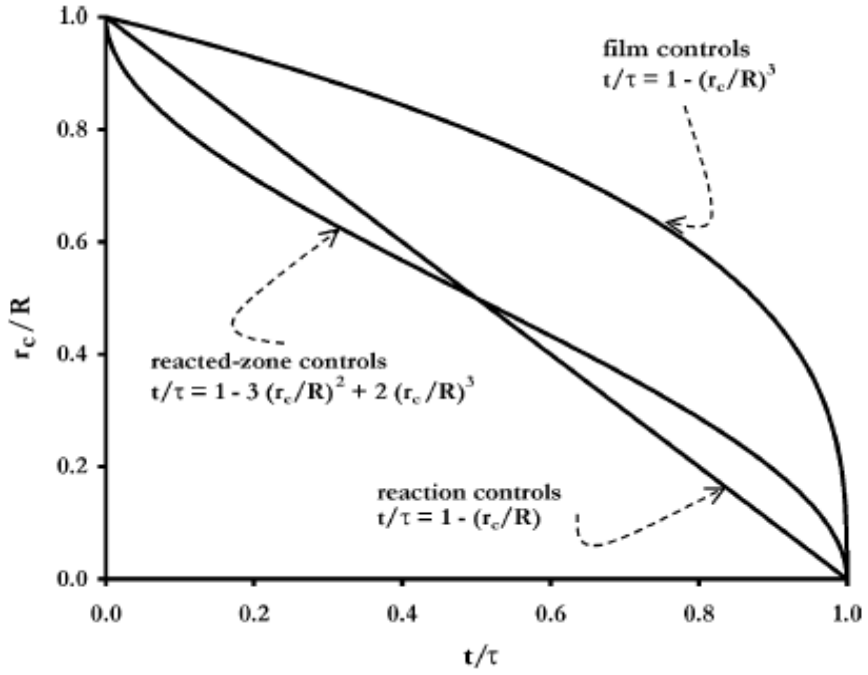


Figure 4. 29. Unreacted-core model equations for possible governing resistances in a sphere and their progress with time (Levenspiel, 1972)

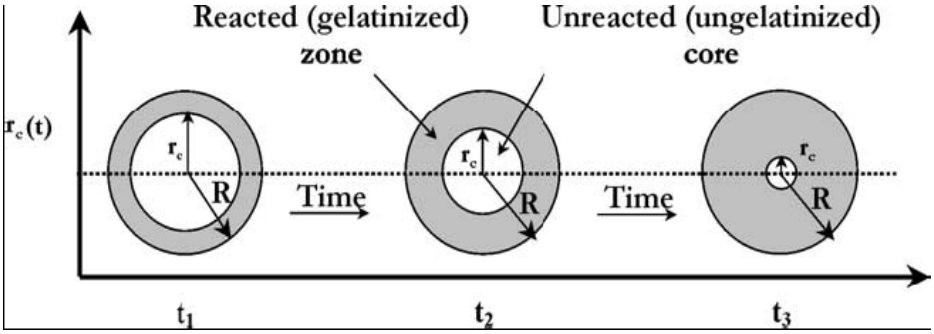


Figure 4.30. Schematic progress of the cooking of chickpea starch according to the unreacted-core model (Sayar et al., 2003)

Table 4.7. Kinetic parameters of starch cooking reaction fitted for unreacted-core model at different times for 87, 92 and 97 °C without and with US cooking of chickpeas

$ln(\frac{-d\alpha_B}{dt}) = ln(k_r) + n(ln(\alpha_B))$				$\frac{t}{\tau} = 1 - (\frac{r_C}{r})$	
Process	**n**	**k_r (s^{-1})x10^4**	**R^2**	**τ_{pre} (min)**	**R^2**
87 °C	0.635	2.35	0.9727	232	0.9693
87 °C 25 kHz 100 W	0.682	3.45	0.9664	186	0.9575
87 °C 25 kHz 300 W	0.641	4.03	0.9380	150	0.9393
92 °C	0.754	4.32	0.9506	183	0.9455
92 °C 25 kHz 100 W	0.695	4.78	0.9429	146	0.8959
92 °C 25 kHz 300 W	0.662	6.53	0.9162	111	0.9101
97 °C	0.711	4.85	0.8961	147	0.8949
97 °C 25 kHz 100 W	0.663	6.62	0.9288	110	0.9000
97 °C 25 kHz 300 W	0.516	8.14	0.9237	76	0.9268

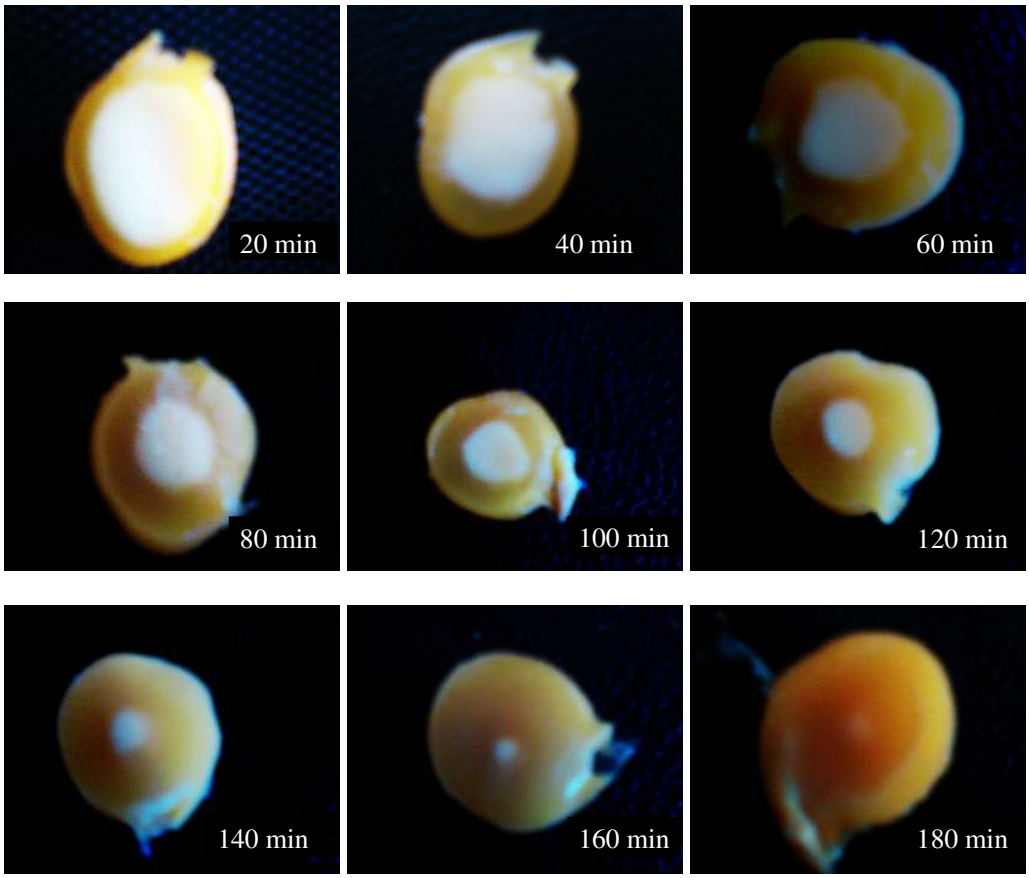


Figure 4.31. Typical progress of the cooking of chickpea starch during cooking in water at 92 °C

The progress of the gelatinization in chickpea samples was determined utilizing the ratio of the core area / total area of the cotyledons. From the area ratio, the ratio of the core radius / cotyledon radius was determined. The radius ratio (r_c / r) versus time (t) plots exhibited linear behavior at all cooking temperatures (87, 92 and 97 ^oC) without and with US (Figure 4.33). Equation 4.28 fitted to the experimental data for chickpea cooking at different time and temperatures without and with US with coefficient of correlations (R^2) between 0.8949 and 0.9693, and with data points randomly scattering around the regression lines. The R^2 values and the random scatterings indicated the good fit of the model to the process and from the slopes of the plots, the cooking time was predicted (τ_{pre}) as tabulated in Table 4.7. The cooking time (τ, min) was found from the slopes of lines as 232, 183 and 147 min for 87, 92 and 97 ^oC, respectively (Table 4.7 and Figure 4.33). Increase in temperature decreased the cooking time of chickpea as expected.

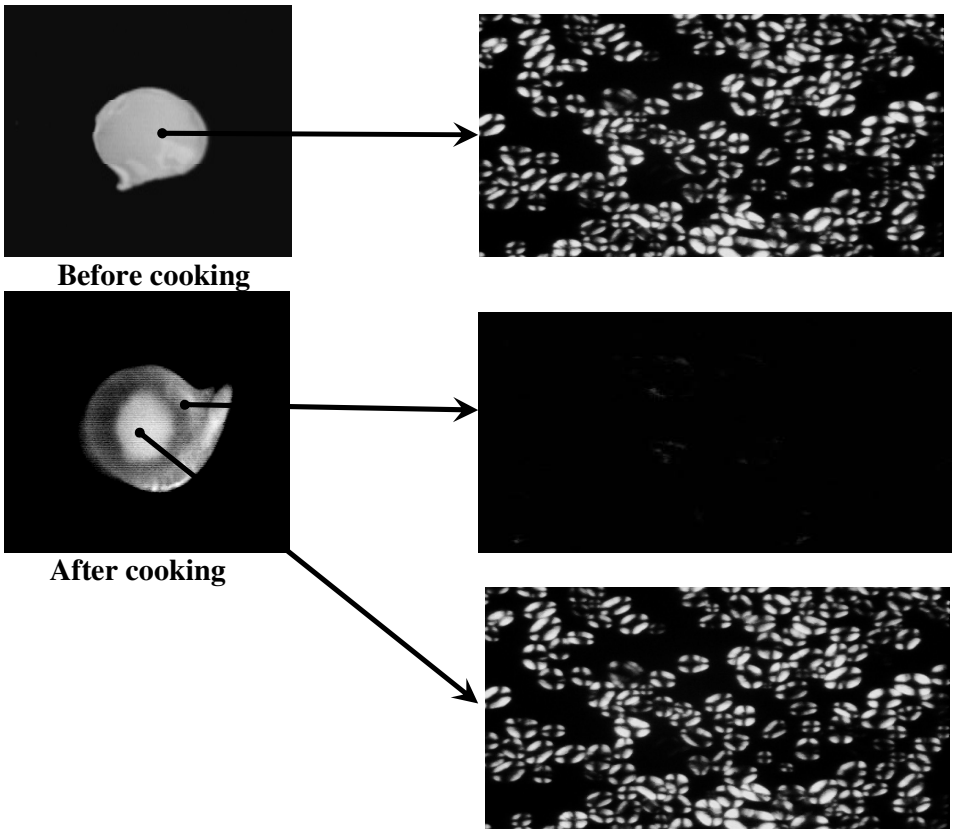


Figure 4. 32. Typical birefringence images for the starch cooking in chickpea before cooking and during cooking in water

The effect of US can be seen from Table 4.7 and Figure 4.33. Also, increase in power of ultrasounds decreased the degree of cooking and cooking times. As the temperature increased from 87 to 97 ^{o}C, the cooking time decreased from 232 to 186 and 150 min, 183 to 146 and 111 min and 147 to 110 and 76 min at 87, 92, 97 ^{o}C temperatures with 25 kHz 100 and 25 kHz 300 W application of ultrasounds to chickpeas, respectively (Table 4.7).

Cooking times were also determined experimentally using the birefringence images at the given temperatures in Section 4.2.2.1 and valeus are given in Table 4.6. With increasing cooking time the distortion and disappearance of Maltase crosses increased, and finally they totally disappeared as shown in Figure 4.31 at 92 ^{o}C. The comparison of the experimental curves in Figure 4.33 with the theoretical curves in Figure 4.29 reveals that cooking of chickpea starch is effectively gelatinization-controlled. The dominancy of the gelatinization reaction during cooking of chickpea was in agreement with the work of Sayar et al. (2001) on the modeling of starch gelatinization in whole chickpea and with other similar works on other whole starchy grains (Bakshi and Singh, 1980; Suzuki et al., 1976). The verification of the unreacted-core model for the gelatinization of starch allows taking more steps further for obtaining information on the kinetics of the starch gelatinization. The time elapsed for the ungelatinized white core in whole grains to disappear during cooking is practically accepted as the cooking time (Williams et al., 1986), i.e. cooking time (τ). The relationship between τ and cooking temperature (T) can be useful for selecting a cooking temperature other than the boiling temperature of water as usually practiced at atmospheric pressure, and for estimating the cooking time at the selected temperature to prevent undercooking or overcooking.

For the chickpea samples used, τ decreased with increasing T as expected (Table 4.7), and the relationship between them was estimated by a linear equation with a satisfactorily with high R^2 (0.9923) value within the given temperature range (τ_{pre}= -8.50T + 969.33).

Assuming the molar density of starch (ρ_B) is same in the unreacted core and reacted zone, the rate of the starch gelatinization can be expressed by the linearized form of the following general reaction rate equation:

$$-\frac{d\alpha_B}{dt} = k_r \alpha_B^n \tag{4.29}$$

$$\ln\left(\frac{-d\alpha_B}{dt}\right) = ln(k_r) + n(ln(\alpha_B)) \tag{4.30}$$

where $\alpha_B = r_C^3 / r^3$ is mol fraction of ungelatinized starch, k_r is gelatinization rate constant (s^{-1}) and n is order of gelatinization reaction.

The fractional decrease in the ungelatinized starch (α_B) was determined from the radius ratio (r_c/r) data given in Tables A17-A19 and Figure 4.34 for each temperature without and with 25 kHz 100 W and 25 kHz 300 W US. It exponentially decreased with increasing time till complete gelatinization, i.e. $\alpha_B = r_C^3 / r^3 = 0$. The unreacted-core model dictates that the reaction is 100% complete when the core disappears at t = τ. This does not comply with the ceasing of starch gelatinization before 100% completion during cooking of whole grains.

Data for regressing Equation 4.30 was obtained from the slopes of the curves taken between successive data in Figure 4.34. The regression resulted in R^2 values ranged from 0.8961 to 0.9727 (Table 4.7), and data randomly scattered around the regression lines as shown for cooking temperatures without and with US in Figure 4.35 which points out the good fit of Equation 4.30 to the kinetics of the starch gelatinization. The order and the rate constant of the gelatinization were estimated from the slopes and intercepts of the regression lines of Equation 4.30, respectively (Tables A17-A19 and Table 4.7).

The value of n was between 0.516 and 0.754 (average 0.7) and it did not exhibit a trend with temperature. It points that the order of the gelatinization is close to but smaller than 1. Though starch gelatinization is practically treated as a first-order reaction in the literature (Bakshi and Singh, 1980; Sayar et al., 2001; Sayar et al., 2003), Lund and Wirakartaksumah (1984) preferred to call it pseudo-first order. Kubota (1979) reported it between 0.87 and 1.45 for the starch gelatinization in whole red bean cooked in water above 60 ^oC. Also, Sayar et al. (2003) reported it between 0.71 and 0.94 for the starch gelatinization in whole chickpea cooked in water above 60 ^oC.

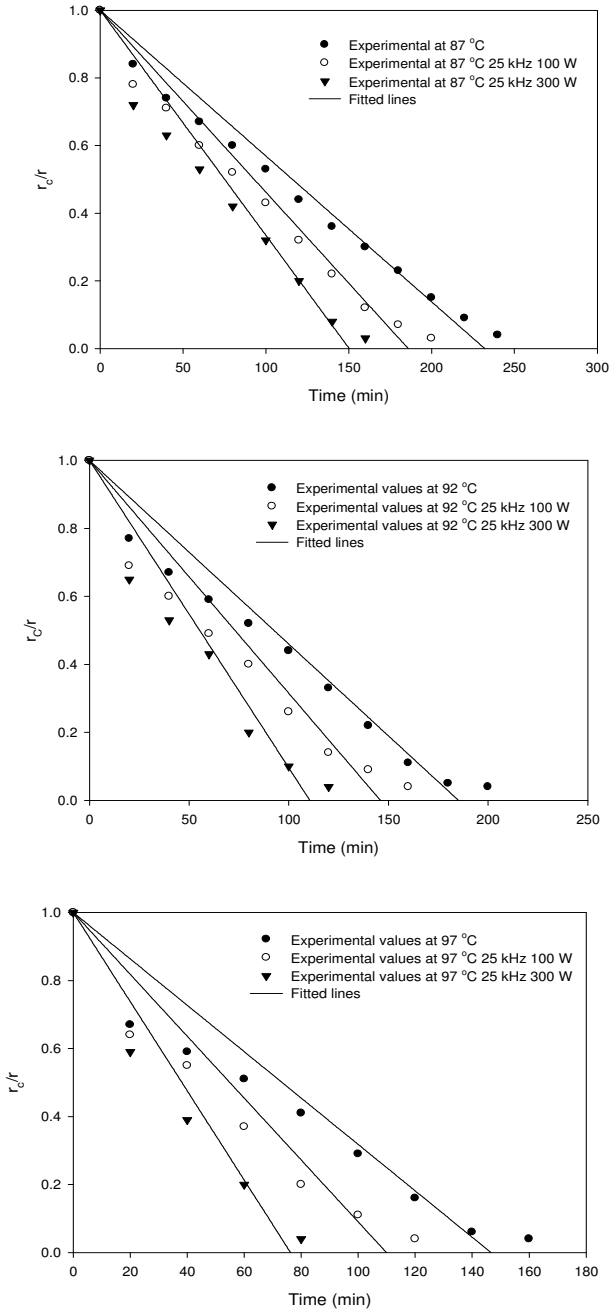


Figure 4.33. Experimental and predicted r_c/r values of cooked chickpea without and with US for different cooking times at 87, 92 and 97 °C

The order of magnitude of reaction constan (k_r) was determined as 10^{-4} s^{-1} (Table 4.7). It was reported in the range of 10^{-5} and 10^{-4} s^{-1} for chickpea samples cooked in water above 60 °C assuming the gelatinization follows a first-order reaction kinetics (Sayar et al., 2001; Sayar et al., 2003).

In unreacted-core model, the degree of cooking also was found by the following equation:

$$DC(\%) = \frac{(4/3)\pi * r^3 - (4/3)\pi * r_C^3}{(4/3)\pi * r^3} = \frac{r^3 - r_C^3}{r^3} * 100 \quad (4.31)$$

where, DC(%) is the degree of cooking, r_c and r are avarage radius of unreacted core and whole chickpeas.

The relationship between the degree of cooking by volume ratio of reacted to whole chickpea and time at 87, 92 and 97 ^oC without and with US is illustrated in Figure 4.36. From the data in Tables A17-A19, the cooking times were also found as 240, 200 and 160 min at 87, 92 and 97 ^oC, respectively. These values are close to values obtained (232, 183 and 147 min) from the regression of r_c/r vs time in Figure 4.33 (Table 4.7).

As the cooking temperature increased, the cooking time decreased. One can see that time for complete gelatinization for unreacted-core and volume ratio models were found to be approximately the same values because of the same mechanism in both case.

The degree of cooking from equation 4.32 for US application are illustrated in Figure 4.35. 25 kHz 100 W and 25 kHz 300 W ultrasound applied chickpeas also decreased cooking times and increased degree of cooking for different cooking temperatures (87-97 ^oC) (Tables A17-A19 and Figure 4.36). Also, increase in power of ultrasound (from 100 to 300 W) decreased cooking time and increased degree of cooking. As the temperature increased from 87 to 97 ^oC with 25 kHz 100 and 25 kHz 300 W application of ultrasounds to chickpeas, the cooking time decreased from 240 to 200 and 160 min, 200 to 160 and 120 min and 160 to 120 and 80 min, respectively (Tables A17-A19 and Figure 4.36). The degree of cooking at 87 ^oC and 20 min cooking of chickpea was found as 41.25 %. At the same conditions (20 min and 87 C), DC (%) increased to 51.81 and 63.40 % with 25 kHz 100 W and 25 kHz 300 W US applications. 25 kHz 100 W and 25 kHz 300 W US applications for 20 min cooking provided 26, 23.5 and 6.5 % benefits to cooking of chickpea at 87, 92 and

97 ^{o}C. 25 kHz 300 W US provided higher benefits than 25 kHz 100 W to cooking operation for all temperatures.

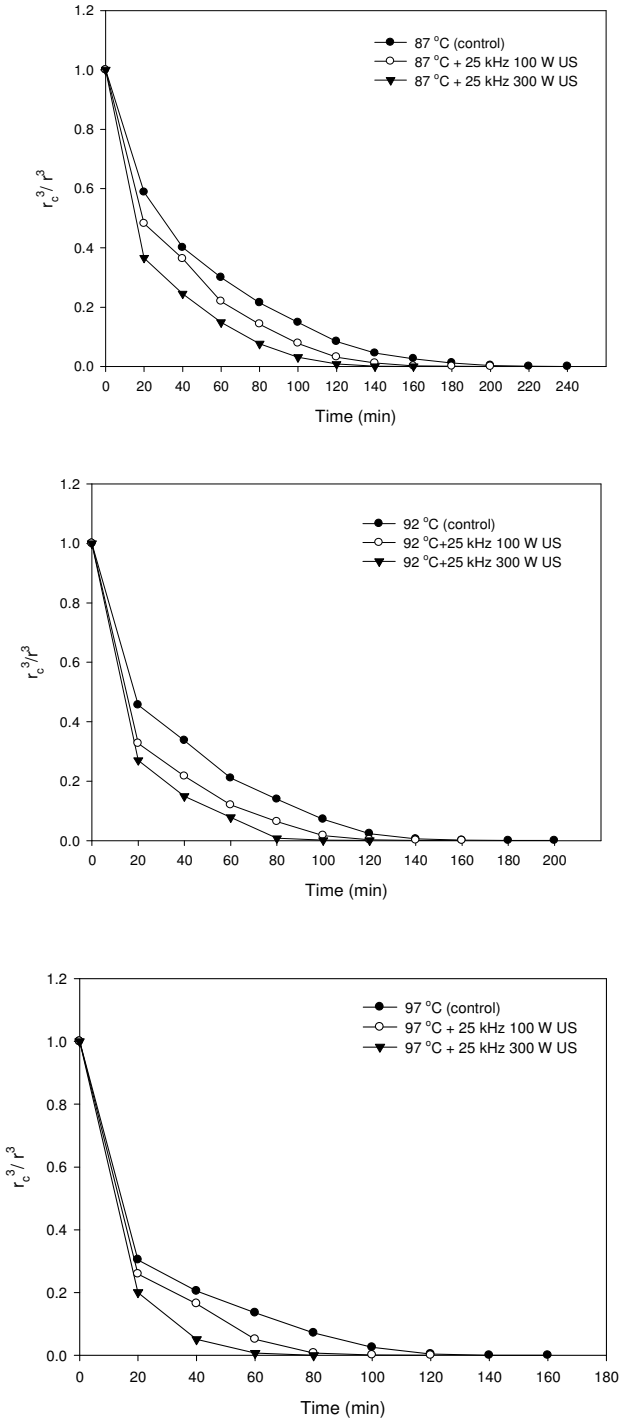
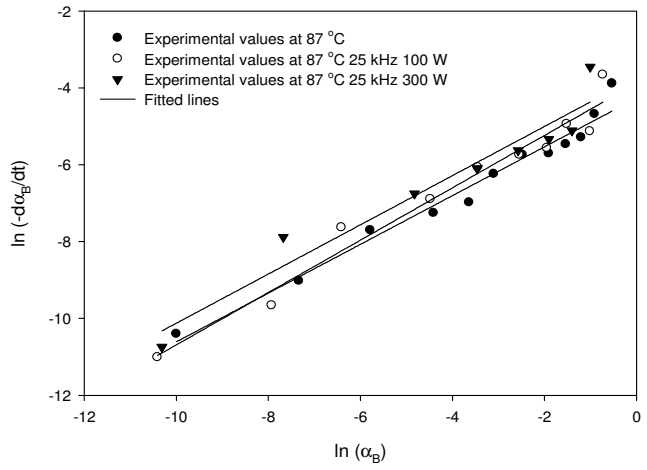
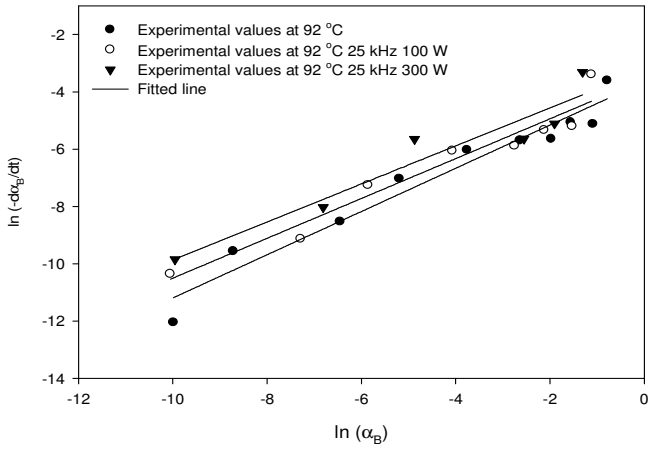


Figure 4.34. Progress of the gelatinization of the chickpea starch with r_c^3/r^3 relation to cooking time without and with US at 87, 92 and 97 ^{o}C





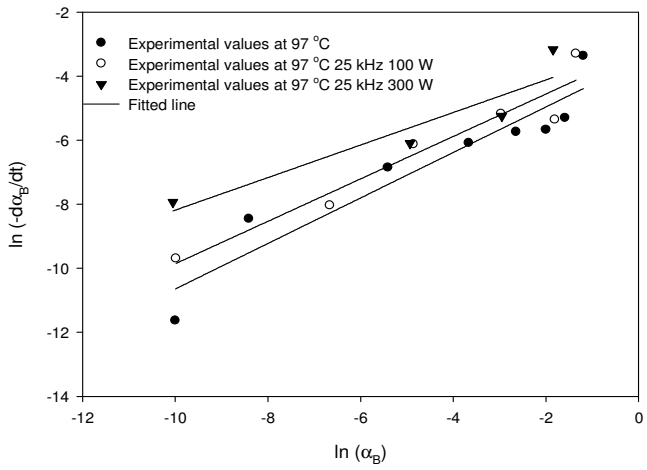


Figure 4.35. Experimental and predicted $\ln(-d\alpha_B/dt)$ vs $\ln(\alpha_B)$ of cooked chickpea without and with US for different cooking times at 87, 92 and 97 °C

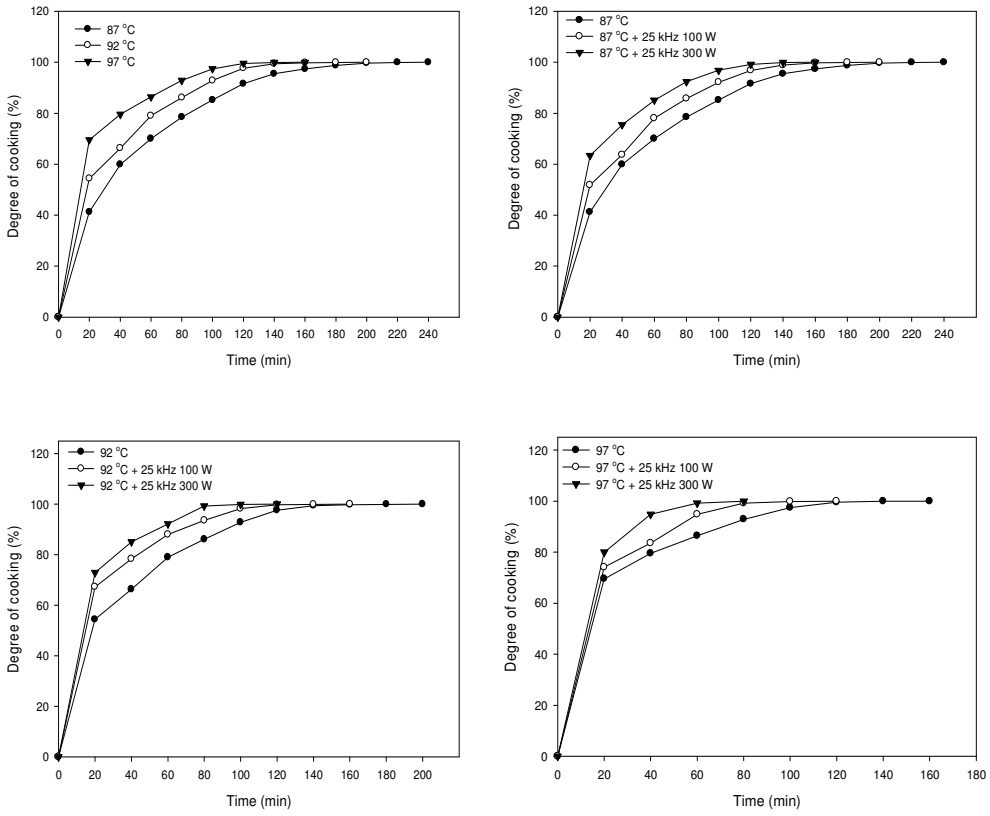


Figure 4.36. Degree of cooking (DC, %) by unreacted-core model of cooked chickpeas at 87, 92 and 97 °C without and with US

4.2.2.3. Degree of cooking using Differential Scanning Calorimetric (DSC) method

Differential Scanning Calorimetry (DSC) is a powerful tool used to investigate thermal properties and phase transition of starch (Roos, 1995). Endo- and exothermal changes in a DSC thermograph reveal transitions or reactions occurring during DSC testing, such as glass transition, gelatinization, and melting. Analysis of DSC data can provide additional information about starch, such as its structure and composition, its interaction with other components, the effects of water, and related properties.

Starch gelatinization is the important factor that determines the overall cooking behavior and product characteristics of foods. During starch heating, there are some changes in properties, enthalpy, specific heat capacity, and cooking temperature, showing the extent of starch gelatinization (Tester and Morrison, 1990). The loss of

molecular order was measured by the endothermic enthalpy of gelatinization. Many studies have been conducted to determine thermal properties of starches for different reasons, including the effect of lipid and protein on starch gelatinization (Hoover et al., 1993; Huang et al., 1994; Radosavljevic et al., 1998), the effect of amylose-lipid complexes (Tester and Morrison, 1990; Morrison et al., 1993), the effect of annealing (Jacobs et al., 1995), and the effect of heat-moisture treatment on starch properties (Hoover and Vasanthan, 1994).

The degree of cooking was determined by comparing the enthalpy change of cooked sample or gelatinized (ΔH_{gel}) to that of raw sample (ΔH_{raw}) as described by Marshall et al. (1993). Therefore the following formula can be used for degree of cooking (DC, %) :

$$DC\ (\%) = [1-(\ \Delta H_{cook} / \Delta H_{raw})]x100 \qquad (4.32)$$

Differential scanning calorimetry (DSC) was used to measure the enthalpy (ΔH_{gel}) of starch gelatinization, cooking temperatures (onset,T_o; peak, T_p; and conclusion, T_c) and peak height index (PHI). DSC thermogram for cooked chickpea at 120 min and 92 ^oC is given in Figure 4.37. From this Figure, T_o, T_p, T_c and ΔH_{gel} values for cooked chickpea at 120 min and 92 ^oC were found as 61.13, 67.12, 75.56 ^oC and 0.95 J/g, respectively. The enthalpy of cooking ΔH_{gel}, onset temperatures (T_o) and degree of cooking for different cooking times were given in Table 4.8. ΔH_{gel} of uncooked chickpea in present study was found as 6.62 kJ/mol. A similar value for uncooked chickpea (6.90 J/g) obtained in the study of Klamczynska et al. (2001). It decreased to 0 kJ/mol at the end of 240 min cooking. The total cooking (100 %) was obtained after 240 min cooking of chickpea by this method.

Starch granules of the chickpeas used in this study kept the integrity of Maltase crosses till 61 ^oC (Figure 4.38). They noticeably started to decrease in number and distort in shape between 60 and 70 ^oC (Figure 4.38) pointing that cooking temperature of chickpeas starts between 60 and 70 ^oC. T_o (onset) temperature values at 92 ^oC were in the range of 59.86-62.33 and the average was 61.13±0.68 (Table 4.8). Singh et al. (2004) has been found T_o, T_p and T_c of chickpea as in the range of 61.5–64.8 ^oC, 66.4–69.0 ^oC, and 71.3–73.8 ^oC, respectively. Also, T_o, T_p and T_c for

chickpea from the study of Hughes et al. (2009) were found as 58.65–59.48 °C, 63.29–65.51 °C, and 77.47–79.28 °C, respectively. The high ΔH_{gel} of starches suggest that the double helices (formed by the outer branches of adjacent amylopectin chains) that unravel and melt during cooking are strongly associated within the native granule.

Table 4.8. Entalphy, onset (T_o) temperature and degree of cooking relation to cooking time at 92 °C

Time (min)	Onset temperature (T_o) (°C)	Entalphy of cooking ΔH_{gel} (J/g)	Degree of cooking (%) $=((1-(\Delta H_{heat}/\Delta H_{raw}))*100$
0	59.86	6.62	0.00
20	60.27	3.81	42.37
40	60.78	3.05	53.90
60	60.84	2.37	64.18
80	60.90	1.66	74.97
100	60.95	1.13	82.88
120	61.13	0.95	85.58
140	61.18	0.72	89.05
160	61.30	0.53	92.00
180	61.37	0.37	94.45
200	61.65	0.18	97.22
220	62.15	0.06	99.15
240	62.33	0.00	100.00

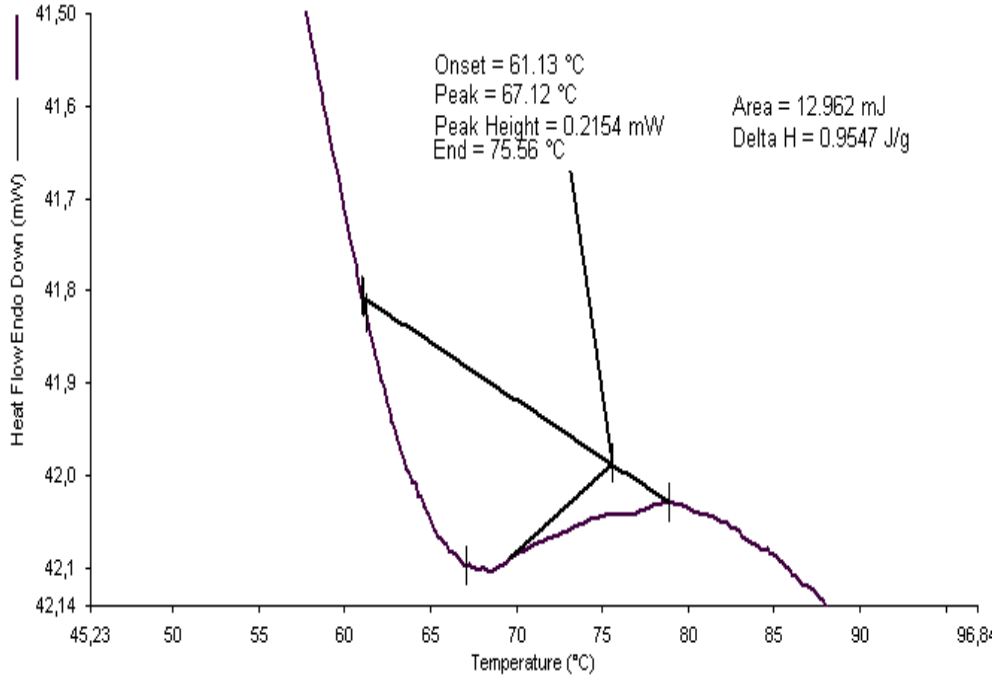


Figure 4.37. Differential Scanning Calorimetry thermogram for 120 min cooked chickpea at 92 °C

Hoover and Ratnayake (2002) reported that T_o, T_p, T_c and ΔH_{gel} values have been found as 59.4-59.7, 64.7-67.7, 71.7-78.2 ^oC and 9.7-12.4 J/g for chickpea starches, respectively. In another study, Miao et al. (2009) reported that the transition temperatures (T_o, T_p and T_c) of chickpea were 62.2, 67.0 and 72.0 ^oC for kabuli starch, and 59.4, 68.8 and 77.8 ^oC for desi starch, respectively. The average cooking temperature (T_o) of chickpea found in this study was in the range of previous studies. Increase in cooking time decreased in ΔH_{gel} values while increased in degree of cooking (DC, %) values (Table 4.8 and Figure 4.39).

The difference in cooking temperature may be attributed to the difference in amylose content, size, form and distribution of starch granules, and to the internal arrangement of starch fractions within the granule. Kaur and Singh (2005) reported that kabuli chickpea flour exhibited lower T_o, T_p, T_c and ΔH_{gel} than the desi type. This could be attributed to difference in cultivars. The cooking temperature of chickpea found by DSC method (61.13 ^oC) in this study was in the range of that obtained with different models in Section 4.1.1.2 (59.96 and 61.47 ^oC) and 4.1.2.2 (60 ^oC).

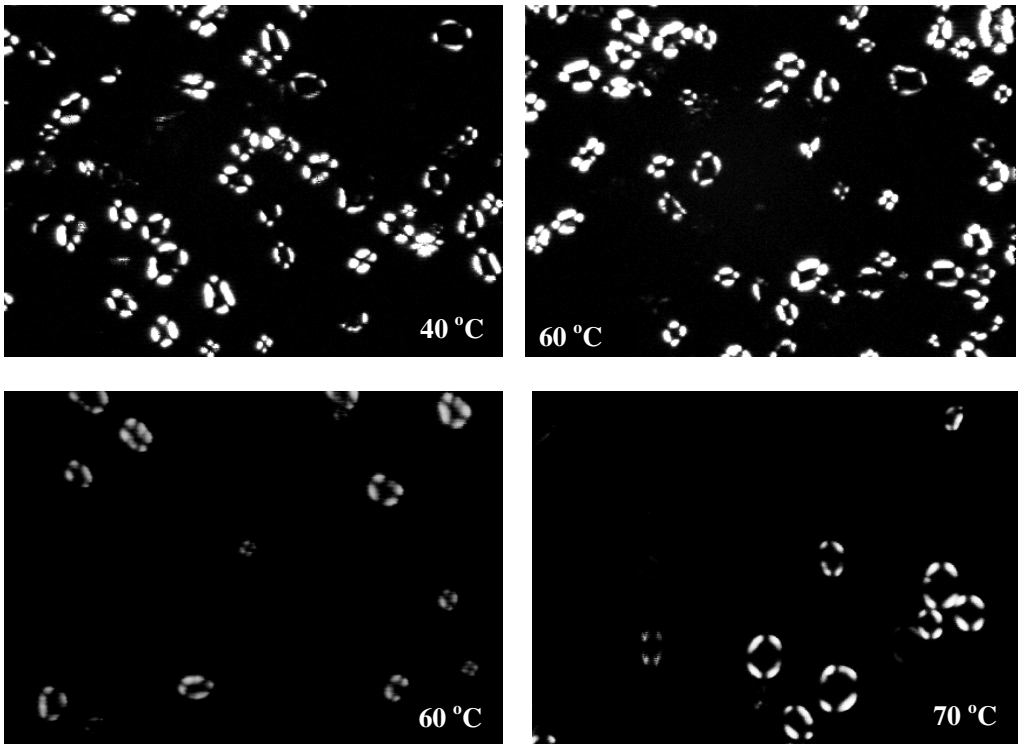


Figure 4.38. Effect of soaking temperature on the birefriengence of chickpea starch at 40, 50, 60 and 70 ^oC

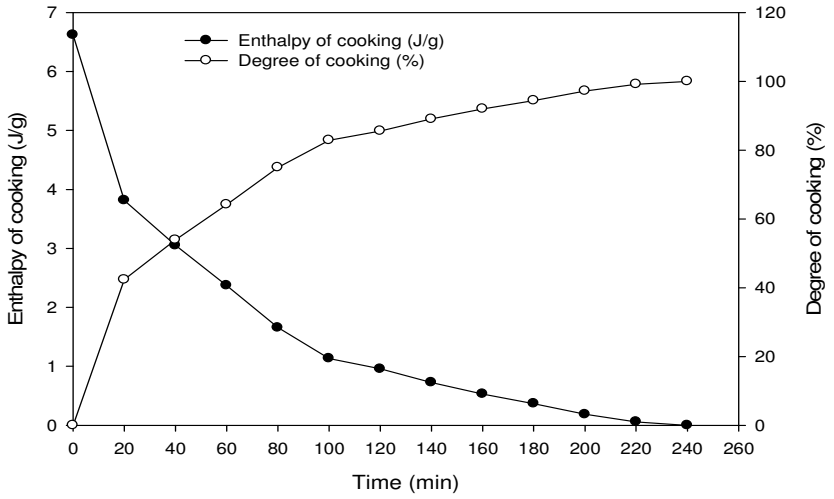


Figure 4.39. Degree of cooking (%) and Enthalpy of gelatinization (J/g) by DSC method of cooked chickpea for different times at 92 ^{o}C

4.2.2.4. Degree of cooking using electrical conductivity (EC) of chickpea and cooking water method: A New method

Electrical conductivity and ohmic heating have been used for degree of cooking by several researchers before (Wang and Sastry, 1997; Chaiwanichsiri et al., 2001; Bauer and Knorr, 2004; Karapantsios et al., 2000; Li et al., 2004). The authors explained the effect of starch gelatinization on electrical conductivity during heating and detected changes in electrical conductivity synchronously with starch gelatinization. Also, they found that at constant time the degree of cooking increased resulting in a gelatinization curve similar to that of thermal gelatinization. For starch gelatinization, Wang and Sastry (1997) found that electrical conductivity increased with temperature, but decreased with degree of starch gelatinization, and indicated a possibility for starch cooking temperature and the degree of cooking to be measured by ohmic heating or electrical conductivity of cooking water.

Karapantsios et al. (2000) studied electrical conductance of starch gelatinization during conventional heating and found that the electrical conductivity had a linear relationship with time until reaching the cooking temperature and presented a decreasing trend. The reason for a decrease in electrical conductivity in the gelatinization range was due to starch granule swelling and viscosity increase, which

resulted in a reduction of area for starch particle movement and an increase in the resistance to motion of the swollen particles.

Li et al. (2004) found that the electrical conductivity and temperature of a starch suspension had a linear relationship before and after gelatinization. Chaiwanichsiri et al., (2001) stated as well that electrical conductivity measurements were an effective method to quantify thermal starch gelatinization, also in on-line applications. The authors explained the rise in electrical conductivity simultaneously with starch gelatinization by an ion release from starch granules corresponding to the breakdown of crystalline structures. The beginning of the ion release was in accordance with the initiation of starch gelatinization and the completion of ion release correlated with the disintegration of the starch granules and the total collapse of the crystalline structure. Bauer and Knorr, (2004) found a good linear relationship between the degree of cooking and the electrical conductivity for wheat and tapioca starch suspensions. So, the electrical conductivity of cooking water and also chickpea can be used for degree of cooking.

Figure 4.40 shows the calibration curve for degree of cooking relation to electrical conductivity of chickpea with a high correlation coefficient (R^2) of 0.9987. From the calibration curve in Figure 4.40, the degree of cooking of chickpea was evaluated at 92 ^{o}C for different cooking times (Figure 4.41). The cooking time at 92 ^{o}C was found as 240 min by electrical conductivity of chickpea seed method. The cooking time of cooked chickpea at 92 ^{o}C was found as the same value (240 min) for birefringes images, DSC and electrical conductivity of chickpea seed methods. The electrical conductivity of chickpea seed decreased with increase of cooking time and degree of cooking at 92 ^{o}C (Figure 4.40 and 4.41). But, unlike electrical conductivity of chickpea seed method, electrical conductivity of cooking water increased with cooking time (Section 4.2.1.1). From Section 4.2.1.1, increase in time, temperature and US applications also increased in electrical conductivity of cooking water (Figure 4.20).

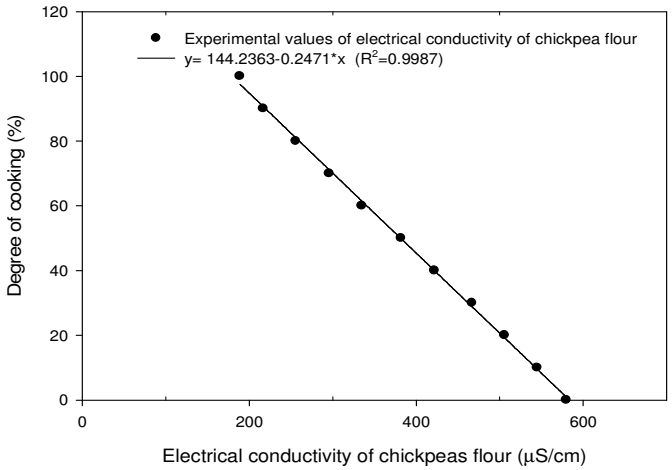


Figure 4.40. Electrical conductivity (µS/cm) versus degree of cooking values for calibration curve of DC by EC of chickpea method

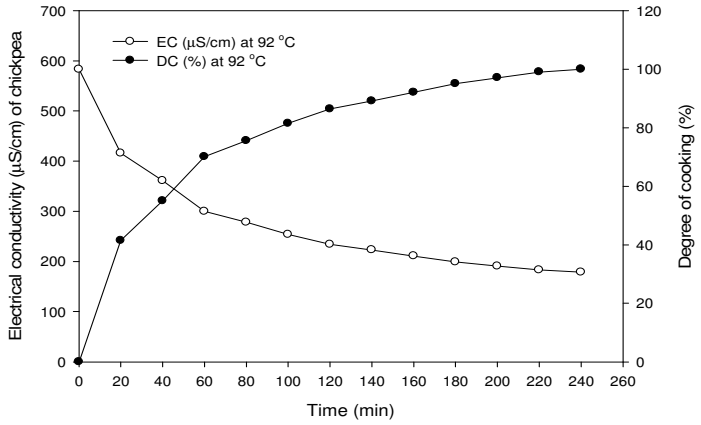


Figure 4.41. Electrical conductivity (mS/cm) and degree of cooking by electrical conductivity (%) of chickpea during cooking at 92 ^{o}C

The electrical conductivity of the cooking water of chickpea rose with increasing time, temperature and US applications, the course of conductivity curve corresponded with the gelatinization curve for all temperatures (Figures 4.42-4.50) (Section 4.2.2.5). So, the electrical conductivity of cooking water can be used for degree of cooking. Furthermore, for application of this method, one other method should be used together with this method. The electrical conductivity values of cooking water at each treatment (87, 92 and 97 ^{o}C w/o and w/ US applications) were converted to percentage electrical conductivity (% EC) with Equation 3.4. In order to

calculate % EC of cooking water, EC values at the cooking time of 100% gelatinization for DSC, Birefringes images, Unreacted-core model and EC of chickpea methods were used. The calculated percentage electrical conductivity of cooking water method is given in Tables A20-A23. Figure 4.49 in Section 4.2.2.5 shows EC (%) by all methods (birefringes images, DSC, unreacted-core model and electrical conductivity of seed methods) relation to cooking time at 92 ^{o}C. As a result, electrical conductivity of both chickpea seed/flour and cooking water during cooking can be used for determination of degree of cooking.

4.2.2.5. Comparison of degree of cooking by EC of cooking water with birefringes images, unreacted core model, EC of chickpea and DSC methods.

The electrical conductivity increased with increase in temperature during cooking of chickpea (Tables A20-A23). The electrical conductivity of cooking water at 87 ^{o}C increased from 0.0016 to 4.82 mS/cm as the time increased from 0 to 280 min (Table A20). The similar increases were observed for 92 and 97 ^{o}C (Tables A21-A23). As the time increased more starch was gelatinized. Because of increase in electrical conductivity increased cooking time, the electrical conductivity values at each time, temperature and treatment were compared with the degree of cooking by birefringence images, DSC, electrical conductivity of chickpea seed and unrected-core model methods at each cooking times (Tables A20-A23 and Figures 4.42-4.56).

Electrical conductivity (mS/cm) of cooking water at 87 and 97 ^{o}C w/o and w/ US by both birefringence images and unreacted-core model showed similar trends of % electrical conductivities (Figures 4.42- 4.44). Figure 4.43 shows the relation between the electrical conductivity (mS/cm) and % EC values of cooking water for birefringes images, DSC, unreacted-core model and electrical conductivity of chickpea seed methods relation to cooking time at 92 ^{o}C. The shapes of EC (mS/cm) versus EC (%) curves for birefringes images, DSC, unreacted-core and electrical conductivity of chickpea seed methods were approximately similar.

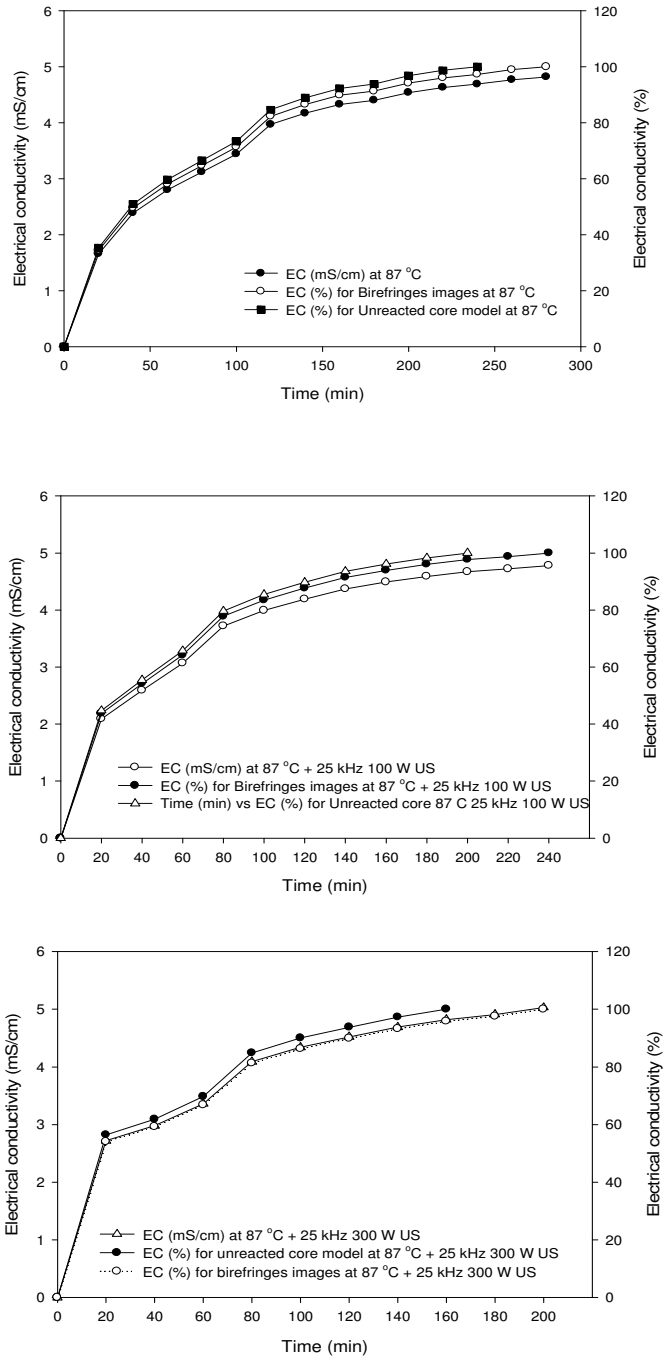


Figure 4.42. Electrical conductivity (mS/cm) and (%) values of cooking water for birefringes images and unreacted-core model methods relation to time at 87 °C without and with US

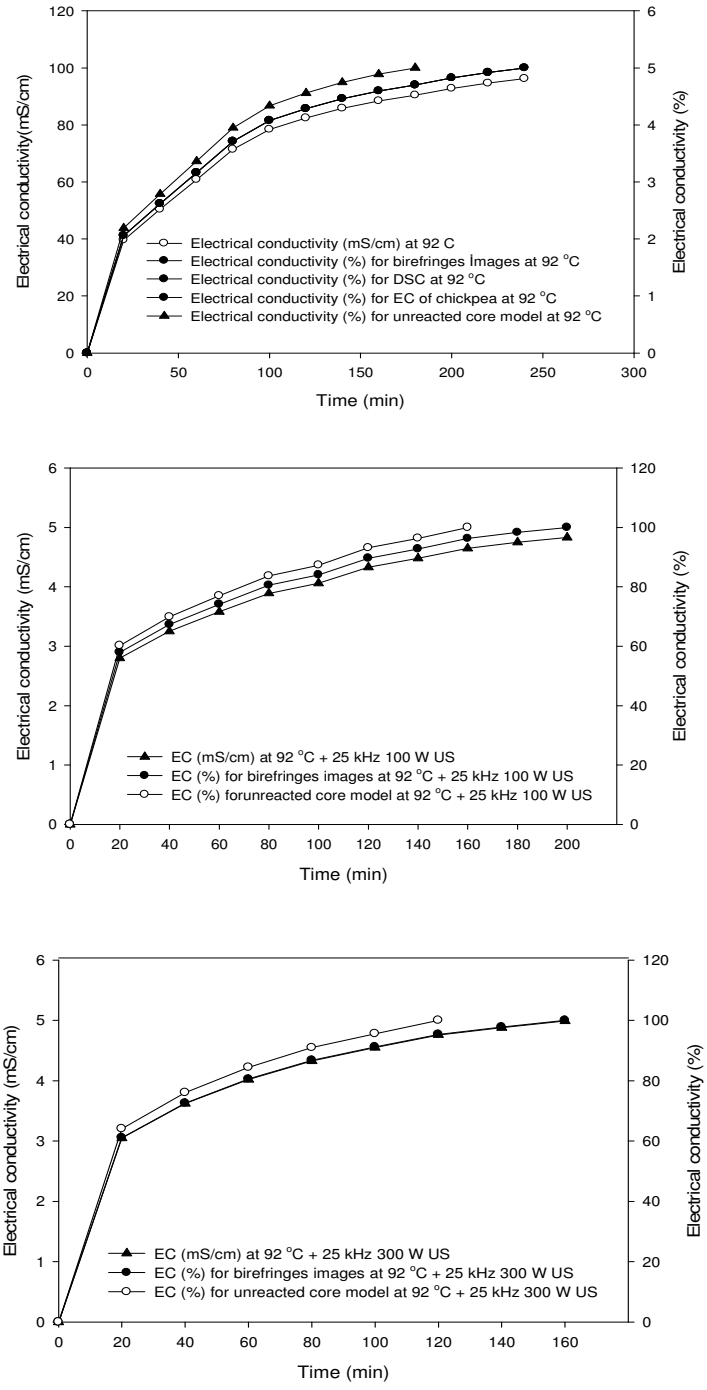


Figure 4.43. Electrical conductivity (mS/cm) and (%) values of cooking water for birefringes images, DSC, unreacted-core model and electrical conductivity of chickpea methods relation to time at 92 °C without and with US

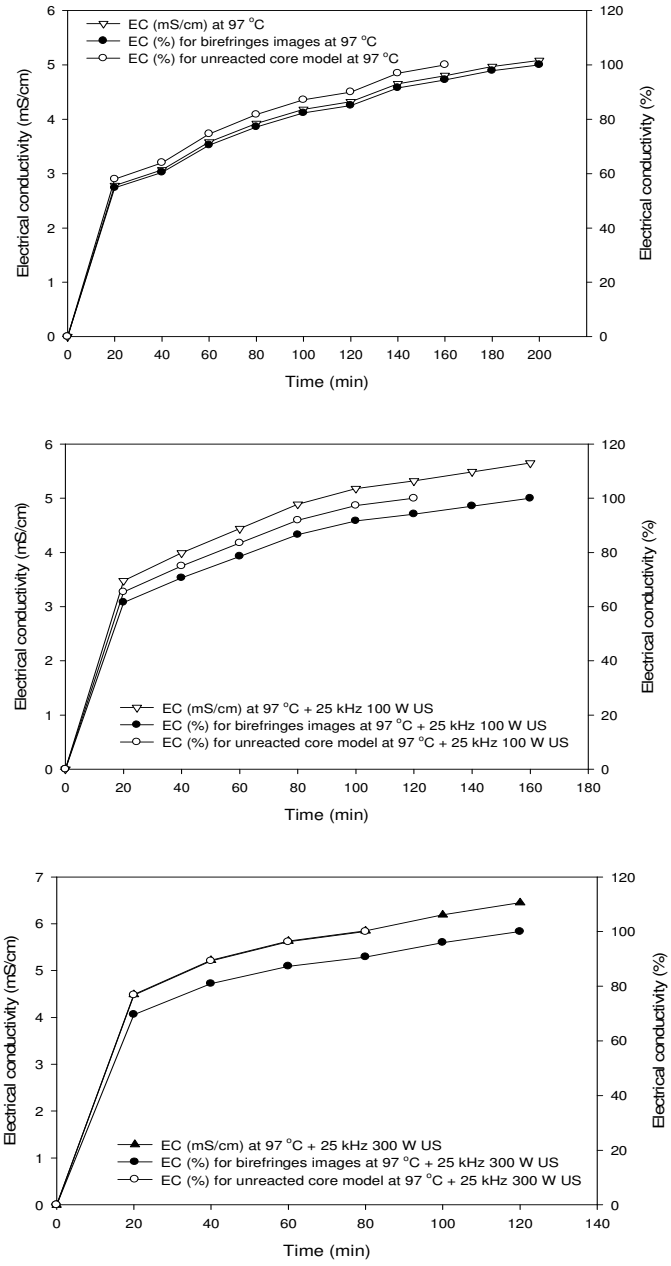
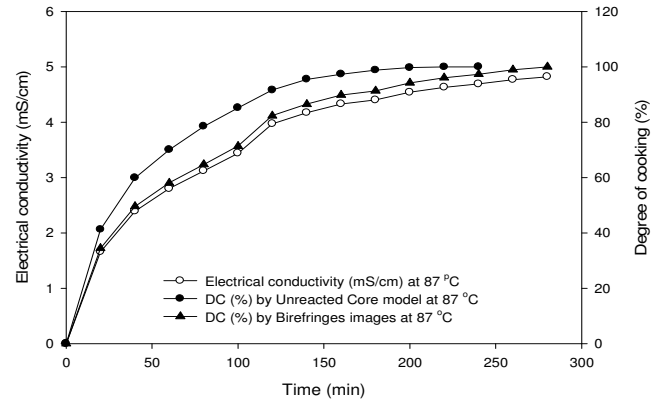
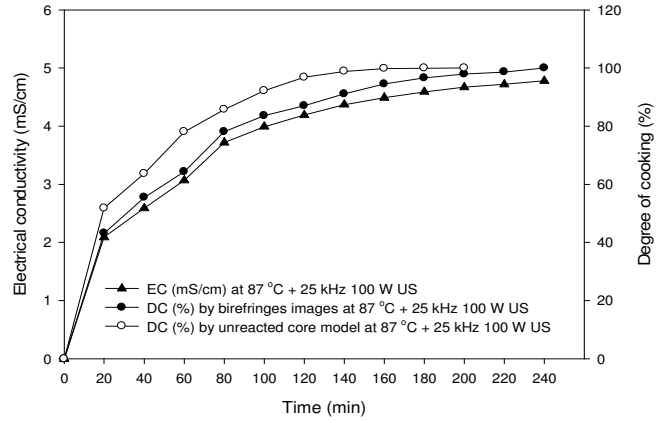


Figure 4.44. Electrical conductivity (mS/cm) and (%) values of cooking water for birefringes images and unreacted-core model methods relation to time at 97 °C without and with US

Electrical conductivity (mS/cm) of cooking water and degree of cooking (%) by unreacted-core model and birefringes images in relation to cooking time at 87, 92 and 97 °C without and with US are also illustrated in Figures 4.45-4.47. The curves obtained from electrical conductivity (mS/cm) of cooking water and degrees of

cooking (%) values were similar. In Figure 4.46, EC (mS/cm) of cooking water was compared with DC (%) by birefringes images, DSC, unreacted-core model and EC of chickpea seed methods at 92 °C.





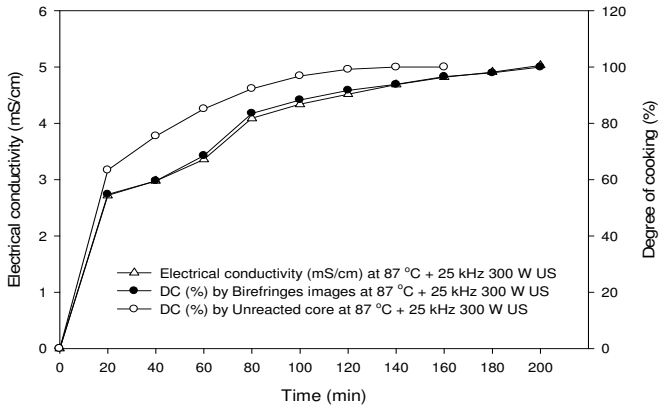


Figure 4.45. Electrical conductivity (mS/cm) of cooking water and degree of cooking (%) by unreacted-core model and birefringes images relation to time at 87 °C without and with US

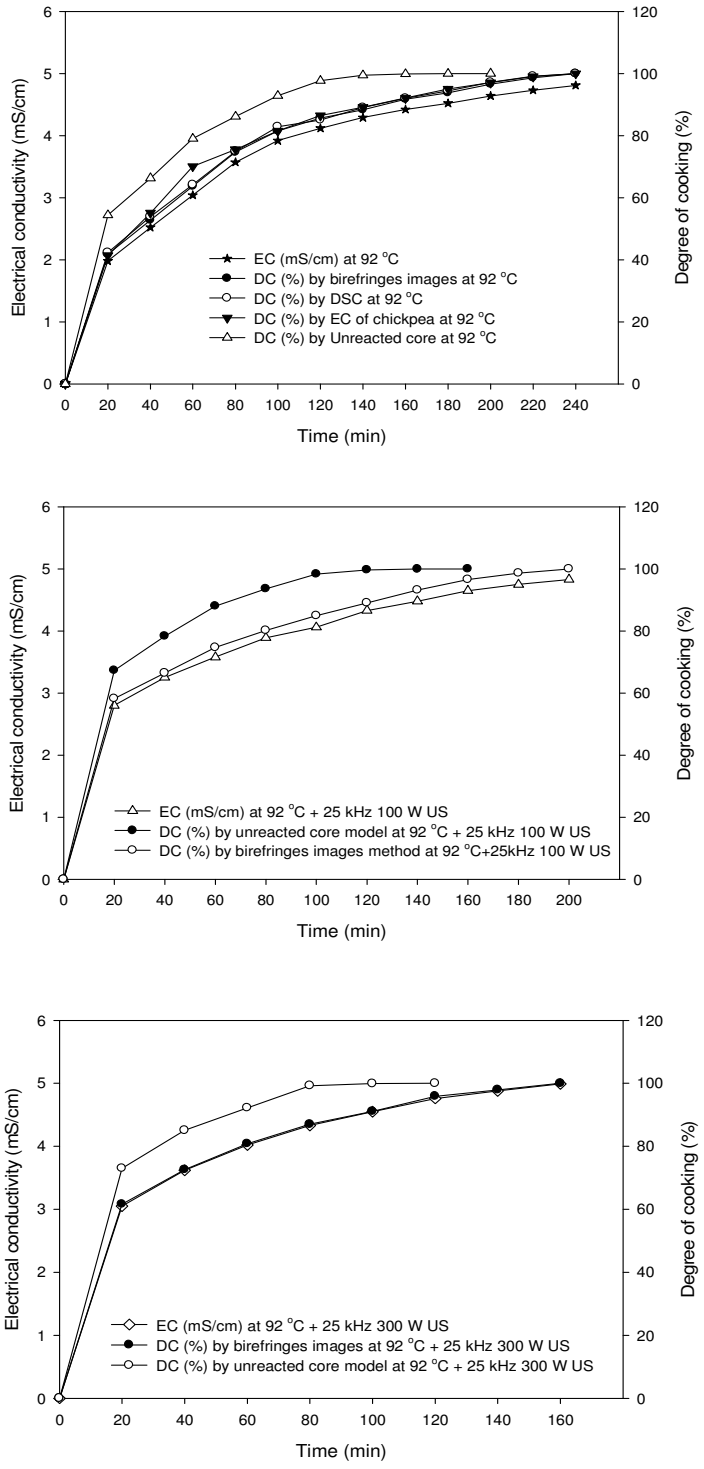


Figure 4.46. Electrical conductivity (mS/cm) of cooking water and degree of cooking (%) by unreacted-core model, birefringes images, DSC and EC of chickpea methods relation to time at 92 °C without and with US

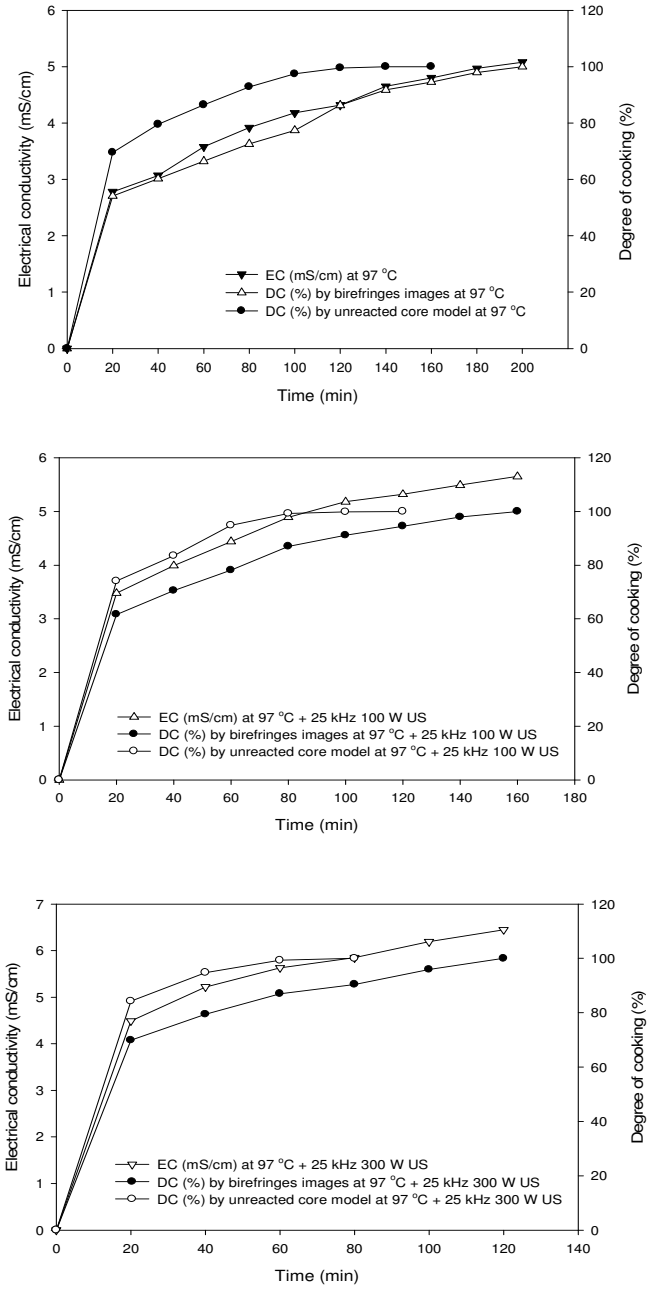


Figure 4.47. Electrical conductivity (mS/cm) of cooking water and degree of cooking (%) by unreacted-core model and birefringes images methods relation to time at 97 ^{o}C without and with US

The degree of cooking (%) and the electrical conductivity (%) of cooking water relation to cooking time at 87, 92 and 97 ^{o}C without and with US for unreacted-core model and birefringes images methods were compared and given in Figures 4.48-4.50. The shape of curves was also similar to sigmoid. Figure 4.48 shows the relation

of degree of cooking (%) and electrical conductivity (%) of cooking water with cooking time at 92 ^{o}C for birefringes images, unreacted-core, DSC and EC of chickpea seed methods. The trend of curves related to degree of cooking (%) versus electrical conductivity (%) of cooking water of chickpea at all temperatures without and with US was similar.

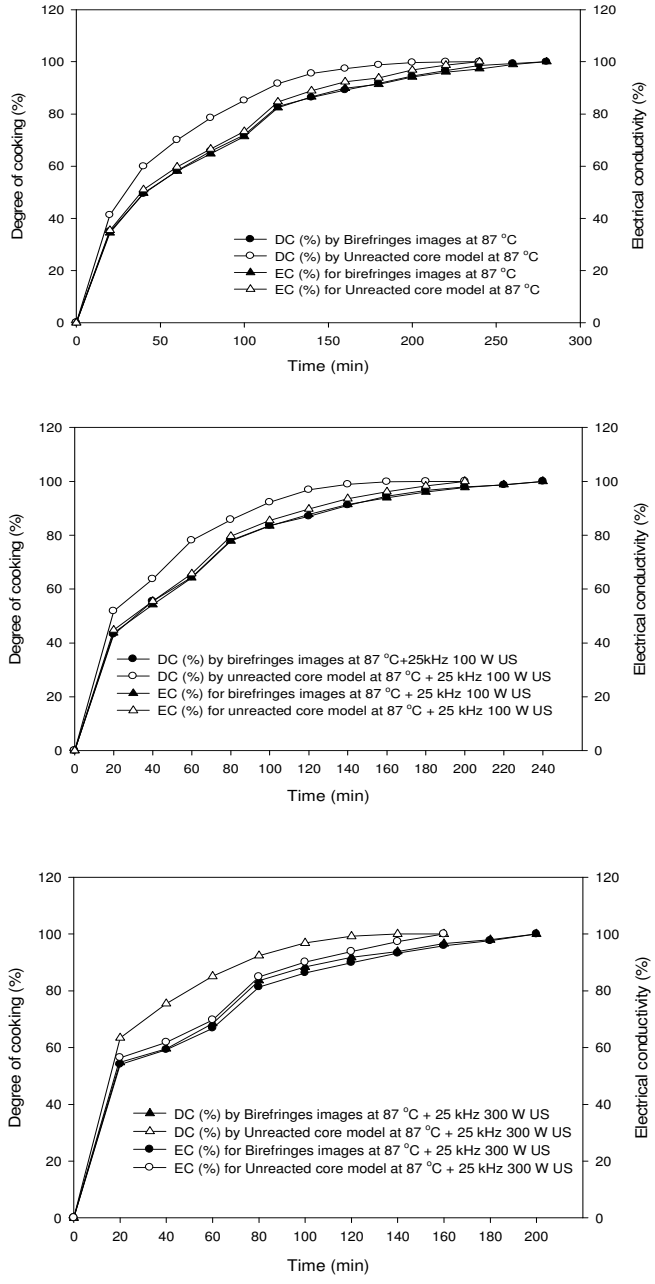


Figure 4.48. Degree of cooking (%) and electrical conductivity (%) of cooking water relation to time at 87 ^{o}C without and with US for unreacted-core model and birefringes images methods

Figure 4.51 shows the correlation of birefringes image and unreacted core model at 87, 92 and 97 °C without and with US. R^2 values from 0.9524 to 0.9943 indicated a good linear relationship between the degree of cooking values of both unreacted-core and birefringes images methods.

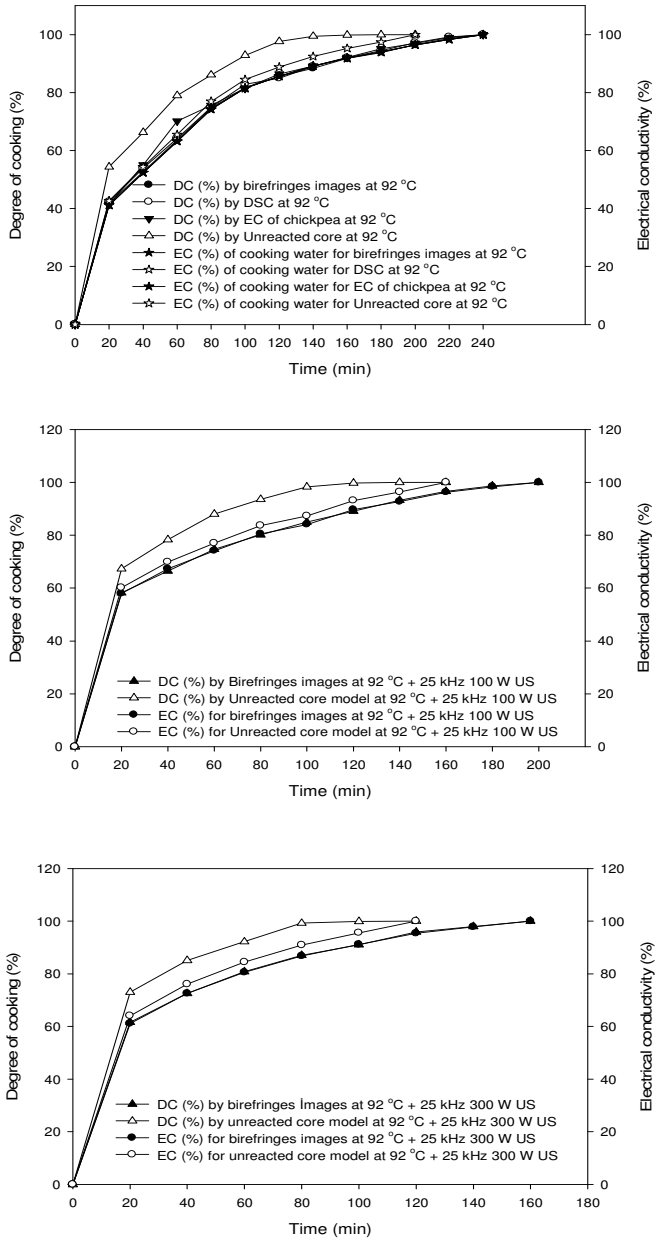


Figure 4.49. Degree of cooking (%) and electrical conductivity (%) of cooking water relation to time at 92 °C without and with US for unreacted-core model, birefringes images, DSC and electrical conductivity of chickpea methods

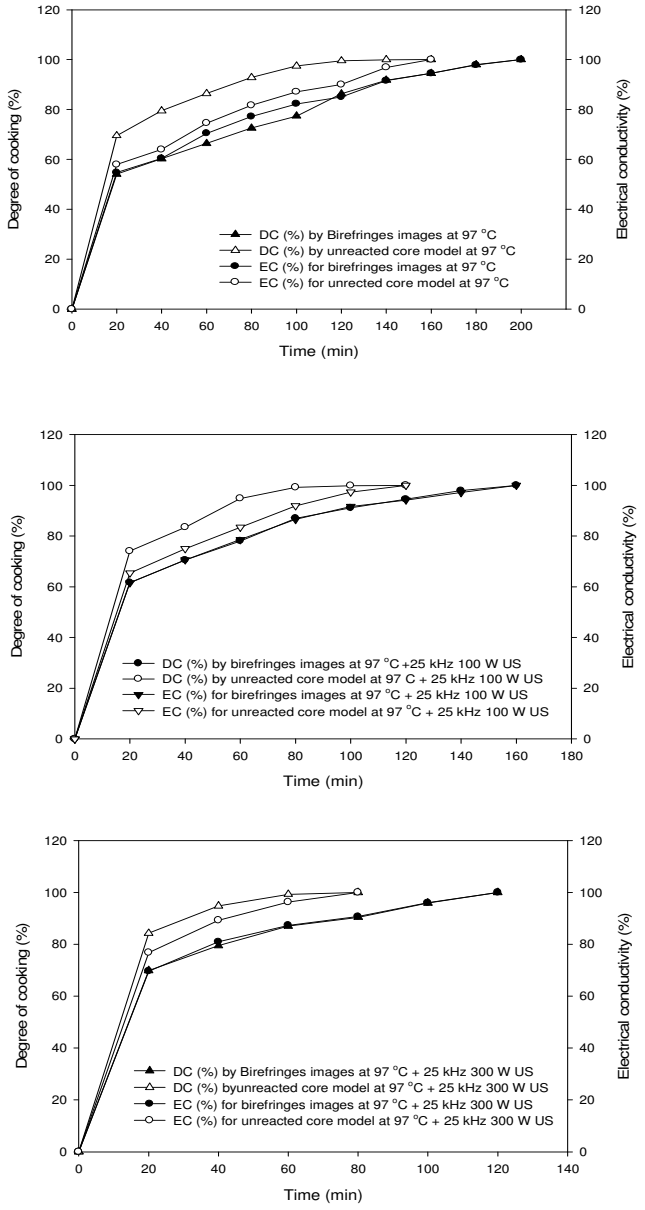


Figure 4.50. Degree of cooking (%) and electrical conductivity (%) of cooking water relation to time at 97 ^{o}C without and with US for unreacted-core model and birefringes images methods

The correlation of the degree of cooking by birefringes images and unreacted-core methods versus electrical conductivity of cooking water at 87, 92 and 97 ^{o}C without and with US is depicted in Figure 4.52. The values of the electrical conductivity data was normalized, whereas the lowest data point was defined as 0 % and the highest as 100 %. R^2 values (0.9941 to 1) showed a good linear relationship between the degree

of cooking values by both unreacted-core and birefringes images methods. These results were similar to study of Bauer and Knorr (2004) with correlation coefficient (R^2) of 0.9653. Moreover, the slopes of the fitted curves were almost 1 (Y ≈X) providing that there was a conformity of the degree of cooking and the electrical conductivity for all methods used in this research.

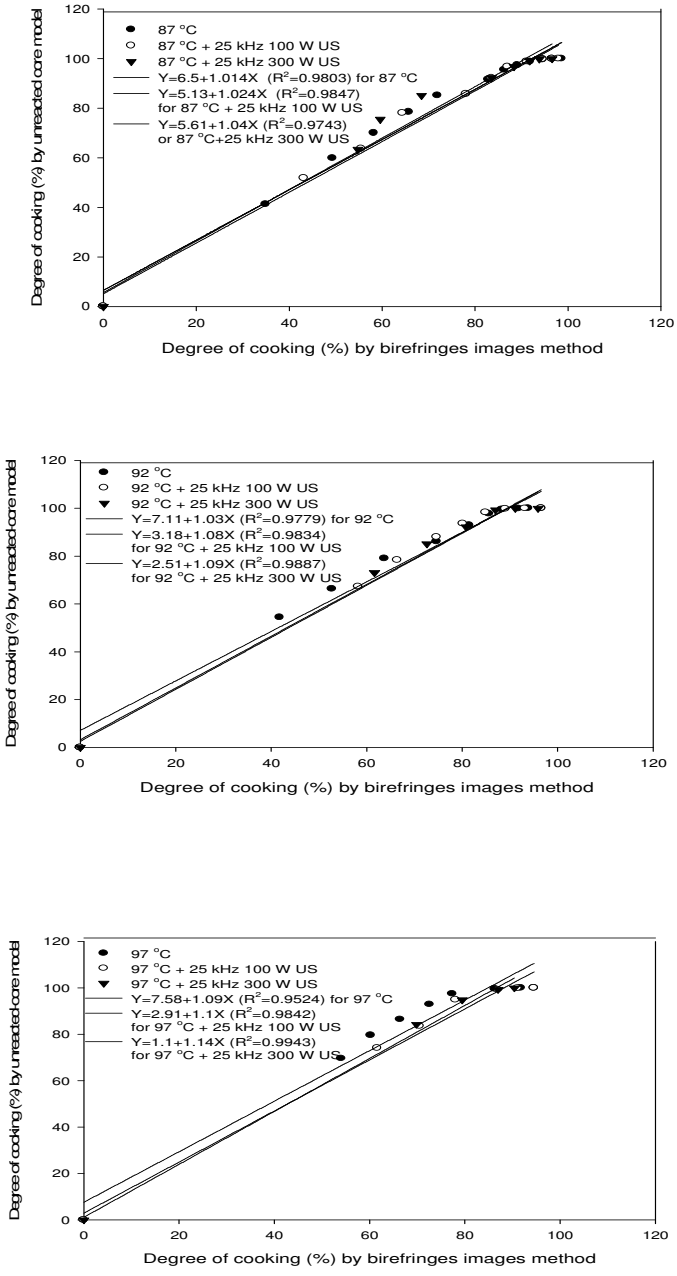


Figure 4.51. DC (%) by unreacted-core model versus DC (%) by birefringes images at 87, 92 and 97 °C without and with US and resulting adjusted curves

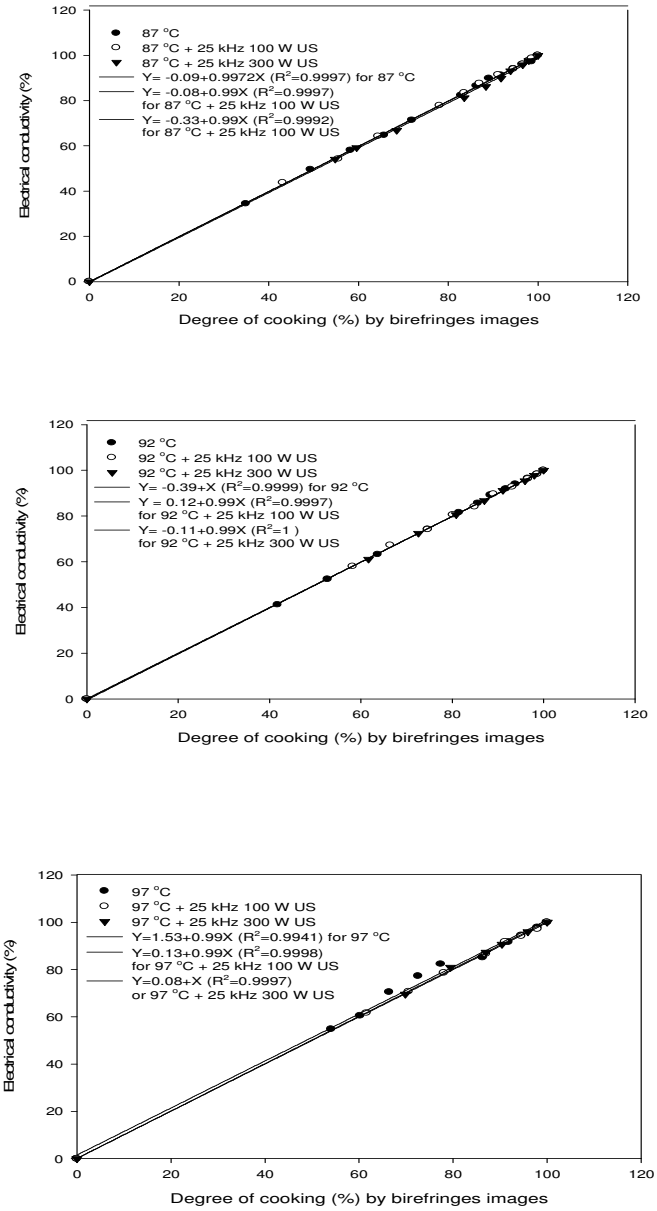


Figure 4.52. DC (%) by birefringes images versus electrical conductivity (%) at 87, 92 and 97 ^{o}C without and with US and the resulting adjusted curves

Degree of cooking (%) by birefringes images, unreacted-core model and EC of chickpea seed methods versus degree of cooking (%) by DSC method at 92 ^{o}C and the resulting adjusted curves are illustrated in Figure 4.53. Similarly, Figure 4.55 shows the relation of degree of cooking (%) by electrical conductivity of chickpea seed, DSC and unreacted-core models versus degree of cooking (%) by birefringes

images method at 92 °C and the resulting adjusted curves. Also, degree of cooking (%) by electrical conductivity of chickpea seed, birefringes images and DSC methods versus degree of cooking (%) by unreacted-core model at 92 °C and the resulting adjusted curves is given in Figure 4.56. From Figures 4.53-4.55, R^2 of fitted curves of all methods at 92 °C were found in between 0.9779 and 0.9997.

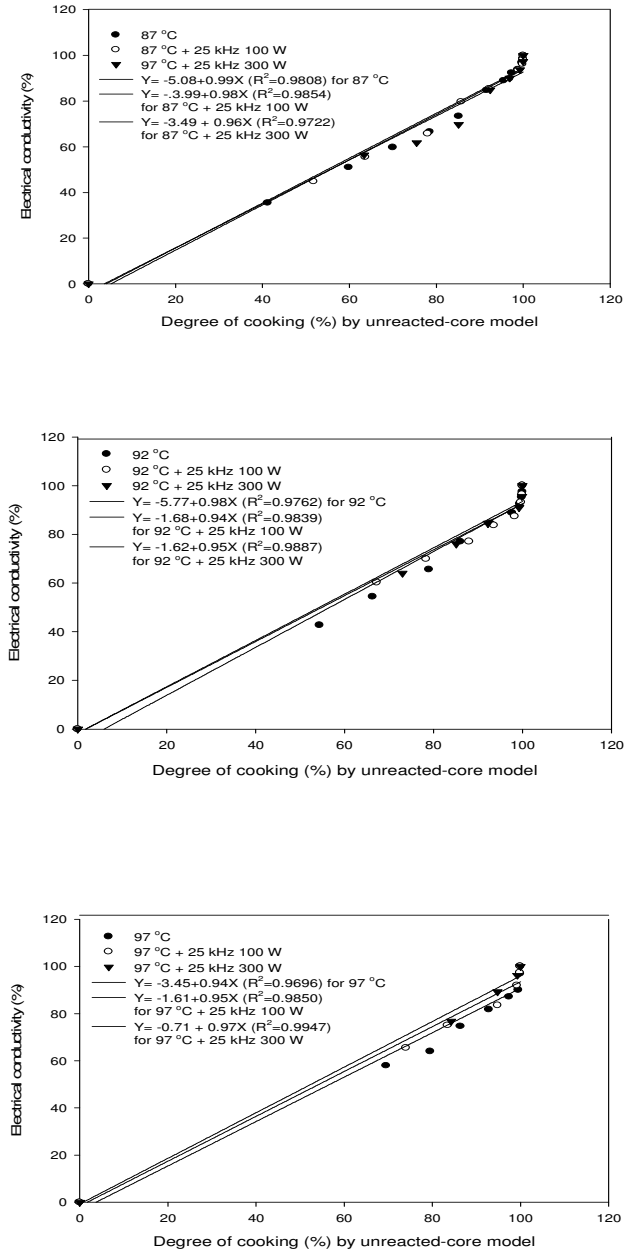


Figure 4.53. DC (%) by unreacted-core model versus electrical conductivity (%) at 87, 92 and 97 °C without and with US and the resulting adjusted curves

Measurement of the degree of cooking as a function of the treatment such as US, power of US, temperature based on birefringence, DSC, unreacted-core and electrical conductivity of chickpea seed resulted in similar curves, because the physicochemical processes involved occur simultaneously.

Consequently, the electrical conductivity corresponds with the degree of cooking of chickpea and an effective method for quick determination of starch gelatinization. The cooking time (τ) of chickpea found at 92 ^{o}C by birefringes images was 240 min which was the same value for the DSC and EC of chickpea seed part. But, at this temperature, τ-value was found as 183 min by unreacted-core model which is lower than 240 min due to different mechanisms of models. 25 kHz 100 W US application represented a 40 min reduction in cooking time at each cooking temperature of chickpea. On the other hand, 25 kHz 300 W US application had 80 min decrease in cooking time of chickpea.

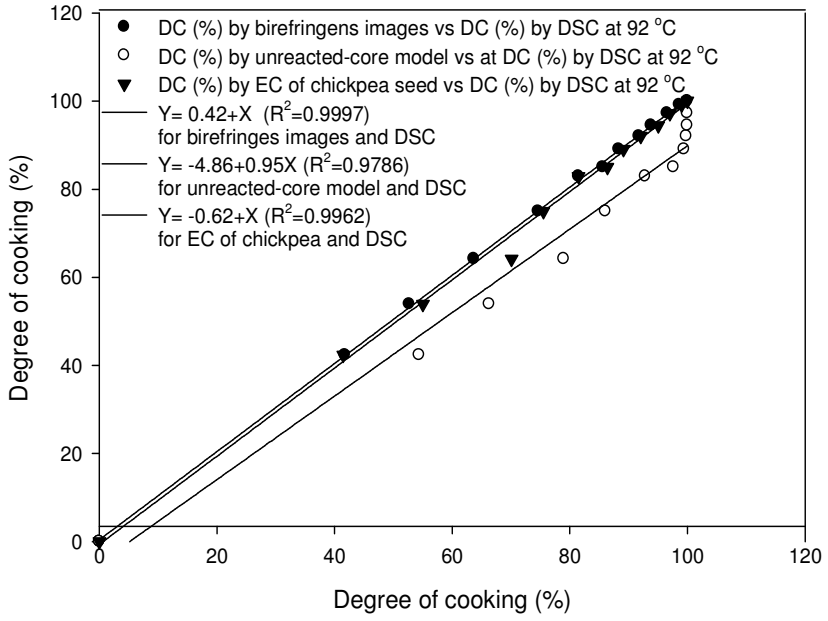


Figure 4.54. DC (%) by birefringes images, unreacted-core model and EC of chickpea methods versus DC (%) by DSC method at 92 ^{o}C and the resulting adjusted curves

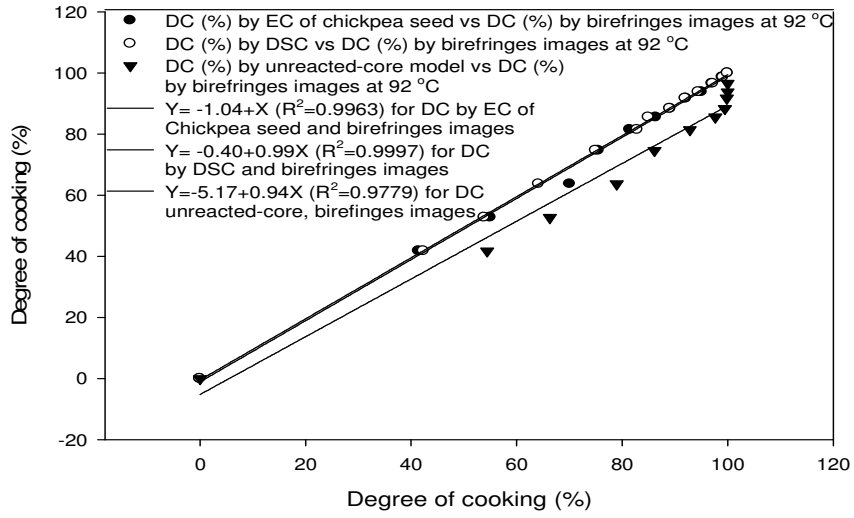


Figure 4.55. DC (%) by EC of chickpea, DSC, and unreacted-core model versus DC (%) by birefringes images method at 92 °C and the resulting adjusted curves

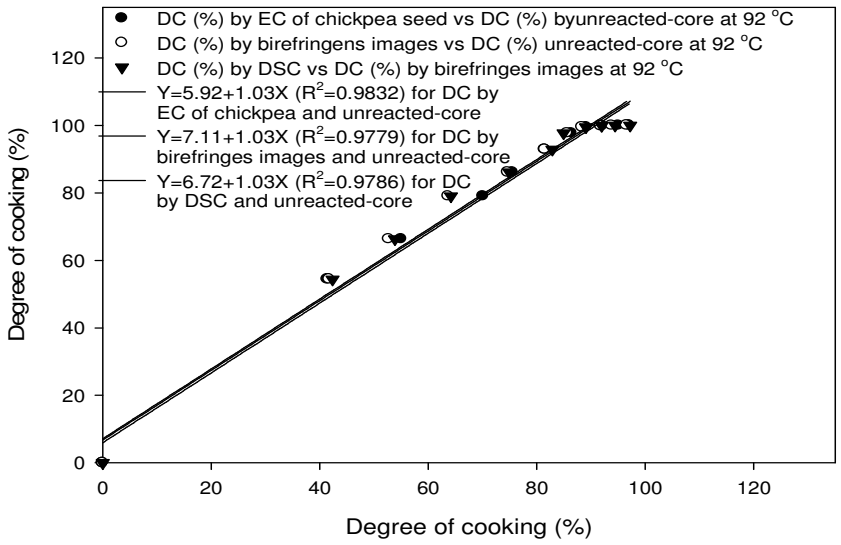


Figure 4.56. DC (%) by EC of chickpea, birefringes images and DSC methods versus DC (%) by unreacted-core model at 92 °C and the resulting adjusted curves

CHAPTER V

CONCLUSIONS

The study on the ultrasounds applied chickpeas revealed the following conclusions:

1. Water absorption rate of chickpea significantly increased ($P<0.05$) with increasing of soaking time, temperature and power of ultrasound (100-300 W). High ultrasound frequencies (40 kHz) did not significantly ($P>0.05$) affect the water absorption of chickpea during soaking. The frequency is inversely proportional to the bubble size. High frequency ultrasound (40 kHz) generates small cavitation bubbles resulting in lower pressures in the cavitation zone. As the frequency increases the cavitation zone becomes less violent and no cavitation is observed anymore.
2. Soaking time, temperature, low frequency ultrasounds (25 kHz) and power of ultrasounds (100 to 300 W) had significant effect ($P<0.05$) on the moisture content and texture (F_{max}) of chickpea. Increase in soaking time and temperature from 0 to 210 min and from 20 to 97 ^{o}C increased the m.c. (% g/g, d.b.) from 11.58 to 151.97 and decreased the texture (F_{max}, N) of chickpea from 67.73 to 1.30. When soaking time (0 to 120 min), temperature (20 to 97 ^{o}C) increased, 25 kHz 100 W US resulted to increase the m.c. (% g/g, d.b.) from 11.58 to 151.23 and to decrease the texture (F_{max}, N) of chickpea from 67.73 to 1.46. Similarly, 25 kHz 300 W US increased the m.c. (% g/g, d.b.) from 11.58 to 157.57 and decreased the texture (F_{max}, N) of chickpea from 67.73 to 1.43.
3. Fick's, Normalized Weibull, Peleg and Asymptotic first order models were successfully fitted to correlate water absorption of chickpea with soaking time and temperature (R^2=0.9894-0.9999). Fick's and Normalized Weibull diffusion constant (D_{eff}), Peleg rate constant (K_1) and hydration rate constant (k_H) of Asymptotic first order model increased with temperature (20 to 97 ^{o}C) and ultrasound treatments (25 kHz 100 W, 40 kHz 100 W and 25 kHz 300 W) due to increasing of water diffusion of chickpea during soaking.

4. During soaking of chickpea, texture of chickpea was modeled as a function of time and temperature with Asymptotic first order model with a good correlation coefficient range of 0.9914-0.9999. Texture model rate constant (k_F) increased with temperature and ultrasound treatments (25 kHz 100 W and 25 kHz 300 W US).
5. Cooking time, temperature, ultrasound treatment and power of ultrasounds used significantly ($P<0.05$) increased the electrical conductivity and turbidity of cooking water part decreased the electrical conductivity of chickpea part during cooking due to dissolved solids, electrolytes such as organic compounds, pigments, protein, sugars, starch, vitamins etc. leaching into the water.
6. During cooking, color of cooking water changed at each temperature with ultrasound treatment and power of ultrasound used due to the coloring compounds and starch leached into water and lightness of water increased during cooking of chickpea in contrast to decrease during cooking of soybean because of its different bran structure and chemical composition.
7. The unreacted-core model very well fitted (R^2=0.8949-0.9727) to the gelatinization of the chickpea starch. The goodness of fit of the model and the estimation of gelatinization kinetic data showed that the model can be used for the gelatinization of chickpea starch.
8. During atmospheric cooking operation without soaking, cooking time (for 100 % cooking) found by birefringes images and unreacted-core models was 280 and 232, 240 and 183, 200 and 147 minutes for chickpea at 87, 92 and 97 °C, respectively. Cooking time of 25 kHz 100 W US treated chickpea found both by birefringes images and unreacted-core models was 240 and 186, 200 and 146, 160 and 110 minutes for chickpea at 87, 92 and 97 ^{o}C, respectively. Cooking time for 25 kHz 300 W US applied chickpea found both by birefringes images and unreacted-core models was 200 and 150, 160 and 111, 120 and 76 minutes at 87, 92 and 97 ^{o}C, respectively.
9. R^2 values for the degree of cooking (%) by birefringes images and unreacted-core model methods versus the electrical conductivity (%) were found between 0.9941 and 1. Moreover, the slopes of the fitted curves were almost 1 ($Y \approx X$) providing that there was a conformity of the degree of cooking and the electrical conductivity for all methods used in this study.

10. R^2 of fitted curves of degree of cooking by Birefringes images, unreacted-core model, DSC and electrical conductivity methods at 92 ^oC were compared and found as between 0.9779 and 0.9997.
11. Measurement of the degree of cooking as a function of the treatment such as US, power of US, temperature based on birefringence, DSC, unreacted-core and electrical conductivity of chickpea seed gave similar curves, because the physicochemical processes involved occur simultaneously.
12. There was a good linear relationship between the degree of cooking and the electrical conductivity data for cooking water and chickpea parts. Electrical conductivity of cooked chickpea part decreased while that of cooking water part increased. Since the electrical conductivity of cooking water and seed parts correlated well with the degree of cooking it could be applied as method for the quick and simple determination of starch gelatinization.
13. The cooking time (τ) of chickpea found at 92 ^oC by birefringes images was 240 min which was the same value for the DSC and EC of chickpea seed part. But, at this temperature, τ-value was found as 183 min by unreacted-core model which is lower than 240 min due to different mechanisms of models. 25 kHz 100 W and 25 kHz 300 W US treatments represented 40 and 80 min benefit for cooking time at each cooking temperature of chickpea.
14. Cooking temperature of chickpea found by DSC method was 61.13 ^oC that is confirmed with values (60-70 ^oC) obtained from birefringes images method, moisture absorption and texture models during soaking.

Thermosonication decreased soaking and cooking times of chickpea, however, complete and detailed energy analysis should be performed to see if the process lowers the energy requirement. As a recommendation, effect of thermosonication on chickpea quality is another area swhich should be studied in depth. Further studies are needed to improve the processing equipment in order to apply this technology in the food industry. Also, frequencies of US lower than 25 kHz and powers higher than 300 W may further decrease time of soaking and cooking operations of chickpea. For optimization of thermosonication, ultrasonic horns can be used with parallel to ultrasonic tanks for soaking and cooking of chickpeas.

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APPENDICES

Table A1. Summary of multiple range analysis (Duncan test) on moisture contents (%, d.b.) of soaked chickpeas as a function of processing time and temperature

Time (min)	Moisture content (%, d.b)								
	20 °C	30 °C	40 °C	50 °C	60 °C	70 °C	87 °C	92 °C	97 °C
0	$11.58^{a,1}$	$11.58^{a,1}$	$11.58^{a,1}$	$11.58^{a,1}$	$11.58^{a,1}$	$11.58^{a,1}$	$11.58^{a,1}$	$11.58^{a,1}$	$11.58^{a,1}$
30	$33.55^{b,1}$	$37.40^{b,2}$	$46.10^{b,3}$	$62.36^{b,4}$	$70.61^{b,5}$	$76.09^{b,6}$	$86.85^{b,7}$	$91.54^{b,8}$	$97.05^{b,9}$
60	$43.88^{c,1}$	$57.54^{c,2}$	$62.58^{c,3}$	$84.70^{c,4}$	$97.89^{c,5}$	$99.01^{c,6}$	$108.58^{c,7}$	$111.16^{c,8}$	$121.06^{c,9}$
90	$56.27^{d,1}$	$66.99^{d,2}$	$80.53^{d,3}$	$95.43^{d,4}$	$108.05^{d,5}$	$110.19^{d,6}$	$122.38^{d,7}$	$125.43^{d,8}$	$136.49^{d,9}$
120	$65.50^{e,1}$	$78.98^{e,2}$	$88.24^{e,3}$	$108.69^{e,4}$	$115.63^{e,5}$	$119.45^{e,6}$	$129.30^{e,7}$	$131.36^{e,8}$	$144.71^{e,9}$
150	$72.52^{f,1}$	$82.27^{f,2}$	$97.30^{f,3}$	$115.84^{f,4}$	$124.02^{f,5}$	$126.35^{f,6}$	$135.41^{f,7}$	$137.76^{f,8}$	$148.59^{f,9}$
180	$76.91^{g,1}$	$84.53^{g,2}$	$101.90^{g,3}$	$120.82^{g,4}$	$126.57^{g,5}$	$129.78^{g,6}$	$138.37^{g,7}$	$142.44^{g,8}$	$150.72^{g,9}$
210	$81.93^{h,1}$	$93.76^{h,2}$	$110.18^{h,3}$	$122.71^{h,4}$	$128.99^{h,5}$	$130.68^{h,6}$	$140.17^{h,7}$	$142.67^{h,8}$	$151.97^{h,9}$

[a-h] Indicate statistical differences between each row at constant times, α=0.05,
[1-9] Indicate statistical differences between each column at constant temperatures, α=0.05.

Table A2. Summary of multiple range analysis (Duncan test) on moisture contents (%, d.b.) of soaked chickpeas at 20 and 30 °C with and without ultrasound treatments

Time (min)	Moisture content (%, d.b)			
	20 °C	20 °C+40 kHz 100 W	20 °C+25 kHz 100 W	20 °C+25 kHz 300 W
0	11.58^{a}	11.58^{a}	11.58^{a}	11.58^{a}
30	33.55^{a}	34.82^{b}	40.61^{c}	43.18^{d}
60	43.88^{a}	44.97^{b}	54.06^{c}	55.93^{d}
90	56.27^{b}	56.24^{a}	65.76^{c}	69.60^{d}
120	65.50^{b}	64.60^{a}	70.64^{c}	74.85^{d}
150	72.52^{b}	70.24^{a}	78.20^{c}	86.92^{d}
180	76.91^{b}	76.55^{a}	85.14^{c}	91.89^{d}
210	81.93^{b}	80.54^{a}	89.48^{c}	95.66^{d}
240	88.39^{b}	86.14^{a}	95.14^{c}	102.30^{d}
270	90.63^{a}	92.05^{b}	99.12^{c}	106.56^{d}
300	98.06^{b}	97.69^{a}	103.11^{c}	111.56^{d}
	30 °C	30 °C+40 kHz 100 W	30 °C+25 kHz 100 W	30 °C+25 kHz 300 W
0	11.58^{a}	11.58^{a}	11.58^{a}	11.58^{a}
30	37.40^{a}	39.79^{b}	41.04^{c}	49.85^{d}
60	57.54^{a}	57.79^{b}	60.40^{c}	60.88^{d}
90	66.99^{b}	66.24^{a}	73.77^{c}	72.19^{d}
120	78.98^{b}	78.37^{a}	79.63^{c}	90.31^{d}
150	82.27^{b}	81.72^{a}	86.40^{c}	100.06^{d}
180	84.53^{a}	84.87^{b}	92.52^{c}	107.72^{d}
210	93.76^{b}	93.20^{a}	98.00^{c}	111.05^{d}
240	104.78^{b}	104.40^{a}	106.25^{c}	113.29^{d}
270	107.75^{b}	107.39^{a}	108.23^{c}	115.60^{d}
300	109.96^{b}	109.75^{a}	112.03^{c}	118.85^{d}

[a-d] Indicate statistical differences between each column at constant temperatures, α=0.05.

Table A3. Summary of multiple range analysis (Duncan test) on moisture contents (%, d.b.) of soaked chickpeas at 40, 50, 60 and 70 °C with and without ultrasound treatments

Time (min)	Moisture content (%, d.b)			
	40 °C	**40 °C+40 kHz 100 W**	**40 °C+25 kHz 100 W**	**40 °C+25 kHz 300 W**
0	11.58^{a}	11.58^{a}	11.58^{a}	11.58^{a}
30	46.10^{b}	45.55^{a}	54.71^{c}	59.86^{d}
60	62.58^{a}	63.92^{b}	72.20^{c}	77.41^{d}
90	80.53^{b}	78.70^{a}	84.23^{c}	97.25^{d}
120	88.24^{a}	89.43^{b}	93.59^{c}	107.08^{d}
150	97.30^{a}	100.21^{b}	109.76^{c}	115.29^{d}
180	101.90^{b}	100.62^{a}	115.10^{c}	121.19^{d}
210	110.18^{b}	109.70^{a}	118.23^{c}	128.12^{d}
240	111.00^{a}	112.58^{b}	122.29^{c}	127.27^{d}
270	117.95^{b}	116.90^{a}	125.34^{c}	128.00^{d}
300	121.84^{b}	120.49^{a}	125.47^{c}	128.12^{d}
	50 °C	**50 °C+40 kHz 100 W**	**50 °C+25 kHz 100 W**	**50 °C+25 kHz 300 W**
0	11.58^{a}	11.58^{a}	11.58^{a}	11.58^{a}
30	62.36^{b}	57.74^{a}	64.74^{c}	75.35^{d}
60	84.70^{a}	86.78^{b}	91.31^{c}	109.25^{d}
90	95.43^{a}	101.14^{b}	106.73^{c}	117.07^{d}
120	108.69^{b}	108.19^{a}	115.86^{c}	121.01^{d}
150	115.84^{a}	117.20^{b}	123.87^{c}	128.71^{d}
180	120.82^{b}	119.15^{a}	126.11^{c}	131.34^{d}
210	122.71^{a}	123.12^{b}	127.22^{c}	134.59^{d}
	60 °C	**60 °C+40 kHz 100 W**	**60 °C+25 kHz 100 W**	**60 °C+25 kHz 300 W**
0	11.58^{a}	11.58^{a}	11.58^{a}	11.58^{a}
30	70.61^{b}	69.73^{a}	72.96^{c}	80.35^{d}
60	97.89^{b}	96.90^{a}	99.89^{c}	111.50^{d}
90	108.05^{a}	108.36^{b}	113.06^{c}	120.27^{d}
120	115.63^{b}	114.91^{a}	119.91^{c}	126.34^{d}
150	124.02^{b}	124.00^{a}	127.76^{c}	130.71^{d}
180	126.57^{b}	126.51^{a}	128.99^{c}	132.14^{d}
210	128.99^{b}	127.93^{a}	130.74^{c}	134.92^{d}
	70 °C	**70 °C+40 kHz 100 W**	**70 °C+25 kHz 100 W**	**70 °C+25 kHz 300 W**
0	11.58^{a}	11.58^{a}	11.58^{a}	11.58^{a}
30	76.09^{b}	74.13^{a}	82.82^{c}	84.81^{d}
60	99.01^{b}	98.09^{a}	105.95^{c}	112.69^{d}
90	110.19^{b}	109.72^{a}	114.24^{c}	124.46^{d}
120	119.45^{b}	115.87^{a}	122.16^{c}	129.46^{d}
150	126.35^{b}	125.11^{a}	129.20^{c}	131.97^{d}
180	129.78^{b}	128.64^{a}	131.50^{c}	133.72^{d}
210	130.68^{b}	129.32^{a}	132.30^{c}	135.78^{d}

[a-d] Indicate statistical differences between each column at constant temperatures, α=0.05.

Table A4. Summary of multiple range analysis (Duncan test) on moisture contents (%, d.b.) of soaked chickpeas at 87, 92 and 97 °C with and without ultrasound treatments

Time (min)	Moisture content (%, d.b)			
	87 °C	**87 °C+40 kHz 100 W**	**87 °C+25 kHz 100 W**	**87 °C+25 kHz 300 W**
0	11.58[a]	11.58[a]	11.58[a]	11.58[a]
30	86.85[b]	85.33[a]	92.25[c]	108.65[d]
60	108.58[b]	107.48[a]	115.49[c]	128.81[d]
90	122.38[b]	122.13[a]	128.16[c]	142.46[d]
120	129.30[a]	130.03[b]	132.48[c]	148.93[d]
150	135.41[a]	136.01[b]	138.23[c]	150.90[d]
	92 °C	**92 °C+40 kHz 100 W**	**92 °C+25 kHz 100 W**	**92 °C+25 kHz 300 W**
0	11.58[a]	11.58[a]	11.58[a]	11.58[a]
30	91.54[b]	89.91[a]	102.61[c]	115.27[d]
60	111.16[a]	112.34[b]	122.37[c]	132.71[d]
90	125.43[b]	124.29[a]	139.77[c]	147.79[d]
120	131.36[b]	131.23[a]	146.11[c]	151.24[d]
150	137.76[b]	137.75[a]	150.54[b]	154.23[c]
	97 °C	**97 °C+40 kHz 100 W**	**97 °C+25 kHz 100 W**	**97 °C+25 kHz 300 W**
0	11.58[a]	11.58[a]	11.58[a]	11.58[a]
30	97.05[b]	96.49[a]	106.98[c]	122.78[d]
60	121.06[b]	119.59[a]	139.07[c]	145.37[d]
90	136.49[b]	136.25[a]	148.67[c]	153.97[d]
120	144.71[a]	144.91[b]	151.23[c]	157.57[d]
150	148.59[a]	148.61[b]	158.93[c]	165.45[d]

[a-d] Indicate statistical differences between each column at constant temperatures, α=0.05.

Table A5. Average experimental F_{max} values, standard deviations and residuals of soaked chickpeas at 20 ^{o}C without and with US at different times for texture model

Time (min)	F_{max} (N)$_{exp}$	Residuals	F_{max} (N)$_{exp}$	Residuals	F_{max} (N)$_{exp}$	Residuals
	20 ^{o}C		20 ^{o}C + 25 kHz 100 W		20 ^{o}C + 25 kHz 300 W	
0	67.73±4.57	1.48	67.73±4.57	2.90	67.73±4.57	4.65
20	52.90±6.34	-1.66	46.27±7.69	-4.24	42.89±5.94	-7.00
40	42.11±4.48	-2.89	41.05±7.39	-2.53	37.97±4.30	-2.56
60	37.29±3.67	0.11	34.25±4.25	0.07	33.95±6.38	0.54
80	33.13±5.68	2.34	30.80±3.02	3.66	28.88±5.70	2.85
100	27.40±3.18	1.84	26.40±3.82	2.45	23.97±3.90	3.95
120	24.05±6.29	2.76	20.49±4.52	1.72	17.81±4.60	1.72
140	18.74±3.19	0.95	15.72±3.37	0.32	13.65±2.65	0.64
160	13.42±2.63	-1.51	11.68 ±2.07	-1.01	9.06±1.91	-1.53
180	10.19±2.49	-2.41	7.91±2.60	-2.49	7.17±2.24	-1.52
200	9.26±1.03	-1.42	6.76±1.87	-1.58	5.55±2.19	-1.75
220	8.31±1.85	-0.81	6.56±2.66	-0.76	5.19±1.93	-0.83
240	7.39±0.56	-0.45	6.11±1.61	-0.07	4.62±1.41	-0.49
260	6.57±2.47	-0.23	5.30±2.11	0.04	4.14±1.38	-0.25
280	5.42±1.27	-0.52	4.17±1.40	-0.35	3.83±1.44	0.01
300	5.21±0.86	-0.03	3.84±1.35	-0.08	3.54±1.14	0.17
320	4.74±1.10	0.07	3.62±1.10	-0.02	3.45±1.29	0.12
340	4.59±1.50	0.39	3.54±0.89	0.09	3.02±1.02	0.27
360	4.23±0.98	0.41	3.38±0.80	0.24	2.76±0.66	0.22
380	3.65±1.28	0.14	3.32±0.97	0.33	2.68±0.93	0.31
400	3.54±1.32	0.29	2.97±0.62	0.39	2.48±0.56	0.24
420	3.46±1.40	0.42	2.53±0.74	0.41	2.25±0.48	0.22
440	3.36±1.01	0.49	2.48±0.69	0.51		
460	2.98±0.59	0.25				
480	2.69±0.73	0.07				
500	2.48±0.63	-0.04				

Table A6. ANOVA for texture (F_{max}) of chickpeas without and with US treatments at different temperatures (^{o}C) and soaking times (min)

Source	Type III SS	df	Mean Square	F	Sig.
Corrected Model	250791.307[a]	386	649.718	4.925×10^{17}	0.000
Intercept	19192.528	1	19192.528	1.455×10^{19}	0.000
Time	228195.528	25	9127.821	6.919×10^{18}	0.000
Temp.	19156.844	8	2394.605	1.815×10^{18}	0.000
USPower	63.488	1	63.488	4.812×10^{16}	0.000
Time * Temp.	10443.516	108	96.699	7.330×10^{16}	0.000
Time * USPower	236.011	21	11.239	8.519×10^{15}	0.000
Temp. * USPower	15.846	8	1.981	1.501×10^{15}	0.000
Time* Temp. * USPower	131.456	87	1.511	1.145×10^{15}	0.000
Error	5.105×10^{-13}	387	1.319×10^{-15}		
Total	369909.203	774			
Corrected Total	250791.307	773			

a. R Squared = 1.000 (Adjusted R Squared = 1.000)

Table A7. Average experimental F_{max} values, standard deviations and residuals of soaked chickpeas at 30 and 40 ^{o}C without and with US at different times for texture model

Time (min)	F_{max} (N)$_{exp}$	Residuals	F_{max} (N)$_{exp}$	Residuals	Force (N)$_{exp}$	Residuals
	30 ^{o}C		**30 ^{o}C + 25 kHz 100 W**		**30 ^{o}C + 25 kHz 300 W**	
0	67.73±4.57	2.90	67.73±4.57	2.65	67.73±4.57	2.47
20	44.10±7.06	-5.12	42.29±3.76	-5.13	40.82±3.60	-5.27
40	36.44±5.30	-1.03	34.09±5.45	-0.58	32.71±3.64	0.02
60	30.14±4.59	1.50	27.08±3.07	1.61	24.89±5.87	1.56
80	25.17±3.48	3.18	22.28±4.75	3.45	20.38±3.39	3.59
100	17.08±1.71	0.10	14.13±2.79	0.10	12.82±2.08	0.60
120	13.90±3.16	0.68	9.86±2.69	-0.71	7.38±2.21	-1.64
140	9.04±1.80	-1.35	7.37±1.80	-0.70	6.09±1.58	-0.70
160	7.10±3.64	-1.15	5.59±1.40	-0.68	4.24±0.95	-0.99
180	6.30±2.34	-0.35	5.17±2.00	0.20	4.03±0.86	-0.11
200	5.71±1.92	0.27	4.06±0.72	0.03	3.48±1.01	0.10
220	5.19±1.57	0.65	3.46±0.81	0.11	3.15±0.65	0.30
240	4.16±0.79	0.31	3.08±0.84	0.22	2.94±0.52	0.46
260	3.95±1.26	0.61	2.58±0.78	0.07	2.52±0.62	0.30
280	2.98±0.74	0.03	2.12±0.49	-0.13	2.08±0.49	0.04
300	2.37±0.63	-0.29	1.92±0.60	-0.15	1.77±0.69	-0.14
320	2.29±0.55	-0.15	1.81±0.36	-0.13	1.59±0.36	-0.23
340	2.15±0.85	-0.13	1.75±0.49	-0.09	1.39±0.31	-0.37
360	1.95±0.37	-0.20	1.64±0.46	-0.13		
380	1.85±0.51	-0.21				
400	1.75±0.44	-0.24				
	40 ^{o}C		**40 ^{o}C + 25 kHz 100 W**		**40 ^{o}C + 25 kHz 300 W**	
0	67.73±4.57	2.51	67.73±4.57	2.92	67.73±4.57	1.57
20	40.42±3.29	-4.78	36.42±2.82	-6.38	34.26±4.55	-4.65
40	31.03±2.98	-0.47	29.08±6.56	0.56	27.40±6.39	2.24
60	23.23±3.79	1.10	20.67±4.61	1.41	18.31±2.78	2.39
80	17.36±5.57	1.65	15.59±4.08	2.34	11.60±3.50	-0.32
100	13.27±3.12	1.96	11.18±5.31	1.83	7.03±2.58	-0.10
120	8.08±3.56	-0.23	6.42±3.14	-0.40	4.85±2.09	-0.89
140	7.13±2.72	0.88	5.89±1.20	0.71	4.11±1.24	-0.12
160	4.21±2.49	-0.63	3.83±1.09	-0.29	3.10±0.91	-0.17
180	3.18±1.10	-0.70	2.87±0.73	-0.56	2.59±0.83	-0.07
200	2.81±0.81	-0.41	2.80±0.54	-0.18	2.37±0.76	0.09
220	2.69±0.52	-0.08	2.64±0.44	-0.05	2.06±0.44	0.02
240	2.57±0.74	0.11	2.37±0.38	-0.13	2.12±0.59	0.23
260	2.46±0.68	0.21	2.16±0.47	-0.22	1.86±0.34	0.07
280	2.09±0.60	-0.01	1.87±0.60	-0.43	1.69±0.34	-0.04
300	1.80±0.79	-0.20	1.70±0.62	-0.55	1.60±0.31	-0.09
320	1.70±0.58	-0.24	1.65±0.53	-0.57		
340	1.59±0.45	-0.30				
360	1.48±0.20	-0.38				

Table A8. Average experimental F_{max} values, standard deviations and residuals of soaked chickpeas at 50, 60 and 70 °C without and with US at different times for texture model

Time (min)	F_{max} (N)$_{exp}$	Residuals	F_{max} (N)$_{exp}$	Residuals	Force (N)$_{exp}$	Residuals
	50 °C		**50 °C + 25 kHz 100 W**		**50 °C + 25 kHz 300 W**	
0	67.73±4.57	1.86	67.73±4.57	1.36	67.73±4.57	1.18
20	33.81±5.13	-4.83	25.99±5.51	-5.10	18.72±3.36	-4.26
40	24.55±5.63	1.37	18.29±3.67	2.82	12.97±3.18	3.08
60	15.12±6.58	0.72	11.36±4.78	2.80	8.73±3.03	2.29
80	10.87±3.13	1.45	7.19±3.10	1.68	6.30±2.43	-1.45
100	7.95±5.05	1.36	6.02±1.97	1.87	4.23±1.27	-0.36
120	6.51±1.70	1.52	4.21±1.26	0.66	3.22±0.87	-0.16
140	5.86±1.70	1.78	3.01±0.65	-0.28	2.42±0.71	-0.19
160	3.61±1.27	0.05	2.58±0.61	-0.59	2.31±0.71	0.11
180	2.75±0.82	-0.51	2.53±0.72	-0.59	2.27±0.72	0.30
200	2.58±0.65	-0.52	2.22±0.56	-0.88	2.02±0.89	0.17
220	2.43±0.73	-0.57	2.00±0.78	-1.09	1.64±0.52	0.06
240	2.32±0.83	-0.63	1.89±0.75	-1.19		
260	2.09±0.53	-0.83	1.61±0.40	-1.47		
280	1.89±0.60	-1.01				
300	1.69±0.17	-1.20				
	60 °C		**60 °C + 25 kHz 100 W**		**60 °C + 25 kHz 300 W**	
0	67.73±4.57	1.41	67.73±4.57	0.62	67.73±4.57	0.19
20	29.17±5.17	-4.25	22.94±3.15	-2.88	14.06±6.57	-1.76
40	18.08±6.88	0.52	12.95±6.14	1.98	9.09±4.44	3.57
60	12.60±5.15	2.68	8.01±3.76	2.38	6.06±2.79	2.59
80	9.49±2.38	3.25	6.05±2.06	2.35	4.23±1.66	1.16
100	5.89±2.48	1.42	4.08±1.59	1.07	3.02±1.41	0.04
120	4.21±2.19	0.60	3.40±1.49	0.64	2.72±1.08	-0.25
140	3.40±1.78	0.20	2.28±1.46	-0.39	1.68±0.27	-1.28
160	2.65±1.38	-0.35	1.60±0.52	-1.04	1.58±0.46	-1.38
180	2.06±1.23	-0.85	1.55±0.62	-1.08	1.52±0.46	-1.44
200	1.81±0.37	-1.05	1.44±0.58	-1.19	1.55±0.26	-1.41
220	1.70±0.83	-1.14	1.42±0.45	-1.20		
240	1.62±0.44	-1.21	1.37±0.56	-1.25		
260	1.59±0.21	-1.23				
	70 °C		**70 °C + 25 kHz 100 W**		**70 °C + 25 kHz 300 W**	
0	67.73±4.57	0.81	67.73±4.57	0.38	67.73±4.57	0.08
20	28.12±3.91	-2.76	22.40±7.80	-2.01	13.28±4.37	-0.82
40	15.57±2.87	0.55	11.85±1.96	2.00	6.29±1.68	1.71
60	10.39±1.71	2.35	6.26±2.36	1.35	5.05±1.97	2.16
80	6.99±2.53	2.03	4.30±1.64	1.06	3.08±1.42	0.49
100	4.68±1.42	1.07	3.08±1.17	0.41	2.67±0.60	0.13
120	3.70±1.17	0.69	2.73±0.87	0.25	2.26±0.56	-0.27
140	2.43±0.89	-0.32	2.03±0.57	-0.38	1.84±0.60	-0.69
160	2.04±1.11	-0.59	1.86±0.27	-0.53	1.77±0.51	-0.76
180	1.81±0.23	-0.77	1.65±0.40	-0.73	1.60±0.27	-0.93
200	1.57±0.35	-0.99	1.51±0.35	-0.87	1.43±0.19	-1.10
220	1.53±0.44	-1.02	1.44±0.28	-0.94		
240	1.50±0.30	-1.05				

Table A9. Average experimental F_{max} values, standard deviations and residuals of soaked chickpeas at 87, 92 and 97 °C without and with US at different times for texture model

Time (min)	F_{max} (N)$_{exp}$	Residuals	F_{max} (N)$_{exp}$	Residuals	Force (N)$_{exp}$	Residuals
	87 °C		**87 °C + 25 kHz 100 W**		**87 °C + 25 kHz 300 W**	
0	67.73±4.57	0.99	67.73±4.57	0.06	67.73±4.57	0.05
20	23.99±5.92	-3.89	19.41±2.78	-0.38	11.37±2.25	-0.58
40	15.53±0.98	2.11	7.05±1.18	0.32	5.30±2.12	1.80
60	8.85±1.40	2.98	3.87±0.99	0.71	2.75±0.78	0.54
80	6.56±0.42	1.89	2.84±0.62	0.65	2.12±0.76	0.10
100	3.14±0.39	-0.33	1.78±0.62	-0.14	1.69±0.38	-0.30
120	3.05±0.42	0.10	1.62±0.30	-0.23	1.48±0.33	-0.51
140	2.15±0.35	-0.58	1.55±0.34	-0.28	1.45±0.44	-0.54
160	1.63±0.19	-1.01	1.47±0.34	-0.35	1.43±0.21	-0.56
180	1.50±0.39	-1.10	1.45±0.27	-0.37		
200	1.42±0.35	-1.16				
	92 °C		**92 °C + 25 kHz 100 W**		**92 °C + 25 kHz 300 W**	
0	67.73±4.57	0.80	67.73±4.57	0.23	67.73±4.57	0.04
20	22.97±2.99	-3.63	15.18±3.66	-1.93	9.60±2.63	-0.71
40	13.97±2.92	2.30	9.39±2.21	3.34	6.50±1.92	2.81
60	9.79±1.58	3.64	6.89±1.17	3.27	4.49±1.17	1.56
80	6.35±0.71	2.25	3.04±0.45	-0.05	2.89±0.48	0.05
100	3.58±0.56	0.23	2.82±0.54	-0.15	2.33±0.54	-0.50
120	2.88±0.48	-0.19	2.46±0.31	-0.48	2.15±0.50	-0.68
140	1.81±0.23	-1.15	1.65±0.33	-1.29	1.54±0.27	-1.19
160	1.59±0.24	-1.35	1.51±0.30	-1.43	1.43±0.27	-1.37
180	1.46±0.26	-1.45	1.43±0.23	-1.51		
200	1.45±0.16	-1.45				
	97 °C		**97 °C + 25 kHz 100 W**		**97 °C + 25 kHz 300 W**	
0	67.73±4.57	0.72	67.73±4.57	0.04	67.73±4.57	0.02
20	21.96±3.69	-3.51	11.01±2.27	-0.59	8.30±1.41	-0.36
40	13.80±0.97	2.81	5.38±1.48	1.70	4.29±1.33	1.66
60	8.95±0.26	3.01	4.03±0.90	1.47	2.86±0.71	0.85
80	6.79±0.33	2.61	3.88±0.36	1.48	1.80±0.24	-0.15
100	3.91±0.34	0.35	2.17±0.25	-0.21	1.65±0.19	-0.29
120	3.85±0.37	0.50	1.46±0.32	-0.91	1.43±0.71	-0.51
140	1.96±0.46	-1.32	1.41±0.25	-0.96	1.36±0.38	-0.58
160	1.65±0.20	-1.60	1.36±0.36	-1.01	1.33±0.31	-0.61
180	1.48±0.27	-1.76	1.35±0.28	-1.02		
200	1.43±0.22	-1.81				

Table A10. Summary of multiple range analysis (Duncan test) of time and temperature for electrical conductivity (mS.cm^{-1}) and turbidity (absorbance at 500 nm) of cooking water of chickpea during cooking

	87 °C		92 °C		97 °C	
Time (min)	**EC[I] (mS cm^{-1})**	**Turbidity (abs.)[J]**	**EC[I] (mS cm^{-1})**	**Turbidity[J] (abs.)**	**EC[I] (mS cm^{-1})**	**Turbidity[J] (abs.)**
0	$0.0016^{a,x}$	$0.000^{a,x}$	$0.0016^{a,x}$	$0.000^{a,x}$	$0.0016^{a,x}$	$0.000^{a,x}$
20	$1.66^{b,x}$	$0.065^{b,x}$	$1.98^{b,y}$	$0.088^{b,y}$	$2.78^{b,z}$	$0.092^{b,z}$
40	$2.39^{c,x}$	$0.085^{c,x}$	$2.52^{c,y}$	$0.094^{c,y}$	$3.07^{c,z}$	$0.144^{c,z}$
60	$2.80^{d,x}$	$0.111^{d,x}$	$3.04^{d,y}$	$0.126^{d,y}$	$3.58^{d,z}$	$0.170^{d,z}$
80	$3.12^{e,x}$	$0.134^{e,x}$	$3.57^{e,y}$	$0.167^{e,y}$	$3.92^{e,z}$	$0.195^{e,z}$
100	$3.44^{f,x}$	$0.168^{f,x}$	$3.92^{f,y}$	$0.195^{f,y}$	$4.18^{f,z}$	$0.247^{f,z}$
120	$3.97^{g,x}$	$0.198^{g,x}$	$4.12^{g,y}$	$0.225^{g,y}$	$4.32^{g,z}$	$0.282^{g,z}$
140	$4.17^{h,x}$	$0.232^{h,x}$	$4.29^{h,y}$	$0.265^{h,y}$	$4.65^{h,z}$	$0.313^{h,z}$
160	$4.33^{i,x}$	$0.267^{i,x}$	$4.42^{i,y}$	$0.315^{i,y}$	$4.80^{i,z}$	$0.375^{i,z}$
180	$4.40^{j,x}$	$0.297^{j,x}$	$4.52^{j,y}$	$0.357^{j,y}$	$4.97^{j,z}$	$0.419^{j,z}$
200	$4.54^{k,x}$	$0.345^{k,x}$	$4.64^{k,y}$	$0.417^{k,y}$	$5.08^{k,z}$	$0.491^{k,z}$
220	$4.63^{l,x}$	$0.382^{l,x}$	$4.73^{l,y}$	$0.470^{l,y}$	$5.27^{l,z}$	$0.596^{l,z}$
240	$4.69^{m,x}$	$0.444^{m,x}$	$4.81^{m,y}$	$0.530^{m,y}$	$5.34^{m,z}$	$0.657^{m,z}$
260	$4.77^{n,x}$	$0.534^{n,x}$	$5.09^{n,y}$	$0.680^{n,y}$	$5.46^{n,z}$	$0.723^{n,z}$

[a-n] Indicate statistical differences between each row at α=0.05,
[x-z] Indicate statistical differences between each column of electrical conductivity (EC) and Turbidity at α=0.05.
I: Electrical conductivity (mS cm^{-1}), J: Absorbance at 500 nm.

Table A11. Summary of multiple range analysis (Duncan test) of ultrasound treatment for electrical conductivity ($mS.cm^{-1}$) and turbidity (absorbance at 500 nm) of cooking water of chickpea during cooking

Electrical conductivity (mS/cm)									
Time (min)	**87 °C**	**87 °C 25 kHz 100 W**	**87 °C 25 kHz 300 W**	**92 °C**	**92 °C 25 kHz 100 W**	**92 °C 25 kHz 300 W**	**97 °C**	**97 °C 25 kHz 100 W**	**97 °C 25 kHz 300 W**
0	0.0016^{a}	0.0016^{a}	0.0016^{a}	0.0016^{a}	0.0016^{a}	0.0016^{a}	0.0016^{a}	0.0016^{a}	0.0016^{a}
20	1.66^{a}	2.09^{b}	3.12^{c}	1.98^{a}	2.80^{b}	3.05^{c}	2.78^{a}	3.48^{b}	4.29^{c}
40	2.39^{a}	2.59^{b}	3.44^{c}	2.52^{a}	3.25^{b}	3.62^{c}	3.07^{a}	3.99^{b}	4.92^{c}
60	2.80^{a}	3.07^{b}	3.86^{c}	3.04^{a}	3.58^{b}	4.02^{c}	3.58^{a}	4.44^{b}	5.63^{c}
80	3.12^{a}	3.72^{b}	4.19^{c}	3.57^{a}	3.89^{b}	4.33^{c}	3.92^{a}	4.89^{b}	6.25^{c}
100	3.44^{a}	3.99^{b}	4.44^{c}	3.92^{a}	4.06^{b}	4.55^{c}	4.18^{a}	5.18^{b}	6.49^{c}
120	3.97^{a}	4.19^{b}	4.58^{c}	4.12^{a}	4.33^{b}	4.76^{c}	4.32^{a}	5.32^{b}	6.69^{c}
140	4.17^{a}	4.37^{b}	4.69^{c}	4.29^{a}	4.48^{b}	4.88^{c}	4.65^{a}	5.49^{b}	6.76^{c}
160	4.33^{a}	4.49^{b}	4.82^{c}	4.42^{a}	4.65^{b}	4.99^{c}	4.80^{a}	5.65^{b}	6.95^{c}
180	4.40^{a}	4.59^{b}	4.91^{c}	4.52^{a}	4.75^{b}	5.11^{c}	4.97^{a}	5.83^{b}	7.28^{c}
200	4.54^{a}	4.67^{b}	5.03^{c}	4.64^{a}	4.83^{b}	5.36^{c}	5.08^{a}	5.97^{b}	7.32^{c}
220	4.63^{a}	4.72^{b}	5.10^{c}	4.73^{a}	5.07^{b}	5.47^{c}	5.27^{a}	6.15^{b}	7.57^{c}
240	4.69^{a}	4.78^{b}	5.15^{c}	4.81^{a}	5.28^{b}	5.68^{c}	5.34^{a}	6.38^{b}	7.79^{c}
260	4.77^{a}	4.87^{b}	5.22^{c}	5.09^{a}	5.37^{b}	5.94^{c}	5.46^{a}	6.47^{b}	7.89^{c}
Turbidity (Absorbance at 500 nm)									
0	0.000^{a}	0.000^{a}	0.000^{a}	0.000^{a}	0.000^{a}	0.000^{a}	0.000^{a}	0.000^{a}	0.000^{a}
20	0.065^{a}	0.108^{b}	0.139^{c}	0.088^{a}	0.111^{b}	0.139^{c}	0.092^{a}	0.129^{b}	0.215^{c}
40	0.085^{a}	0.138^{b}	0.187^{c}	0.094^{a}	0.148^{b}	0.224^{c}	0.144^{a}	0.185^{b}	0.279^{c}
60	0.111^{a}	0.166^{b}	0.227^{c}	0.126^{a}	0.194^{b}	0.288^{c}	0.170^{a}	0.239^{b}	0.369^{c}
80	0.134^{a}	0.218^{b}	0.289^{c}	0.167^{a}	0.235^{b}	0.348^{c}	0.195^{a}	0.315^{b}	0.434^{c}
100	0.168^{a}	0.274^{c}	0.328^{c}	0.195^{a}	0.298^{b}	0.429^{c}	0.247^{a}	0.378^{b}	0.517^{c}
120	0.198^{a}	0.313^{b}	0.368^{c}	0.225^{a}	0.355^{b}	0.489^{c}	0.282^{a}	0.428^{b}	0.568^{c}
140	0.232^{a}	0.364^{b}	0.437^{c}	0.265^{a}	0.408^{b}	0.545^{c}	0.313^{a}	0.488^{b}	0.623^{c}
160	0.267^{a}	0.392^{b}	0.51^{c}	0.315^{a}	0.459^{b}	0.607^{c}	0.375^{a}	0.539^{b}	0.689^{c}
180	0.297^{a}	0.444^{b}	0.556^{c}	0.357^{a}	0.527^{b}	0.656^{c}	0.419^{a}	0.590^{b}	0.731^{c}
200	0.345^{a}	0.484^{b}	0.611^{c}	0.417^{a}	0.565^{b}	0.717^{c}	0.491^{a}	0.632^{b}	0.788^{c}
220	0.382^{a}	0.517^{b}	0.627^{c}	0.470^{a}	0.598^{b}	0.798^{c}	0.596^{a}	0.676^{b}	0.829^{c}
240	0.444^{a}	0.562^{b}	0.683^{c}	0.530^{a}	0.695^{b}	0.854^{c}	0.657^{a}	0.758^{b}	0.868^{c}
260	0.534^{a}	0.627^{b}	0.725^{c}	0.680^{a}	0.745^{b}	0.895^{c}	0.723^{a}	0.823^{b}	0.925^{c}

$^{a-c}$Indicate statistical differences between each column at same temperature, α=0.05.

Table A12. Summary of multiple range analysis (Duncan test) of time and temperature for L^*, a^* and b^* values of chickpea and cooking water during cooking operation

Time (min)	Cooking water								
	L^*			a^*			b^*		
	87 °C	92 °C	97 °C	87 °C	92 °C	97 °C	87 °C	92 °C	97 °C
0	$2.06^{a,x}$	$2.06^{a,x}$	$2.06^{a,x}$	$0.58^{k,x}$	$0.58^{j,x}$	$0.58^{h,x}$	$-0.63^{a,x}$	$-0.63^{a,x}$	$-0.63^{a,x}$
20	$3.83^{b,x}$	$4.49^{b,y}$	$5.30^{b,z}$	$-0.40^{a,x}$	$-0.36^{a,y}$	$-0.26^{a,z}$	$1.19^{b,x}$	$1.32^{b,y}$	$2.01^{b,z}$
40	$4.13^{c,x}$	$4.85^{c,y}$	$5.96^{c,z}$	$-0.38^{b,x}$	$-0.31^{b,y}$	$-0.23^{b,z}$	$1.34^{c,x}$	$1.48^{c,y}$	$2.94^{c,z}$
60	$4.85^{d,x}$	$5.26^{d,y}$	$6.37^{e,z}$	$-0.34^{c,x}$	$-0.22^{c,y}$	$-0.18^{c,z}$	$2.57^{d,x}$	$3.09^{d,y}$	$4.31^{d,z}$
80	$5.55^{e,x}$	$6.38^{e,z}$	$6.89^{,y}$	$-0.33^{d,x}$	$-0.18^{d,y}$	$-0.08^{d,z}$	$2.65^{e,x}$	$3.31^{e,y}$	$4.43^{e,z}$
100	$5.81^{f,x}$	$7.11^{f,z}$	$7.57^{g,y}$	$-0.03^{e,x}$	$0.13^{e,y}$	$0.29^{e,z}$	$2.74^{f,x}$	$4.09^{f,y}$	$4.54^{f,z}$
120	$5.94^{g,x}$	$7.31^{g,z}$	$7.78^{f,y}$	$0.10^{f,x}$	$0.34^{f,y}$	$0.46^{f,z}$	$3.13^{g,x}$	$4.38^{g,y}$	$4.93^{g,z}$
140	$6.64^{h,x}$	$7.59^{h,y}$	$7.91^{h,z}$	$0.21^{g,x}$	$0.45^{g,y}$	$0.55^{g,z}$	$3.71^{h,x}$	$4.64^{h,y}$	$5.24^{h,z}$
160	$6.82^{i,x}$	$7.74^{i,y}$	$8.16^{ı,z}$	$0.35^{h,x}$	$0.48^{h,y}$	$0.65^{i,z}$	$3.93^{i,x}$	$5.57^{i,y}$	$6.37^{i,z}$
180	$7.70^{j,x}$	$8.24^{j,y}$	$8.54^{i,y}$	$0.43^{i,x}$	$0.52^{i,y}$	$0.88^{j,z}$	$4.44^{j,x}$	$6.37^{j,y}$	$6.62^{j,z}$
200	$7.97^{k,x}$	$8.65^{k,z}$	$9.41^{j,y}$	$0.55^{j,x}$	$0.61^{k,y}$	$1.07^{k,z}$	$4.64^{k,x}$	$6.83^{k,y}$	$7.22^{k,z}$
220	$8.53^{l,z}$	$8.96^{l,x}$	$9.48^{k,y}$	$0.61^{l,x}$	$0.79^{l,y}$	$1.79^{l,z}$	$5.33^{l,x}$	$6.94^{l,y}$	$8.15^{l,z}$
240	$8.96^{m,x}$	$9.32^{m,y}$	$9.78^{l,z}$	$0.74^{m,x}$	$0.87^{m,y}$	$1.97^{m,z}$	$5.86^{m,x}$	$7.85^{m,y}$	$8.59^{m,z}$
260	$10.44^{n,x}$	$10.70^{n,y}$	$10.85^{m,z}$	$0.81^{n,x}$	$1.02^{n,y}$	$2.02^{n,z}$	$7.42^{n,x}$	$8.43^{n,y}$	$8.97^{n,z}$
	Chickpea								
0	$55.43^{n,x}$	$55.43^{n,x}$	$55.43^{n,x}$	$9.30^{a,x}$	$9.30^{a,x}$	$9.30^{a,x}$	$22.58^{a,x}$	$22.58^{a,x}$	$22.58^{a,x}$
20	$50.88^{i,y}$	$52.27^{l,z}$	$49.78^{h,x}$	$10.06^{b,x}$	$10.23^{b,y}$	$11.03^{b,z}$	$26.03^{b,x}$	$27.56^{b,y}$	$28.09^{b,z}$
40	$52.02^{m,z}$	$50.88^{h,x}$	$51.84^{k,y}$	$10.25^{c,x}$	$10.48^{c,y}$	$11.27^{c,z}$	$27.93^{c,x}$	$28.72^{e,y}$	$28.86^{c,z}$
60	$51.60^{l,y}$	$53.58^{m,z}$	$50.68^{j,x}$	$10.38^{d,x}$	$10.57^{d,y}$	$11.41^{d,z}$	$28.02^{d,x}$	$28.14^{c,y}$	$28.88^{d,z}$
80	$51.32^{k,x}$	$51.88^{k,y}$	$52.43^{m,z}$	$10.42^{e,x}$	$10.69^{e,y}$	$11.63^{e,z}$	$28.12^{e,x}$	$28.19^{d,y}$	$28.97^{e,z}$
100	$49.57^{d,x}$	$51.59^{j,z}$	$50.50^{i,y}$	$10.57^{f,x}$	$10.87^{f,y}$	$11.79^{f,z}$	$28.60^{f,x}$	$29.26^{f,y}$	$29.55^{f,z}$
120	$50.84^{h,y}$	$50.72^{f,x}$	$51.86^{l,z}$	$10.70^{g,x}$	$10.92^{g,y}$	$11.91^{g,z}$	$28.90^{g,x}$	$29.71^{ı,z}$	$29.68^{g,y}$
140	$50.35^{f,y}$	$50.92^{i,z}$	$47.71^{e,x}$	$10.87^{h,x}$	$11.09^{h,y}$	$12.01^{h,z}$	$29.32^{ı,x}$	$29.63^{h,y}$	$29.74^{h,z}$
160	$51.28^{i,z}$	$49.57^{e,y}$	$49.38^{g,x}$	$10.97^{ı,x}$	$11.25^{ı,y}$	$12.22^{ı,z}$	$29.28^{h,x}$	$29.33^{g,y}$	$29.99^{ı,z}$
180	$48.53^{b,y}$	$48.19^{b,x}$	$49.11^{f,z}$	$11.05^{i,x}$	$11.45^{i,y}$	$12.39^{i,z}$	$29.45^{i,x}$	$30.56^{k,y}$	$30.65^{k,z}$
200	$50.19^{e,z}$	$49.34^{d,y}$	$47.48^{d,x}$	$11.19^{j,x}$	$11.59^{j,y}$	$12.47^{j,z}$	$29.64^{j,x}$	$30.48^{i,y}$	$30.58^{i,z}$
220	$50.44^{g,z}$	$46.55^{a,x}$	$47.01^{c,y}$	$11.25^{k,x}$	$11.66^{k,y}$	$12.61^{k,z}$	$29.87^{k,x}$	$30.53^{j,y}$	$30.62^{j,z}$
240	$47.21^{a,y}$	$50.76^{g,z}$	$46.93^{b,x}$	$11.30^{l,x}$	$11.73^{l,y}$	$12.67^{l,z}$	$29.96^{l,x}$	$30.70^{l,y}$	$30.83^{l,z}$
260	$48.67^{c,z}$	$48.48^{c,y}$	$46.72^{a,x}$	$11.49^{m,x}$	$11.85^{m,y}$	$11.89^{m,z}$	$30.23^{m,x}$	$30.88^{m,y}$	$31.03^{m,z}$

[a-n] Indicate statistical differences between each row at constant temperatures, α=0.05.
[x-z] Indicate statistical differences of L^*, a^* and b^* at different temperatures, α=0.05.

Table A13. Summary of multiple range analysis (Duncan test) of time and US for L*-value of chickpea and cooking water during cooking

Time (min)	87 °C	87 °C 25 kHz 100 W	87 °C 25 kHz 300 W	92 °C	92 °C 25 kHz 100 W	92 °C 25 kHz 300 W	97 °C	97 °C 25 kHz 100 W	97 °C 25 kHz 100 W
	L*-value of cooking water								
0	$2.06^{a,x}$	$2.06^{a,x}$	$2.06^{a,x}$	$2.06^{a,x}$	$2.06^{a,x}$	$2.06^{a,x}$	$2.06^{a,x}$	$2.06^{a,x}$	$2.06^{a,x}$
20	$3.83^{b,x}$	$4.57^{b,y}$	$5.28^{b,z}$	$4.49^{b,x}$	$6.10^{b,y}$	$6.44^{b,z}$	$5.30^{b,x}$	$5.54^{b,y}$	$6.77^{b,z}$
40	$4.13^{c,x}$	$5.47^{c,y}$	$5.67^{c,z}$	$4.85^{c,x}$	$6.50^{d,y}$	$6.74^{c,z}$	$5.96^{c,x}$	$6.61^{c,y}$	$7.41^{c,z}$
60	$4.85^{d,x}$	$5.99^{d,y}$	$6.26^{d,z}$	$5.26^{d,x}$	$6.34^{c,y}$	$6.96^{d,z}$	$6.37^{d,x}$	$6.79^{d,y}$	$7.70^{d,z}$
80	$5.55^{e,x}$	$6.08^{e,y}$	$6.55^{e,z}$	$6.38^{e,x}$	$6.91^{e,y}$	$7.46^{e,z}$	$6.89^{e,x}$	$6.94^{e,y}$	$8.39^{e,z}$
100	$5.81^{f,x}$	$6.50^{f,y}$	$6.96^{f,z}$	$7.11^{f,x}$	$7.10^{f,y}$	$7.89^{f,z}$	$7.57^{f,x}$	$7.94^{f,y}$	$8.83^{f,z}$
120	$5.94^{g,x}$	$6.61^{g,y}$	$7.37^{g,z}$	$7.31^{g,x}$	$7.72^{g,y}$	$8.29^{g,z}$	$7.78^{g,x}$	$8.35^{g,y}$	$9.01^{g,z}$
140	$6.64^{h,x}$	$6.95^{h,y}$	$7.72^{h,z}$	$7.59^{h,x}$	$8.51^{h,y}$	$8.95^{h,z}$	$7.91^{h,x}$	$8.73^{h,y}$	$11.16^{h,z}$
160	$6.82^{i,x}$	$7.08^{i,y}$	$8.36^{i,z}$	$7.74^{i,x}$	$8.71^{i,y}$	$9.49^{i,z}$	$8.16^{i,x}$	$9.95^{i,y}$	$12.41^{i,z}$
180	$7.70^{j,x}$	$7.94^{j,y}$	$8.63^{j,z}$	$8.24^{j,x}$	$9.23^{i,y}$	$9.92^{i,z}$	$8.54^{j,x}$	$10.45^{j,y}$	$12.87^{j,z}$
200	$7.97^{k,x}$	$8.11^{k,y}$	$8.97^{k,z}$	$8.65^{k,x}$	$9.96^{j,y}$	$10.33^{j,z}$	$9.41^{k,x}$	$10.99^{k,y}$	$13.12^{k,z}$
220	$8.53^{l,x}$	$8.76^{l,y}$	$9.46^{l,z}$	$8.96^{l,x}$	$10.14^{k,y}$	$10.87^{k,z}$	$9.48^{l,x}$	$11.16^{l,y}$	$13.67^{l,z}$
240	$8.96^{m,x}$	$9.42^{m,y}$	$10.17^{m,z}$	$9.32^{m,x}$	$10.84^{l,y}$	$11.94^{l,z}$	$9.78^{m,x}$	$11.88^{m,y}$	$13.89^{m,z}$
260	$10.44^{n,x}$	$10.84^{n,y}$	$11.79^{n,z}$	$10.70^{n,x}$	$12.43^{m,y}$	$12.86^{m,z}$	$10.85^{n,x}$	$13.42^{n,y}$	$14.16^{n,z}$
	L*-value of chickpea								
0	$55.43^{m,x}$	$55.43^{m,x}$	$55.43^{m,x}$	$55.43^{m,x}$	$55.43^{m,x}$	$55.43^{m,x}$	$55.43^{m,x}$	$55.43^{m,x}$	$55.43^{m,x}$
20	$50.88^{l,y}$	$50.67^{l,x}$	$51.48^{k,z}$	$52.27^{k,z}$	$51.98^{l,y}$	$51.39^{l,x}$	$49.78^{h,y}$	$50.08^{i,z}$	$49.71^{l,x}$
40	$52.02^{l,z}$	$51.96^{l,y}$	$51.65^{l,x}$	$50.88^{h,y}$	$50.06^{g,x}$	$51.26^{k,z}$	$51.84^{j,z}$	$50.04^{i,y}$	$48.75^{k,x}$
60	$51.60^{k,z}$	$50.92^{i,y}$	$50.69^{i,x}$	$53.58^{l,z}$	$50.92^{i,x}$	$51.12^{j,y}$	$50.68^{i,y}$	$52.62^{l,z}$	$47.92^{i,x}$
80	$51.32^{j,z}$	$51.71^{k,y}$	$51.15^{j,x}$	$51.88^{j,z}$	$51.06^{j,y}$	$50.62^{i,x}$	$52.43^{l,z}$	$49.09^{f,y}$	$45.72^{g,x}$
100	$49.57^{d,y}$	$50.40^{h,z}$	$49.13^{g,x}$	$51.59^{i,z}$	$51.49^{k,y}$	$50.54^{i,x}$	$50.50^{i,z}$	$49.63^{h,y}$	$48.60^{j,x}$
120	$50.84^{h,y}$	$50.01^{e,x}$	$51.12^{i,z}$	$50.72^{f,}$	$49.47^{f,}$	$50.15^{h,}$	$51.86^{k,z}$	$48.84^{e,y}$	$46.54^{i,x}$
140	$50.35^{f,y}$	$51.10^{j,z}$	$49.39^{h,x}$	$50.92^{i,z}$	$50.12^{h,y}$	$49.34^{g,x}$	$47.71^{e,y}$	$50.73^{k,z}$	$45.73^{h,x}$
160	$51.28^{i,z}$	$50.11^{f,y}$	$49.12^{f,x}$	$49.57^{e,z}$	$49.35^{e,y}$	$47.79^{c,x}$	$49.38^{g,y}$	$50.41^{j,z}$	$45.03^{f,x}$
180	$48.53^{b,y}$	$49.70^{b,z}$	$48.05^{e,x}$	$48.19^{b,y}$	$47.78^{c,x}$	$48.73^{f,z}$	$49.11^{f,y}$	$49.34^{g,z}$	$44.89^{e,x}$
200	$50.19^{e,z}$	$49.75^{c,y}$	$47.87^{d,x}$	$49.34^{d,y}$	$50.27^{i,z}$	$48.02^{d,x}$	$47.48^{d,y}$	$48.33^{c,z}$	$44.78^{d,x}$
220	$50.44^{g,z}$	$49.64^{a,y}$	$46.58^{c,x}$	$46.55^{a,x}$	$47.28^{a,y}$	$48.07^{e,z}$	$47.01^{c,y}$	$47.55^{b,z}$	$44.67^{c,x}$
240	$47.21^{a,y}$	$49.86^{d,z}$	$44.33^{a,x}$	$50.76^{g,z}$	$48.10^{d,y}$	$45.34^{a,x}$	$46.93^{b,y}$	$48.68^{d,z}$	$44.23^{b,x}$
260	$48.67^{c,y}$	$50.17^{g,z}$	$45.15^{b,x}$	$48.48^{c,z}$	$47.55^{b,y}$	$45.67^{b,x}$	$46.72^{a,z}$	$46.31^{a,y}$	$43.05^{a,x}$

[a-n] Indicate statistical differences between each row at constant temperatures and US, α=0.05.
[x-z] Indicate statistical differences of L* at different US, α=0.05.

Table A14. Summary of multiple range analysis (Duncan test) of time and US for a*-value of chickpea and cooking water during cooking

Time (min)	87 °C	87 °C 25 kHz 100 W	87 °C 25 kHz 300 W	92 °C	92 °C 25 kHz 100 W	92 °C 25 kHz 300 W	97 °C	97 °C 25 kHz 100 W	97 °C 25 kHz 100 W
	a*-value of cooking water								
0	$0.58^{k,x}$	$0.58^{h,x}$	$0.58^{f,x}$	$0.58^{j,x}$	$0.58^{g,x}$	$0.58^{f,x}$	$0.58^{h,x}$	$0.58^{f,x}$	$0.58^{c,x}$
20	$-0.40^{a,x}$	$-0.29^{a,y}$	$-0.17^{a,z}$	$-0.36^{a,x}$	$-0.22^{a,y}$	$-0.12^{a,z}$	$-0.26^{a,x}$	$-0.19^{a,y}$	$-0.12^{a,z}$
40	$-0.38^{b,x}$	$-0.21^{b,y}$	$-0.16^{b,z}$	$-0.31^{b,x}$	$-0.14^{b,y}$	$-0.09^{b,z}$	$-0.23^{b,x}$	$-0.11^{b,y}$	$-0.04^{b,z}$
60	$-0.34^{c,x}$	$-0.12^{c,y}$	$-0.05^{c,z}$	$-0.22^{c,x}$	$-0.06^{c,y}$	$0.11^{c,z}$	$-0.18^{c,x}$	$-0.07^{c,y}$	$0.97^{d,z}$
80	$-0.33^{d,x}$	$-0.03^{d,y}$	$0.37^{d,z}$	$-0.18^{d,x}$	$0.08^{d,y}$	$0.25^{d,z}$	$-0.08^{d,x}$	$0.37^{d,y}$	$1.10^{e,z}$
100	$-0.03^{e,x}$	$0.01^{e,y}$	$0.45^{e,z}$	$0.13^{e,x}$	$0.35^{e,y}$	$0.41^{e,z}$	$0.29^{e,x}$	$0.54^{e,y}$	$1.33^{f,z}$
120	$0.10^{f,x}$	$0.24^{f,y}$	$0.75^{g,z}$	$0.34^{f,x}$	$0.57^{f,y}$	$0.75^{g,z}$	$0.46^{f,x}$	$0.65^{g,y}$	$1.47^{g,z}$
140	$0.21^{g,x}$	$0.46^{g,y}$	$0.97^{h,z}$	$0.45^{g,x}$	$0.89^{h,y}$	$0.92^{h,z}$	$0.55^{g,x}$	$0.73^{h,y}$	$1.78^{h,z}$
160	$0.35^{h,x}$	$0.61^{i,y}$	$0.98^{i,z}$	$0.48^{h,x}$	$0.95^{i,y}$	$1.15^{i,z}$	$0.65^{i,x}$	$0.99^{i,y}$	$2.10^{i,z}$
180	$0.43^{i,x}$	$0.86^{j,y}$	$1.29^{j,z}$	$0.52^{i,x}$	$0.99^{j,y}$	$1.27^{j,z}$	$0.88^{j,x}$	$1.24^{j,y}$	$2.39^{j,z}$
200	$0.55^{j,x}$	$0.93^{k,y}$	$1.31^{k,z}$	$0.61^{k,x}$	$1.13^{k,y}$	$1.32^{k,z}$	$1.07^{k,x}$	$1.41^{k,y}$	$2.65^{k,z}$
220	$0.61^{l,x}$	$1.12^{l,y}$	$1.77^{l,z}$	$0.79^{l,x}$	$1.27^{l,y}$	$1.58^{l,z}$	$1.69^{l,x}$	$1.93^{l,y}$	$2.89^{l,z}$
240	$0.74^{m,x}$	$1.36^{m,y}$	$1.95^{m,z}$	$0.87^{m,x}$	$1.36^{m,y}$	$1.96^{m,z}$	$1.97^{m,y}$	$2.29^{m,y}$	$3.03^{m,z}$
260	$0.81^{n,x}$	$1.65^{n,y}$	$2.09^{n,z}$	$1.02^{n,x}$	$2.09^{n,y}$	$2.78^{n,z}$	$2.02^{n,y}$	$2.88^{n,y}$	$3.45^{n,z}$
	a*-value of chickpea								
0	$9.30^{a,x}$	$9.30^{a,x}$	$9.30^{a,x}$	$9.30^{a,x}$	$9.30^{a,x}$	$9.30^{a,x}$	$9.30^{a,x}$	$9.30^{a,x}$	$9.30^{a,x}$
20	$10.06^{b,x}$	$11.23^{m,z}$	$11.02^{l,y}$	$10.23^{b,x}$	$11.54^{m,z}$	$10.76^{e,y}$	$11.03^{b,z}$	$10.81^{j,y}$	$9.86^{d,x}$
40	$10.25^{c,x}$	$10.62^{i,z}$	$10.27^{h,y}$	$10.48^{c,x}$	$11.08^{k,z}$	$10.86^{g,y}$	$11.27^{c,z}$	$10.17^{d,y}$	$10.06^{e,x}$
60	$10.38^{d,y}$	$10.79^{k,z}$	$9.90^{e,x}$	$10.57^{d,y}$	$10.11^{c,x}$	$10.92^{i,z}$	$11.41^{d,y}$	$10.70^{i,x}$	$11.48^{k,z}$
80	$10.42^{e,y}$	$11.08^{l,z}$	$9.31^{b,x}$	$10.69^{e,x}$	$10.87^{j,y}$	$10.93^{i,z}$	$11.63^{e,z}$	$10.91^{k,y}$	$9.71^{c,x}$
100	$10.57^{f,z}$	$10.26^{g,x}$	$10.39^{i,y}$	$10.87^{f,y}$	$10.25^{d,x}$	$10.95^{j,z}$	$11.79^{f,z}$	$10.67^{i,y}$	$9.51^{b,x}$
120	$10.70^{g,z}$	$10.01^{e,x}$	$10.30^{i,y}$	$10.92^{g,x}$	$11.85^{i,z}$	$10.97^{k,y}$	$11.91^{g,z}$	$10.56^{g,x}$	$10.69^{f,y}$
140	$10.87^{h,z}$	$9.99^{d,x}$	$10.06^{g,y}$	$11.09^{h,z}$	$10.27^{e,x}$	$10.99^{l,y}$	$12.01^{h,z}$	$9.60^{b,x}$	$10.72^{g,y}$
160	$10.97^{i,z}$	$9.73^{b,y}$	$9.36^{c,x}$	$11.25^{i,z}$	$10.60^{i,x}$	$10.71^{d,y}$	$12.22^{i,z}$	$10.26^{e,x}$	$10.92^{h,y}$
180	$11.05^{i,z}$	$10.21^{f,x}$	$10.64^{j,y}$	$11.45^{i,z}$	$9.77^{b,x}$	$10.89^{h,y}$	$12.39^{i,z}$	$9.99^{c,x}$	$10.99^{i,y}$
200	$11.19^{j,z}$	$9.77^{c,x}$	$9.98^{f,y}$	$11.59^{j,z}$	$10.42^{f,x}$	$10.79^{f,y}$	$12.47^{j,z}$	$10.57^{h,x}$	$11.13^{i,y}$
220	$11.25^{k,z}$	$10.41^{h,x}$	$10.98^{k,y}$	$11.66^{k,z}$	$11.36^{l,y}$	$10.68^{c,x}$	$12.61^{k,z}$	$10.99^{m,x}$	$11.27^{j,y}$
240	$11.30^{l,z}$	$10.76^{j,y}$	$11.70^{m,x}$	$11.73^{l,z}$	$10.45^{g,y}$	$9.64^{b,x}$	$12.67^{l,z}$	$10.54^{f,x}$	$11.78^{l,y}$
260	$11.49^{m,z}$	$10.68^{i,y}$	$9.78^{d,x}$	$11.85^{m,z}$	$10.57^{h,x}$	$10.76^{e,y}$	$11.89^{m,y}$	$10.93^{l,x}$	$12.13^{m,z}$

[a-n] Indicate statistical differences between each row at constant temperatures and US, α=0.05.
[x-z] Indicate statistical differences of a* at different US, α=0.05.

Table A15. Summary of multiple range analysis (Duncan test) of time and US for b*-value of chickpea and cooking water during cooking

Time (min)	87 °C	87 °C 25 kHz 100 W	87 °C 25 kHz 300 W	92 °C	92 °C 25 kHz 100 W	92 °C 25 kHz 300 W	97 °C	97 °C 25 kHz 100 W	97 °C 25 kHz 100 W
	b*-value of cooking water								
0	$-0.63^{a,x}$	$-0.63^{a,x}$	$-0.63^{a,x}$	$-0.63^{a,x}$	$-0.63^{a,x}$	$-0.63^{a,x}$	$-0.63^{a,x}$	$-0.63^{a,x}$	$-0.63^{a,x}$
20	$1.19^{b,x}$	$1.32^{b,y}$	$1.99^{b,z}$	$1.32^{b,x}$	$1.73^{b,y}$	$1.92^{b,z}$	$2.01^{b,x}$	$2.23^{b,y}$	$3.22^{b,z}$
40	$1.34^{c,x}$	$2.54^{c,y}$	$3.39^{c,z}$	$1.48^{c,x}$	$2.96^{c,y}$	$3.41^{c,z}$	$2.94^{c,x}$	$3.84^{c,y}$	$4.44^{c,z}$
60	$2.57^{d,x}$	$3.17^{d,y}$	$3.73^{d,z}$	$3.09^{d,x}$	$3.43^{d,y}$	$3.94^{d,z}$	$4.31^{d,x}$	$4.81^{d,y}$	$5.36^{d,z}$
80	$2.65^{e,x}$	$4.18^{e,y}$	$4.93^{e,z}$	$3.31^{e,x}$	$4.25^{e,y}$	$4.98^{e,z}$	$4.43^{e,x}$	$5.47^{e,y}$	$6.57^{g,z}$
100	$2.74^{f,x}$	$4.27^{f,y}$	$5.17^{f,z}$	$4.09^{f,x}$	$4.58^{f,y}$	$5.89^{f,z}$	$4.54^{f,x}$	$5.87^{f,y}$	$6.89^{e,z}$
120	$3.13^{g,x}$	$4.49^{g,y}$	$5.55^{g,z}$	$4.38^{g,x}$	$4.82^{g,y}$	$6.35^{g,z}$	$4.93^{g,x}$	$6.37^{g,y}$	$7.07^{f,z}$
140	$3.71^{h,x}$	$4.69^{h,y}$	$6.65^{h,z}$	$4.64^{h,x}$	$6.00^{h,y}$	$6.65^{h,z}$	$5.24^{h,x}$	$6.83^{h,y}$	$7.82^{h,z}$
160	$3.93^{i,x}$	$4.95^{i,y}$	$6.90^{i,z}$	$5.57^{i,x}$	$6.24^{i,y}$	$6.97^{i,z}$	$6.37^{i,x}$	$7.22^{i,y}$	$8.34^{\iota,z}$
180	$4.44^{j,x}$	$5.14^{j,y}$	$7.28^{j,z}$	$6.37^{j,x}$	$6.88^{j,y}$	$7.61^{j,z}$	$6.62^{j,x}$	$7.35^{j,y}$	$8.63^{i,z}$
200	$4.64^{k,x}$	$5.73^{k,y}$	$8.20^{k,z}$	$6.83^{k,x}$	$7.26^{k,y}$	$7.94^{k,z}$	$7.22^{k,x}$	$8.00^{k,y}$	$8.99^{j,z}$
220	$5.33^{l,x}$	$6.00^{l,y}$	$9.80^{l,z}$	$6.94^{l,x}$	$7.43^{l,y}$	$8.71^{l,z}$	$8.15^{l,x}$	$8.69^{l,y}$	$9.36^{k,z}$
240	$5.86^{m,x}$	$6.88^{m,y}$	$9.90^{m,z}$	$7.85^{m,x}$	$8.21^{m,y}$	$9.23^{m,z}$	$8.59^{m,x}$	$8.94^{m,y}$	$9.97^{l,z}$
260	$7.42^{n,x}$	$8.44^{n,y}$	$9.97^{n,z}$	$8.43^{n,x}$	$8.89^{n,y}$	$10.33^{n,z}$	$8.97^{n,x}$	$9.39^{n,y}$	$11.08^{m,z}$
	b*-value of chickpea								
0	$22.58^{a,x}$	$22.58^{a,x}$	$22.58^{a,x}$	$22.58^{a,x}$	$22.58^{a,x}$	$22.58^{a,x}$	$22.58^{a,x}$	$22.58^{a,x}$	$22.58^{a,x}$
20	$26.03^{b,x}$	$27.76^{d,y}$	$29.14^{j,z}$	$27.56^{b,x}$	$30.14^{l,z}$	$28.78^{f,y}$	$28.09^{b,z}$	$27.63^{b,y}$	$25.01^{b,x}$
40	$27.93^{c,z}$	$27.67^{c,y}$	$26.53^{d,x}$	$28.72^{e,z}$	$28.68^{h,y}$	$27.56^{e,x}$	$28.86^{c,z}$	$27.71^{c,y}$	$26.17^{c,x}$
60	$28.02^{d,y}$	$30.63^{l,z}$	$26.82^{e,x}$	$28.14^{c,z}$	$26.95^{c,x}$	$27.55^{d,y}$	$28,88^{d,y}$	$29,37^{m,z}$	$26.35^{d,x}$
80	$28.12^{e,y}$	$31.17^{m,z}$	$27.58^{f,x}$	$28.19^{d,y}$	$27.92^{e,x}$	$29.04^{\iota,z}$	$28.97^{e,y}$	$28.98^{j,y}$	$26.65^{e,x}$
100	$28.60^{f,z}$	$28.43^{g,y}$	$27.89^{h,x}$	$29.26^{f,y}$	$26.72^{b,x}$	$29.34^{j,z}$	$29.55^{f,z}$	$28.14^{e,y}$	$26.81^{f,x}$
120	$28.90^{g,y}$	$26.90^{b,x}$	$29.10^{\iota,z}$	$29.71^{\iota,x}$	$30.49^{m,z}$	$30.22^{l,y}$	$29.68^{g,z}$	$28.60^{\iota,y}$	$28.45^{g,x}$
140	$29.32^{\iota,z}$	$27.79^{e,x}$	$29.11^{i,y}$	$29.63^{h,y}$	$29.01^{j,x}$	$30.65^{m,z}$	$29.74^{h,z}$	$27.75^{d,x}$	$28.47^{h,y}$
160	$29.28^{h,z}$	$28.73^{\iota,y}$	$26.24^{c,x}$	$29.33^{g,y}$	$28.84^{i,x}$	$29.33^{i,y}$	$29.99^{\iota,y}$	$28.18^{f,x}$	$31.32^{i,z}$
180	$29.45^{i,z}$	$28.05^{f,x}$	$29.24^{k,y}$	$30.56^{k,z}$	$27.05^{d,x}$	$29.67^{k,y}$	$30.65^{k,y}$	$28.20^{g,x}$	$30.87^{\iota,z}$
200	$29.64^{j,z}$	$28.62^{h,y}$	$27.78^{g,x}$	$30.48^{i,z}$	$28.63^{g,x}$	$28.99^{h,y}$	$30.58^{i,y}$	$28.30^{h,x}$	$32.11^{k,z}$
220	$29.87^{k,z}$	$29.18^{i,x}$	$29.37^{l,y}$	$30.53^{j,z}$	$29.13^{k,y}$	$28.81^{g,x}$	$30.62^{j,y}$	$28.97^{i,x}$	$31.89^{j,z}$
240	$29.96^{l,z}$	$29.73^{j,x}$	$29.94^{m,y}$	$30.70^{l,z}$	$28.81^{\iota,y}$	$26.18^{b,x}$	$30.83^{l,y}$	$29.04^{k,x}$	$32.26^{l,z}$
260	$30.23^{m,z}$	$29.81^{k,y}$	$25.67^{b,x}$	$30.88^{m,z}$	$27.97^{f,y}$	$27.23^{c,x}$	$31.03^{m,y}$	$29.06^{l,x}$	$32.67^{m,z}$

[a-n] Indicate statistical differences between each row at constant temperatures and US, α=0.05.
[x-z] Indicate statistical differences of b* at different US, α=0.05.

Table A16. Experimental values and standard deviations of maltase crosses at any time (N_t) and calculated DC (%) by birefringes images model for cooking of chickpeas at 87, 92 and 97 ^oC without and with US

Time (min)	N_t	DC (%)	N_t	DC (%)	N_t	DC (%)
	87 ^oC		**87 ^oC + 25 kHz 100 W US**		**87 ^oC + 25 kHz 300 W US**	
0	146±18.84	0.00	146±18.84	0.00	146±18.84	0.00
20	95±4.75	34.93	83±7.85	43.15	54±12.27	63.01
40	74±8.56	49.32	65±8.47	55.48	43±7.05	70.55
60	61±6.66	58.22	52±7.28	64.38	32±6.14	78.08
80	50±7.73	65.75	32±2.93	78.08	21±11.70	85.62
100	41±6.05	71.92	24±3.29	83.56	13±2.87	91.10
120	25±5.58	82.88	19±2.68	86.99	9±2.64	93.84
140	20±4.15	86.30	13±2.49	91.10	5±1.64	96.58
160	16±3.63	89.04	8±1.49	94.52	2±0.64	98.63
180	12±3.17	91.78	5±1.37	96.58	1±0.64	99.32
200	8±2.24	94.52	3±0.67	97.95	0±0.66	100.00
220	5±2.44	96.58	2±0.66	98.63		
240	2±0.66	98.63	0± 0.40	100.00		
260	1±0.80	99.32				
280	0±0.40	100.00				
	92 ^oC		**92 ^oC + 25 kHz 100 W US**		**92 ^oC + 25 kHz 300 W US**	
0	146±18.84	0.00	146±18.84	0.00	146±18.84	0.00
20	81±9.85	44.52	61±8.09	58.22	44±8.50	69.86
40	69±7.32	52.74	49±6.56	66.44	30±5.12	79.45
60	53±5.57	63.70	37±9.64	74.66	20±8.14	86.30
80	37±6.20	74.66	29±6.20	80.14	15±6.36	89.73
100	27±3.50	81.51	22±7.14	84.93	10±1.85	93.15
120	21±3.14	85.62	16±3.03	89.04	6±1.55	95.89
140	17±1.78	88.36	10±3.92	93.15	3±0.80	97.95
160	12±3.66	91.78	5±2.39	96.58	0±0.66	100.00
180	9±2.60	93.84	2±1.17	98.63		
200	5±1.08	96.58	0±0.66	100.00		
220	2±1.02	98.63				
240	0±0.49	100.00				
	97 ^oC		**97 ^oC + 25 kHz 100 W US**		**97 ^oC + 25 kHz 300 W US**	
0	146±18.84	0.00	146±18.84	0.00	146±18.84	0.00
20	72±8.26	50.68	55±12.05	62.33	31±8.25	78.77
40	60±7.62	58.90	49±10.34	66.44	19±7.10	86.99
60	51±7.14	65.07	34±6.04	76.71	10±2.75	93.15
80	42±6.69	71.23	21±3.50	85.62	6±1.92	95.89
100	32±5.36	78.08	15±3.32	89.73	3±1.58	97.95
120	21±3.98	85.62	10±3.74	93.15	0±0.66	100.00
140	12±3.80	91.78	3±1.60	97.95		
160	8±4.50	94.52	0±0.49	100.00		
180	3±2.42	97.95				
200	0±0.46	100.00				

Table A17. Average experimental, standard deviation and calculated values of parameters (DC (%), α_β, D_c, D, r_c, r and r_c/r) for unreacted-core model of cooked chickpeas at 87 °C without and with US

Time (min)	D (mm)	D_C (mm)	r (mm)	r_C (mm)	r_C/r	DC(%)	$\alpha_B = \frac{r_C^3}{r^3}$	$ln(\alpha_B)$	$ln[-\frac{\Delta(\frac{r_C^3}{r^3})}{\Delta t}]$
				87 °C					
0	7.77(±0.46)	7.77(±0.46)	3.89	3.89	1.00	0.00	1.00000		
20	8.31(±0.34)	6.96(±0.38)	4.16	3.48	0.84	41.25	0.58752	-0.53	-3.88
40	8.65(±0.12)	6.38(±0.40)	4.33	3.19	0.74	59.88	0.40125	-0.91	-4.68
60	8.80(±0.22)	5.89(±0.67)	4.40	2.95	0.67	70.02	0.29985	-1.20	-5.28
80	8.98(±0.47)	5.38(±0.56)	4.49	2.69	0.60	78.50	0.21504	-1.54	-5.46
100	9.01(±0.47)	4.77(±0.72)	4.51	2.39	0.53	85.16	0.14838	-1.91	-5.70
120	9.11(±0.38)	3.99(±0.32)	4.56	2.00	0.44	91.60	0.08402	-2.48	-5.74
140	9.17(±0.45)	3.26(±0.64)	4.59	1.63	0.36	95.51	0.04493	-3.10	-6.24
160	9.25(±0.58)	2.75(±0.72)	4.62	1.37	0.30	97.37	0.02628	-3.64	-6.98
180	9.27(±0.28)	2.13(±0.93)	4.64	1.07	0.23	98.79	0.01213	-4.41	-7.25
200	9.36(±0.43)	1.36(±0.84)	4.68	0.68	0.15	99.69	0.00307	-5.79	-7.70
220	9.45(±0.33)	0.82(±0.56)	4.73	0.41	0.09	99.93	0.00065	-7.33	-9.02
240	9.52(±0.32)	0.34(±0.47)	4.76	0.17	0.04	100.00	0.00005	-10.00	-10.40
				87 °C + 25 kHz 100 W US					
0	7.77(±0.46)	7.77(±0.46)	3.89	3.885	1.00	0.00	1.00000		
20	8.38(±0.25)	6.57(±0.45)	4.19	3.29	0.78	51.81	0.48191	-0.73	-3.65
40	8.62(±0.16)	6.15(±0.24)	4.31	3.08	0.71	63.68	0.36316	-1.01	-5.13
60	8.77(±0.35)	5.29(±0.36)	4.39	2.65	0.60	78.05	0.21947	-1.52	-4.94
80	9.07(±0.33)	4.74(±0.66)	4.54	2.37	0.52	85.73	0.14273	-1.95	-5.56
100	9.19(±0.43)	3.93(±0.72)	4.60	1.97	0.43	92.18	0.07820	-2.55	-5.74
120	9.32(±0.22)	2.95(±0.63)	4.66	1.48	0.32	96.83	0.03171	-3.45	-6.06
140	9.43(±0.30)	2.12(±0.32)	4.72	1.06	0.22	98.86	0.01136	-4.48	-6.89
160	9.50(±0.27)	1.12(±0.24)	4.75	0.56	0.12	99.84	0.00164	-6.41	-7.63
180	9.55(±0.28)	0.68(±0.57)	4.78	0.34	0.07	99.96	0.00036	-7.93	-9.66
200	9.63(±0.23)	0.30(±0.35)	4.82	0.15	0.03	100.00	0.00003	-10.41	-11.01
				87 °C + 25 kHz 100 W US					
0	7.77(±0.46)	7.77(±0.46)	3.89	3.89	1.00	0.00	1.00000		
20	8.50(±0.18)	6.08(±0.50)	4.25	3.04	0.72	63.40	0.36598	-1.01	-3.45
40	8.66(±0.47)	5.42(±0.62)	4.33	2.71	0.63	75.48	0.24516	-1.41	-5.11
60	8.85(±0.25)	4.69(±0.47)	4.43	2.35	0.53	85.12	0.14883	-1.90	-5.34
80	9.14(±0.26)	3.88(±0.44)	4.57	1.94	0.42	92.35	0.07650	-2.57	-5.62
100	9.25(±0.30)	2.92(±0.33)	4.63	1.46	0.32	96.85	0.03146	-3.46	-6.10
120	9.44(±0.23)	1.89(±0.20)	4.72	0.95	0.20	99.20	0.00802	-4.83	-6.75
140	9.56(±0.33)	0.74(±0.61)	4.78	0.37	0.08	99.95	0.00046	-7.68	-7.88
160	9.65(±0.29)	0.31(±0.37)	4.825	0.16	0.03	100.00	0.00003	-10.31	-10.75

Table A18. Average experimental, standard deviation and calculated values of parameters (DC (%), α_β, D_c, D, r_c, r and r_c/r) for unreacted-core model of cooked chickpeas at 92 °C without and with US

Time (min)	D (mm)	D_C (mm)	r (mm)	r_C (mm)	r_C/r	DC(%)	$\alpha_B = \frac{r_C^3}{r^3}$	$ln(\alpha_B)$	$ln[-\frac{\Delta(\frac{r_C^3}{r^3})}{\Delta t}]$
				92 °C					
0	7.77(±0.46)	7.77(±0.46)	3.89	3.89	1.00	0.00	1.00000		
20	8.60(±0.51)	6.62(±0.13)	4.30	3.31	0.77	54.39	0.45612	-0.79	-3.60
40	8.81(±0.32)	6.13(±0.41)	4.41	3.07	0.70	66.31	0.33686	-1.09	-5.12
60	9.10(±0.41)	5.41(±0.52)	4.55	2.71	0.59	78.99	0.21012	-1.56	-5.06
80	9.19(±0.41)	4.76(±0.33)	4.60	2.38	0.52	86.10	0.13895	-1.97	-5.64
100	9.32(±0.37)	3.87(±0.86)	4.66	1.94	0.42	92.84	0.07159	-2.64	-5.69
120	9.49(±0.36)	2.71(±0.47)	4.75	1.36	0.29	97.67	0.02329	-3.76	-6.03
140	9.55(±0.35)	1.69(±0.52)	4.78	0.85	0.18	99.45	0.00554	-5.20	-7.03
160	9.62(±0.32)	1.12(±0.09)	4.81	0.56	0.12	99.84	0.00158	-6.45	-8.53
180	9.69(±0.38)	0.53(±0.38)	4.85	0.27	0.05	99.98	0.00016	-8.72	-9.56
200	9.73(±0.46)	0.35(±0.29)	4.87	0.18	0.04	100.00	0.00005	-9.98	-12.05
				92 °C + 25 kHz 100 W US					
0	7.77(±0.46)	7.77(±0.46)	3.89	3.89	1.00	0	1.00000		
20	8.65(±0.26)	5.96(±0.29)	4.33	2.98	0.69	67.29	0.32711	-1.12	-3.39
40	9.01(±0.37)	5.41(±0.46)	4.51	2.71	0.60	78.35	0.21648	-1.53	-5.20
60	9.21(±0.33)	4.54(±0.72)	4.61	2.27	0.49	88.02	0.11978	-2.12	-5.33
80	9.30(±0.36)	3.72(±0.60)	4.65	1.86	0.40	93.60	0.06400	-2.75	-5.88
100	9.48(±0.41)	2.44(±0.33)	4.74	1.22	0.26	98.29	0.01705	-4.07	-6.05
120	9.59(±0.27)	1.36(±0.28)	4.80	0.68	0.14	99.71	0.00285	-5.86	-7.25
140	9.65(±0.29)	0.85(±0.76)	4.83	0.43	0.09	99.93	0.00068	-7.29	-9.13
160	9.70(±0.42)	0.34(±0.52)	4.85	0.17	0.04	100.00	0.00004	-10.05	-10.35
				92 °C + 25 kHz 100 W US					
0	7.77(±0.46)	7.77(±0.46)	3.89	3.89	1.00	0	1.00000		
20	8.71(±0.37)	5.63(±0.51)	4.36	2.82	0.65	72.99	0.27007	-1.31	-3.31
40	9.11(±0.39)	4.83(±0.65)	4.56	2.42	0.53	85.10	0.14903	-1.90	-5.11
60	9.32(±0.28)	3.98(±0.78)	4.66	1.99	0.43	92.21	0.07788	-2.55	-5.64
80	9.39(±0.19)	1.85(±0.50)	4.70	0.93	0.20	99.24	0.00765	-4.87	-5.65
100	9.58(±0.28)	0.99(±0.70)	4.79	0.50	0.10	99.89	0.00110	-6.81	-8.02
120	9.66(±0.13)	0.35(±0.52)	4.83	0.18	0.04	100.00	0.00005	-9.95	-9.85

Table A19. Average experimental, standard deviation and calculated values of parameters (DC (%), α_β, D_c, D, r_c, r and r_c/r) for unreacted-core model of cooked chickpeas at 97 °C without and with US

Time (min)	D (mm)	D_C (mm)	r (mm)	r_C (mm)	r_C/r	DC(%)	$\alpha_B = \frac{r_C^3}{r^3}$	$ln(\alpha_B)$	$ln[-\frac{\Delta(\frac{r_C^3}{r^3})}{\Delta t}]$
				97 °C					
0	7.77(±0.46)	7.77(±0.46)	3.89	3.89	1.00	0	1.00000		
20	8.86(±0.46)	5.96(±0.38)	4.43	2.98	0.67	69.56	0.30439	-1.19	-3.36
40	9.13(±0.26)	5.38(±0.39)	4.57	2.69	0.59	79.54	0.20461	-1.59	-5.30
60	9.32(±0.25)	4.79(±0.41)	4.66	2.40	0.51	86.42	0.13576	-2.00	-5.67
80	9.43(±0.33)	3.91(±0.33)	4.72	1.96	0.41	92.87	0.07128	-2.64	-5.74
100	9.56(±0.36)	2.82(±0.74)	4.78	1.41	0.29	97.43	0.02567	-3.66	-6.08
120	9.64(±0.15)	1.59(±0.48)	4.82	0.80	0.16	99.55	0.00449	-5.41	-6.85
140	9.73(±0.23)	0.59(±0.61)	4.87	0.30	0.06	99.98	0.00022	-8.41	-8.45
160	9.80(±0.27)	0.35(±0.37)	4.90	0.18	0.04	100.00	0.00005	-10.00	-11.63
				97 °C + 25 kHz 100 W US					
0	7.77(±0.46)	7.77(±0.46)	3.89	3.89	1.00	0	1.00000		
20	9.08(±0.35)	5.79(±0.25)	4.54	2.90	0.64	74.07	0.25928	-1.35	-3.30
40	9.21(±0.23)	5.05(±0.56)	4.61	2.53	0.55	83.51	0.16485	-1.80	-5.36
60	9.41(±0.32)	3.50(±0.56)	4.71	1.75	0.37	94.85	0.05146	-2.97	-5.17
80	9.54(±0.27)	1.89(±0.42)	4.77	0.95	0.20	99.22	0.00777	-4.86	-6.13
100	9.67(±0.22)	1.05(±0.39)	4.84	0.53	0.11	99.87	0.00128	-6.66	-8.03
120	9.76(±0.20)	0.35(±0.29)	4.88	0.18	0.04	100.00	0.00005	-9.98	-9.69
				97 °C + 25 kHz 100 W US					
0	7.77(±0.46)	7.77(±0.46)	3.89	3.89	1.00	0	1.00000		
20	9.21(±0.32)	5.39(±0.41)	4.61	2.70	0.59	79.96	0.20044	-1.61	-3.22
40	9.39(±0.23)	3.49(±0.73)	4.70	1.75	0.37	94.87	0.05134	-2.97	-4.90
60	9.56(±0.32)	1.85(±0.42)	4.78	0.93	0.19	99.28	0.00725	-4.93	-6.12
80	9.69(±0.42)	0.34(±0.61)	4.85	0.17	0.04	100.00	0.00004	-10.05	-7.93

Table A20. Average electrical conductivity (mS/cm) of cooking water. DC-BI (%), EC-CW-BI (%), DC-UC (%) and EC-CW-UC (%) for cooking chickpeas at 87 °C without and with US

	87 °C					87 °C + 25 kHz 100 W					87 °C + 25 kHz 300 W				
Time min	EC-CW (mS/cm)	DC-BI (%)	DC-UC (%)	EC-CW-BI (%)	EC-CW-UC (%)	EC (mS/cm)	DC-BI (%)	DC-UC (%)	EC-CW-BI (%)	EC-CW-UC (%)	EC (mS/cm)	DC-BI (%)	DC-UC (%)	EC-CW-BI (%)	EC-CW-UC (%)
0	0.00	0.0	0.0	0.0	0.0	0.00	0.0	0.0	0.0	0.0	0.00	0.0	0.0	0.0	0.0
20	1.66	34.9	41.2	34.4	35.4	2.09	43.1	51.8	43.7	44.7	2.72	54.8	63.4	54.1	56.4
40	2.39	49.3	59.9	49.6	51.0	2.59	55.5	63.7	54.2	55.5	2.98	59.6	75.5	59.2	61.8
60	2.80	58.2	70.0	58.1	59.7	3.07	64.4	78.0	64.2	65.7	3.36	68.5	85.1	66.8	69.7
80	3.12	65.7	78.5	64.7	66.5	3.72	78.1	85.7	77.8	79.7	4.09	83.6	92.3	81.3	84.8
100	3.44	71.9	85.2	71.4	73.3	3.99	83.6	92.2	83.5	85.4	4.34	88.4	96.8	86.3	90.0
120	3.97	82.9	91.6	82.4	84.6	4.19	87.0	96.8	87.7	89.7	4.52	91.8	99.2	89.9	93.8
140	4.17	86.3	95.5	86.5	88.9	4.37	91.1	98.9	91.4	93.6	4.69	93.8	99.9	93.2	97.3
160	4.33	89.1	97.4	89.8	92.3	4.49	94.5	99.8	93.9	96.1	4.82	96.6	100	95.8	100
180	4.40	91.8	98.8	91.3	93.8	4.59	96.6	99.9	96.0	98.3	4.91	97.9		97.6	
200	4.54	94.5	99.7	94.2	96.8	4.67	97.9	100	97.7	100	5.03	100		100	
220	4.63	96.6	99.9	96.1	98.7	4.72	98.6		98.7						
240	4.69	98.6	100	97.3	100	4.78	100		100						
260	4.77	99.3		99.0											
280	4.82	100		100											

EC-CW (mS/cm): Electrical conductivity of cooking water. EC-C(mS/cm): Electrical conductivity of chickpea. BI: Birefringes Imeges. UC:Unreacted Core. DC-BI(%):Degree of cooking by birefringes images. DC-UC(%): Degree of cooking by unreacted core model. DC-DSC(%): Degree of cooking by DSC. DC-EC-C(%): Degree of cooking by electrical conductivity of chickpea. EC-CW-BI(%): Electrical conductivity on the basis of Birefringes images. EC-CW-UC (%): Electrical conductivity on the basis of Unreacted core model. EC-CW-DSC(%):Electrical conductivity on the basis of DSC. EC-CW-C (%):Electrical conductivity on the basis of electrical conductivity of chickpea method.

Table A21. Average electrical conductivity (mS/cm) of cooking water (EC-CW) and chickpea (EC-C), DC-BI(%), DC-UC(%), DC-DSC(%), DC-EC-C(%), EC-CW-BI(%), EC-CW-UC(%), EC-CW-DSC(%) and EC-CW-C(%) at 92 °C

Time (min)	EC-CW (mS/cm)	EC-C (µS/cm)	DC-BI (%)	DC-UC (%)	DC-DSC (%)	DC-EC-C (%)	EC-CW-BI (%)	EC-CW-UC (%)	EC-CW-DSC (%)	EC-CW-C (%)
0	0.00	583	0.0	0.0	0.00	0.00	0.00	0	0.00	0.00
20	1.98	416	41.8	54.4	42.37	41.45	41.16	43.8	41.16	41.16
40	2.52	361	52.7	66.3	53.90	55.04	52.39	55.8	52.39	52.39
60	3.04	300	63.7	79.0	64.18	70.11	63.20	67.3	63.20	63.20
80	3.57	278	74.7	86.1	74.97	75.55	74.22	79.0	74.22	74.22
100	3.92	254	81.5	92.8	82.88	81.48	81.50	86.7	81.50	81.50
120	4.12	234	85.6	97.7	84.98	86.42	85.65	91.2	85.65	85.65
140	4.29	223	88.4	99.4	89.05	89.14	89.19	94.9	89.19	89.19
160	4.42	211	91.8	99.8	92.00	92.10	91.89	97.8	91.89	91.89
180	4.52	199	93.8	100.0	94.45	95.07	93.97	100.0	93.97	93.97
200	4.64	192	96.6		97.22	97.04	96.47		96.47	96.47
220	4.73	183	98.6		99.15	99.02	98.34		98.34	98.34
240	4.81	179	100.0		100.00	100.00	100.00		100.00	100.00

Table A22. Average electrical conductivity (EC, mS/cm), DC-BI (%), DC-EC-BI(%), DC-UC(%) and DC-EC-UC(%) for chickpeas at 92 °C without and with US

	92 °C					92 °C + 25 kHz 100 W					92 °C + 25 kHz 300 W				
Time min	EC-CW (mS/cm)	DC-BI (%)	DC-UC (%)	EC-CW-BI (%)	EC-CW-UC (%)	EC-CW (mS/cm)	DC-BI (%)	DC-UC (%)	EC-CW-BI (%)	EC-CW-UC (%)	EC-CW (mS/cm)	DC-BI (%)	DC-UC (%)	EC-CW-BI (%)	EC-CW-UC (%)
0	0.00	0.0	0.0	0.0	0	0.00	0.0	0.0	0.0	0.0	0.00	0.0	0.0	0.0	0.0
20	1.98	41.8	54.4	41.2	43.8	2.80	58.2	67.3	58.0	60.2	3.05	61.6	73.0	61.1	64.1
40	2.52	52.7	66.3	52.4	55.8	3.25	66.4	78.3	67.3	69.9	3.62	72.6	85.1	72.5	76.0
60	3.04	63.7	79.0	63.2	67.3	3.58	74.7	88.0	74.1	77.0	4.02	80.8	92.2	80.6	84.4
80	3.57	74.7	86.1	74.2	79.0	3.89	80.1	93.6	80.5	83.7	4.33	87.0	99.2	86.8	91.1
100	3.92	81.5	92.8	81.5	86.7	4.06	84.9	98.3	84.1	87.3	4.55	91.1	99.9	91.2	95.6
120	4.12	85.6	97.7	85.6	91.2	4.33	89.0	99.7	89.6	93.1	4.76	95.9	100	95.4	100
140	4.29	88.4	99.4	89.2	94.9	4.48	93.1	99.9	92.7	96.3	4.88	97.9		97.8	
160	4.42	91.8	99.8	91.9	97.8	4.65	96.6	100	96.3	100	4.99	100		100	
180	4.52	93.8	100	94.0	100	4.75	98.6		98.3						
200	4.64	96.6		96.5		4.83	100		100						
220	4.73	98.6		98.3											
240	4.81	100		100											

Table A23. Average electrical conductivity (EC, mS/cm), DC-BI (%), DC-EC-BI (%), DC-UC (%) and DC-EC-UC (%) for chickpeas at 97 °C without and with US

	97 °C					97 °C + 25 kHz 100 W					97 °C + 25 kHz 300 W				
Time min	EC-CW (mS/cm)	DC-BI (%)	DC-UC (%)	EC-CW-BI (%)	EC-CW-UC (%)	EC-CW (mS/cm)	DC-BI (%)	DC-UC (%)	EC-CW-BI (%)	EC-CW-UC (%)	EC-CW (mS/cm)	DC-BI (%)	DC-UC (%)	EC-CW-BI (%)	EC-CW-UC (%)
0	0.00	0.0	0.0	0.0	0.0	0.00	0.0	0.0	0.0	0.0	0.00	0.0	0.0	0.0	0.0
20	2.78	54.1	69.6	54.7	57.9	3.48	61.6	74.1	61.6	65.4	4.29	69.9	84.2	64.1	68.6
40	3.07	60.3	79.5	60.4	64.0	3.99	70.5	83.5	70.6	75.0	4.92	79.4	94.8	73.5	78.7
60	3.58	66.4	86.4	70.5	74.6	4.44	78.1	94.8	78.6	83.5	5.63	87.0	99.3	84.2	90.1
80	3.92	72.6	92.9	77.2	81.7	4.89	87.1	99.2	86.5	91.9	6.25	90.4	100	93.4	100
100	4.18	77.4	97.4	82.3	87.1	5.18	91.1	99.9	91.7	97.4	6.49	95.9		97.0	
120	4.32	86.3	99.5	85.0	90.0	5.32	94.5	100	94.2	100	6.69	100		100	
140	4.65	91.8	99.9	91.5	96.9	5.49	97.9		97.2						
160	4.80	94.5	100	94.5	100	5.65	100		100						
180	4.97	97.9		97.8											
200	5.08	100		100											

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