ASSESSMENT OF THE RENEWABILITY OF BLACK, INSTANT AND ICE TEA PRODUCTION AND WASTE VALORIZATION PROCESSES

by

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ASSESSMENT OF THE RENEWABILITY OF BLACK, INSTANT AND ICE TEA PRODUCTION AND WASTE VALORIZATION PROCESSES

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Dedicated to my mum and dad…

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ABSTRACT

ASSESSMENT OF THE RENEWABILITY OF BLACK, INSTANT AND ICE TEA PRODUCTION AND WASTE VALORIZATION PROCESSES

Energy and exergy utilization, carbon dioxide (CO_2) emission and exergy destruction were calculated for the "*orchard to the retail market*" industrial production of the black tea in Turkey and pilot scale production of the instant and ice tea. Energy and exergy utilization was 12,748 and 45,532 MJ/t of black tea produced, being consistent with the results given in the literature. The total amount of the CO_2 emission in the entire process was 1,732 kg/t of black tea. In the entire black tea process, 70 per cent of the total energy and 86 per cent of the total exergy utilization was allocated to the processing of the tea, which also accounted for 72 per cent of the total amount of the carbon dioxide emission. The largest amounts of energy and exergy were used in the drying, withering and packaging stages of the processes, respectively. The total exergy utilized in drying process was 22,424 MJ/t, corresponding to 52 per cent of the total exergy utilization. HVAC units employed in withering were causing the largest exergy destruction, 2,542 MJ/t of black tea, followed by 318 MJ/t of black tea of exergy destruction during drying.

Energy and exergy utilization from agriculture to packaging were 1,431 MJ/kg and 3,987 MJ/kg of instant tea and 3,571 MJ/kg and 4,464 MJ/kg of ice tea, respectively. The total amount of the CO_2 emission in the entire process was 140 kg/ kg of instant tea and 267 kg/ kg of ice tea. Waste from the extraction step was analyzed further for potential conversion into value added products - activated carbon, hydrogen and adsorbent. Energy and exergy requirement for the activated carbon production from tea waste was 59.8 MJ/kg and 249.5 MJ/kg of waste tea and for the adsorbent production 3.7 MJ/kg and 15.2 MJ/kg of waste tea, respectively. Instant tea production was the most and the brewed tea was the least energy and exergy utilizing process among all the cases studied. The cumulative degree of perfection (CDP) and renewability indicator of the products showed that all of these processes were nonrenewable.

ÖZET

SİYAH, İNSTANT VE SOĞUK ÇAY ÜRETİMİ VE ÇIKAN ATIKLARIN DEĞERLENDİRİLMESİ SÜREÇLERİNİN YENİLENEBİLİRLİĞİNİN ARAŞTIRILMASI

Bu çalışmada, Türkiye'deki siyah çay üretimi "*tarladan çatala*" yaklaşımı ile endüstriyel boyutta, instant ve soğuk çay üretimi ise pilot ölçekli olarak enerji, ekserji ve karbondioksit (CO_2) salınımları açısından incelenmiştir. Siyah çay üretimi için enerji ve ekserji tüketimleri, literatürle uygunluk gösterir şekilde 12,748 and 45,532 MJ/t siyah çay olarak hesaplanmıştır. "*Tarladan çatala*" yaklaşımı ile hesaplanan CO_2 salınımı ise 1,732 kg/t siyah çaydır. Tüm süreç değerlendirildiğinde, yüzde 70 enerji, yüzde 86 ekserji ve yüzde 72 CO_2 salınımı ile siyah çayın fabrikada işlenmesi en çok enerji harcanan basamak olarak belirlenmiştir. En çok enerji ve ekserji sırası ile kurutma, soldurma ve paketleme basamaklarında harcanmaktadır. Kurutma basamağında harcanan ekserji 22,424 MJ/t siyah çay olup, toplamın yüzde 52'sine denk gelmektedir. Soldurmada kullanılan ısıtma ünitesi ekserji kaybında ilk sırada iken (2,542 MJ/t siyah çay), kurutmada kullanılan ısıtma ünitesi ise ikinci sırada gelmektedir (318 MJ/t siyah çay).

İnstant ve soğuk çayın, tarladan paketlenen ürün dahil enerji ve ekserji tüketimleri sırası ile 1,431 MJ/kg ve 3,987 MJ/kg of instant çay ve 3,571 MJ/kg ve 4,464 MJ/kg of soğuk çay olarak hesaplanmıştır. Toplam CO_2 salınımları ise 140 kg/ kg of instant çay ve 267 kg/ kg of soğuk çay olarak hesaplanmıştır. Ekstraksiyon aşamasında açığa çıkan atık çayın katma değerli ürünlere (aktif karbon, hidrojen ve adsorban) dönüştürülmesi de çalışma kapsamında değerlendirilmiştir. Atık çaydan; aktif karbon ve adsorban üretebilmek için gereken enerji ve ekserji sırasıyla 59.8 MJ/kg atık çay, 249.5 MJ/kg atık çay ve 3.7 MJ/kg atık çay, 15.2 MJ/kg atık çay olarak hesaplanmıştır. Instant çayın içime hazır hale getirilmesi en çok enerji tüketen ürün iken, demleme çay en az enerji tüketen ürün olarak bulunmuştur. Ürünlerin yenilenebilirlik değerleri ve toplam mükkemmeliyet dereceleri, incelenen tüm proseslerin yenilenebilir olmadığını göstermektedir.

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b	Flow availability of a stream
b^{ch}	Sum of the chemical exergies
eq	Equivalent
Ex	Exergy (kJ/kg)
EX	Exergy (kJ)
H	Enthalpy (kJ/kg)
h	Enthalpy (kJ)
ha	Hectar
I_r	Renewability indicator
k	Index of heat sources
m	Mass
Q	Heat
S	Entropy (kJ/kg.K)
s	Entropy (kJ/K)
T	Temperature (°C)
T_0	Reference temperature
t	Ton
W	Work
W_p	Useful work obtained by the product
W_r	Restoration work
X	Molar fraction
X_{loss}	Exergy loss
X_p	Exergy of the product
ΔT	Temperature difference
AUC	Area under the fluorescein decay curve
CBM	Cubic metres
CCO_2E	Cumulative carbon dioxide emission
CDP	Cumulative degree of perfection

CEENE	Cumulative exergy extraction from the natural environment-
CEnC	Cumulative energy consumption
CExC	Cumulative exergy consumption
COP21	United Nations Climate Change Conference
GAE	Gallic acdi equivalent
GHG	Greenhouse gas
HDPE	High density polyethylene
HVAC	Heating, ventilation, and air conditioning
LDPE	Low density polyethylene
MT	Metric ton
ORAC	Oxygen radical absorbance capacity
PET	Polyethylene terephthalate
SD	Standard deviation
TE	Trolox equivalent

1. INTRODUCTION

Tea is the second most consumed non-alcoholic drink, after water, in the world [1, 2]. Global tea production was 5.1 million tons in 2013 [3]; China is the world's largest producer contributing 36 per cent to the total global production, followed by India (21.2 per cent), Kenya (7.8 per cent), Sri Lanka (7.0 per cent), Turkey (4.8 per cent), Vietnam (4.6 per cent), and Iran (3.3 per cent). Other countries provide the remaining 15.3 per cent. Turkey, as the fifth largest producer has an annual production of 212,400 MT [4] and top per capita tea consumer [5]. Black tea, which is consumed mainly in the Western countries accounts for about 78 per cent to the global tea production. Tea is marketed in different forms, including green tea, black tea, instant tea and ice tea [6].

1.1. BLACK TEA PRODUCTION PROCESS

Black tea, which is produced by fermenting the tea leaves is the most preferred variety in Turkey. Stages of the black tea production process are given in Figure 2.2. Non-renewable chemicals, e.g., fertilizers and diesel-oil are among the inputs of the tea agriculture; pesticides are not used in tea production in Turkey.

There are four main steps in almost all of the black tea production processes: withering, rolling, fermentation, and drying [7]. The Turkish version of the Orthodox method is also called the "Çaykur method" by referring to the biggest black tea manufacturer "Çaykur" in Turkey [8]. The word withering implies controlled fading, decaying and shrinking and loss of freshness and vigor of the leaves. In the typical Turkish tea production process green tea leaves which initially has 70-83 per cent of moisture content are withered to a moisture content of 58-67 per cent at the maximum temperature of 32 °C for 6 hours [9]. During the withering process humidity, temperature and air-flow are closely monitored, the density of the withered leaves are tried to be kept even in the processing unit to allow for the development of uniform aroma and flavor compounds. The withered leaves are rolled for 40 - 45 minutes with a maceration equipment, rotorvane. The macerated leaves pieces are sieved, and then the large pieces are rolled in a pressed roller for 15-20 minutes more and then the macerated leaves are sent to the fermentation unit. Fermentation is carried out at 24-28 °C and 90 per cent relative humidity for 30 minutes. Duration of the fermentation process has significant effect on the chemical composition, and therefore the quality of the tea produced [10]. The last step of the black tea production process is drying, where air flows into the unit at an inlet temperature of 95-100 °C and flows out at 50-55 °C making final moisture content of black tea about 3 per cent. The final product is sieved for grading and packed into large Kraft bags and then sent to another plant for making the retail packages [9]. Most of the black tea is packed in 500 g or 1000 g packages. Packed black tea is placed into cardboard crates and send to the markets for sale. The industrial black tea manufacturing process in Turkey is similar to what is known globally as the Orthodox method, where the integrity and flavor of tea leaves are preserved in all stages of the production, whereas in the Turkey the leaves are subject to size reduction.

1.2. INSTANT TEA PRODUCTION PROCESS

Plain or flavor-enriched instant tea is emerging as a new fast growing commodity. It is easy to prepare it with single-serve packaging in hot or cold water without any waste. The ice and black tea products in the market have changed the customer preferences positively and made the global market grow faster [11]. China was the world leader in instant tea sector with US$ 2.2 billion sales in 2013, and followed by Japan with US$ 138.6 million [12]. The reports show that instant tea had a 25 per cent retail value in Chinese tea sector [12]. Due to rising health awareness and increasing popularity of instant tea, Europe is projected to be a potential market with fastest growing potential, whereas North America is regarded as a maturated market [11].

There are four main steps in the instant tea production processes. First loose tea, such as black tea, is produced from the tea leaves, and then the loose tea is brewed to produce a tea extract, which is then concentrated by evaporation of water to obtain a granular solid concentrate [13]. Energy and exergy utilization, carbon dioxide emission and exergy destruction in industrial black tea production process was studied recently by Pelvan Pelitli *et al*. [14], within the scope of this PhD study. The solid granular concentrate, which is obtained after drying of the tea extract may be packed in to bags, e.g., one g of concentrate may be packed in one g of paper bag and 2 g black tea and 1 g of instant tea is dipped into 200 mL of hot water for reconstitution. The tea extract may also be sold as “ice tea”, e.g., a canned product, for cold consumption. In extraction of black tea one of the most efficient and commercially preferred techniques is continuous extraction. Three types of conventional methods, spray, freeze, and vacuum drying, are employed to produce instant tea powder [15]. Spray drying is a widely used and well-established technique to produce powder from liquid and semi-liquid foods [16], due to being a short and a controllable process, and the products retain high quality properties such as color, flavor, and nutrients. Instant tea powder may be agglomerated to increase the solubility. Agglomeration can be performed with fluidized bed dryer. Drying aids or carrier materials, such as maltodextrin, modified starches, and arabic gum, are used in spray drying to provide stability and improve the product recovery [17].

1.3. ICE TEA PRODUCTION PROCESS

Ice tea is a cold consumed product, enriched generally with flavors such as sweetens, lemon, peach, vanilla, etc. Ice tea can be produced by extracting tea leaves to a desired concentration or by diluting the tea extract concentrate or instant tea powder. A potential cloudiness problem in ice tea production may be prevented by many different processes such as centrifugation, enzyme treatment and precipitation [18, 19]. Ice tea is generally served as ready to drink in cans or bottles. According to review of Tea Association of the USA Inc. [20] ice tea is the top tea beverage consumed away from home. In the USA, approximately 85 per cent of the tea consumption is in the form of ice tea and over the last ten years, ready-to-drink tea market has grown by more than 15-folds.

Improving the energy efficiency of food production, as in the black tea, instant tea and ice tea production, without deteriorating the quality is among the major goals of the current research. In every moment of the process the prevailing physical conditions, e.g., the temperature, and the composition of the food should be in perfect combination [21]. In a typical example while trying to find an energy efficient process for frying the potato chips, van Loon *et al*. [22] reduced the cellular water content of the potatoes by using alternative technologies, such as superheated steam, pre-drying with air and vacuum freezing and achieved a more energy efficient process, but the new processes did not produce the crispy crust like the ones produced with the conventional process, therefore the new process was not used in the industry. The taste development constraints needs to be satisfied while carrying out the energy savings studies in the food industry. Gupta *et al*. [23]

suggested a fuzzy logic approach to achieve these combinations during the withering process.

The recent publications by Xu and Flapper [24], Wu *et al*. [25] and Rodriguez-Gonzales *et al.* [26] offered recommendations for substituting the less energy efficient steps of food production with the more energy efficient ones representing the general trend towards increasing the energy efficiency by decreasing the energy utilization. Exergy destruction in the individual processing units decreases the overall exergy efficiency of the processes. The process units where exergy destruction is the highest is determined by exergy analysis. Within this context Bayrak *et al*. [27] assessed the exergetic performance of sherbet production, distillation, thickening, and crystallization stages the sugar process, and found their exergetic efficiencies as 49.3 per cent, 62.1 per cent, 91.9 per cent, and 61.7 per cent, respectively. Exergy analysis of the entire chains of pork mincemeat, pea-protein based product, and pea soup production processes were determined by Apaiah *et al*. [28] as 0.09 per cent, 0.2 per cent, and 0.48 per cent, respectively. Waheed *et al.* [29] studied the energy consumption pattern in the orange juice manufacturing industry Nigeria, where the pasteurizer was found to be responsible for more than 90 per cent of the irreversibility. Özilgen and Sorgüven [30] assessed energy and exergy utilization and carbon dioxide emission during production of soybean, sunflower, and olive oils using farm-to-fork approach. The CExC (cumulative exergy consumption) associated with the production of the olive, sunflower, and soybean oils was found to be 43,050.3, 17,638.2, and 45,256.8 MJ/t, respectively. In a similar study, Sorgüven and Özilgen [31] applied the exergy analysis to compute the CExC for assessing the environmental impact of the flavored yogurt production process. The analysis covered three important stages of the yogurt production i.e., agriculture, dairy farming, and industrial processes. The total exergy loss was found to be 7,5791.6 MJ/t of flavored yogurt. The results showed that the milk production (dairy farming) had the highest contribution to the total exergy loss, accounting for 53 per cent of the overall exergy loss. Quijera and Labidi [32] and Yildirim and Genç [33] carried out exergy analysis to improve the exergy efficiency of the pasteurization of milk by employing solar and thermal energy, respectively. Zisopoulos *et al.* [34] employed exergy analysis to compare efficiency of three industrial bread production chains, Değerli *et al.* [35] employed a similar methodology to calculate the farm to fork exergy efficiency of wheat and rye bread production processes in Turkey and Germany. In another survey, Genc and Hepbasli [36] assessed the exergetic performance of a potato crisp frying system consisting of a combustor, a heat exchanger, and a fryer. The exergetic efficiencies of the combustor, heat exchanger, and fryer were calculated as 58 per cent, 82 per cent, and 77 per cent, respectively, while the exergy efficiency of the whole frying system was 4 per cent.

Drying is among the higher amounts of energy utilizing food processing operations, due to the energy requirement of the phase change of water, therefore there are very large number of exergy analysis studies regarding drying [37- 41] including drying of macaroni in the industry [42] and rough rice drying process in a laboratory scale plug flow fluidized bed dryer [43] where the exergy efficiency of the process was determined in the range of 4.18 - 12.00 per cent. Icier *et al.* [44] carried out exergy efficiency studies by using tray, fluidized bed, and heat pump dryers during processing of broccoli florets and found that the fluidized bed dryer had the highest exergy efficiency (90.86 per cent) among all of the drying systems. Aghbashlo *et al.* [45] studied the exergy efficiency of the fish oil microencapsulation process by spray drying and reported that the process exergy efficiency was between 1.64 per cent and 14.43 per cent. Tea processing consists of numerous drying stages. Individual stages of the tea production had been the subject of the thermodynamic analysis, including withering [8] and drying [39, 46, 47] proposed a model for energetic and exergetic analyses of a batch type fluidized bed dryer. Erbay and Koca [37] studied the performance of a pilot scale spray dryer during white cheese powder production. Saygı *et al.* [41] evaluated the performance of spray drying process of a fruit puree by means of energy and exergy analyses. Ozgener and Ozgener [42] studied drying of macaroni in the industry, Khanali *et al.* [43] studied rough rice drying process in a laboratory scale plug flow fluidized bed dryer, where the exergy efficiency of the process was in the range of 4.18 -12.00 per cent. Experimental exergy analysis is a time-consuming and costly process. With the use of mass, momentum, energy, entropy and exergy balance equations the time and costs can be reduced in determination of most efficient conditions [40].

Thermodynamic analysis of the instant and ice tea process is important to achieve reductions in energy utilization. Taste development should not be neglected while carrying out these analyses. The optimum process conditions for pilot scale instant tea production were assessed by a sensory panel [48] in association the energy and exergy utilization and carbon dioxide emissions in this study were carried out based on that conditions.

The United Nations Climate Change Conference (COP21), also known as the 2015 Paris Climate Conference took place in December 2015, with the aim of keeping the rise in average global temperature below 2 ºC by 2100. During the COP21, 196 countries agreed to stabilize their greenhouse gas (GHG) emissions by 2020 before starting to decrease them. There are many studies regarding the GHG emissions in industry. Investigation of the "*cradle to grave*" GHG emissions of food products is important since food related activities make up nearly 20 per cent of the total climate related emissions of the households in Germany [49]. Azapagic *et al.* [5] studied "*cradle to grave*" global warming potential of production and consumption of the Kenyan tea and found the impact 12.45 and 12.08 kg CO_2 eq./kg for the large and the small-scale production, respectively. The 85 per cent of the impact was due to boiling of water for preparation. Tea cultivation and processing constituted 10 per cent to the total, whereas the share of transportation was 4 per cent. Cichorowski *et al.* [49] after studying the life cycle GHG emission of Darjeeling tea reported that the carbon footprint was 38 g CO_2 eq./250 mL and found the largest share, 51 per cent, was generated while boiling of water. In most countries, progress toward clean environment is achieved only with the support of the public, which comes only after informing the people. In this study, the energy utilization and the carbon dioxide emission during production of the black tea is assessed and the Turkish version of the Orthodox method of black tea production and pilot scale instant and ice tea production has been assessed by referring to energy and exergy utilization and the carbon dioxide emission. This study is different than the others carried out in the similar field [8, 50- 52] since it covers the entire "orchard to the retail market" of the black tea production process, including packaging and transportation, presents the values of all the thermodynamic parameters CEnC, CExC and CCO_2E of these stages together with the associated exergy destruction. Theoretical values are also compared with the industrial data published in Turkey.

A comprehensive review of the potential of the valorization of the waste products was presented by Grace *et al.* [53]. Currently, tea and coffee wastes are either composted or send to the landfills [53]. Production of activated carbon and adsorbent material from the tea waste are viable options [53- 55]. Removal of metals, dyes, phenols have been achieved by the adsorbents produced from tea and coffee waste [53]. Production of the activated carbon from the industrial grape processing [56] and palm solid [57] wastes and hydrogen from the food wastes [58- 60] is described in the literature.

In the present study, instant tea and ice tea production processes were analyzed by using energy and exergy analysis to determine the efficiencies in each step. Energy and exergy utilization and CO_2 emission were compared for the "*cradle to grave*" production and consumption of the Turkish style brewed tea, brewed tea with tea bag, instant tea and ice tea. Renewability and cumulative degree of perfection (CDP) of black tea, instant tea and ice tea with further processing of the waste tea for adsorbent, active carbon and hydrogen are also carried out.

2. METHODOLOGY

2.1. ENERGY, EXERGY AND CO_2 EMISSION CALCULATIONS

Tea is grown in the Black Sea Region of Turkey, whereas major consuming areas are big cities such as İstanbul, Ankara, and İzmir. Tea processing factories are mainly located in Black Sea Region of Turkey, especially around the province of Rize. The average distances between the fields - factories and factories - consumers were taken as 20 km and 1,150 km, respectively. The distances were calculated by using the maps and the Çaykur reports [61]. The product delivery trucks are considered to be making one-way trip only, since in the practice they usually carry other products on the way back. Black tea production process system and its boundary used in this study is given in Figure 2.1.

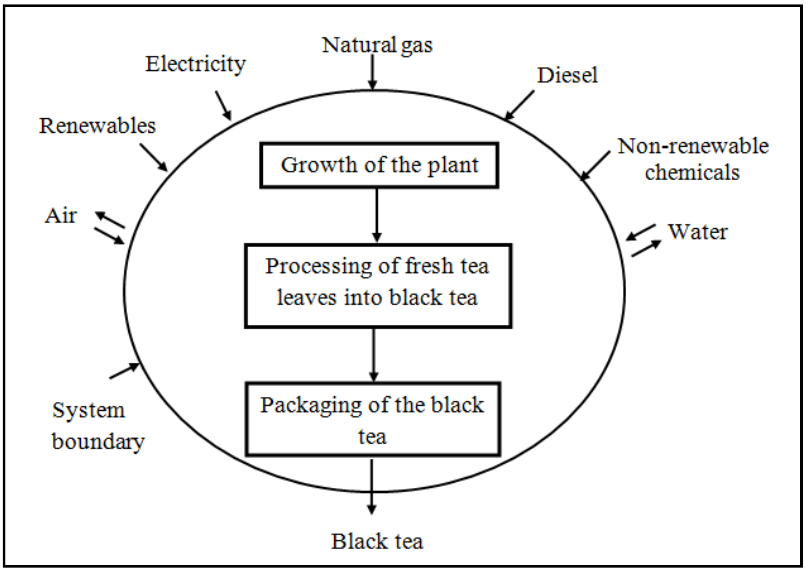

Figure 2.1. Description of the black tea production process system and its boundary

The process flow diagram of the black tea production process is described in Figure 2.2. Energy utilization by the equipment of each production steps, e.g. conveying, withering, rolling, fermentation, drying, and packaging are obtained from the web site of the equipment providers and the heating, ventilation, and air conditioning (HVAC) units is based on theoretical calculations.

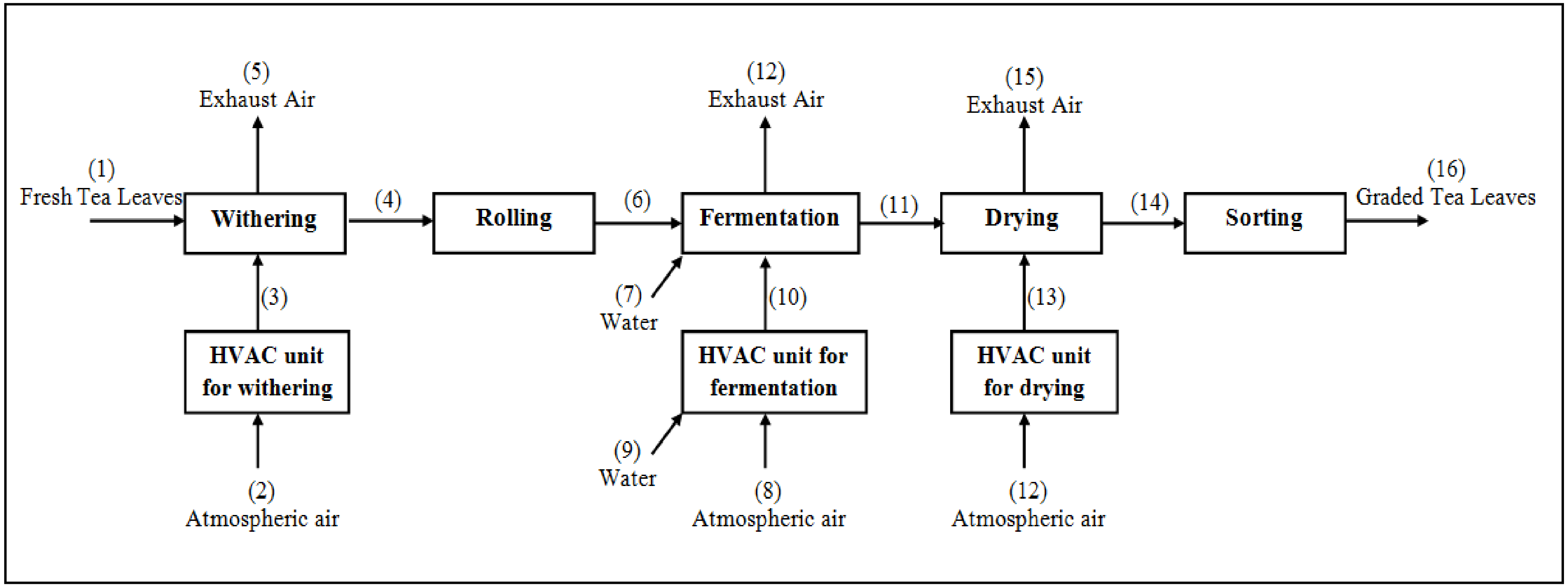

Figure 2.2. Flow diagram of the black tea production process

The energy and exergy utilization in each process was computed by using the flow diagram presented in Figure 2.2. Each process step in agriculture, production and packaging of black tea is analyzed with mass, energy and exergy balance equations to determine the CEnC, CExC, total CO_2 emission (CCO_2E). The governing equations employed here are:

Mass balance:

$$\sum(\mathrm{m})_{in} - \sum(\mathrm{m})_{out} = 0 \tag{2.1}$$

Energy balance:

$$\sum(\mathrm{mh})_{in} - \sum(\mathrm{mh})_{out} = Q - W \tag{2.2}$$

Exergy balance:

$$\sum(\mathrm{mb})_{in} - \sum(\mathrm{mb})_{out} - \sum_{k} Q_k \left(1 - \frac{T_0}{T_k}\right) - W = X_{loss} \tag{2.3}$$

Where k is the index of heat sources and b is the flow availability of a stream (neglecting the potential and kinetic energy contribution):

$$b = h - T_0 s - \sum x_i\, \mu_i^0 \tag{2.4}$$

The chemical availability can be obtained from tables, if available or computed via group contribution method, if the chemical structure of the compound is known. The group contribution method estimates b^{ch} as the sum of the chemical exergies of the simple groups, which make up the compound. Chemical composition of non-fermented green tea and fermented black tea is taken from the study of Harbowy *et al.* [62]. Chemical energy and exergy of organic compounds are calculated based on their composition and standard chemical exergy of the organic groups are taken from Szargut *et al.* [63]. Epigallocatechingallate, theaflavin and gallic acid were taken as the representing compound in cathechins, theaflavins and other polyphenols group, respectively.

The overall flow diagram of the steps of the production chain from agriculture to the end products is given in Figure 2.3. The agriculture and black tea processing steps were studied in detail by Pelvan Pelitli et al. [14], within the scope of this study. The process flow diagram of the instant tea production process is described in Figure 2.4. Energy utilization by the equipment of each production steps, e.g. extractor, separator, spray dryer and fluidized bed dryer were obtained from the user’s manual of the equipment. The process flow diagram of the ice tea production process is described in Figure 2.5. Energy utilization by the equipment of each production step, e.g. extractor, separator, mixing and bottling were obtained from the user's manual of the equipment or from internet. All the production calculations were carried out for batch systems. The energy and exergy utilization in each process was computed by using the flow diagram presented in Figure 2.4 and Figure 2.5. Thermodynamic properties of the streams, heat and work flows of the processes were calculated for instant and ice tea. In a batch process the outlet temperature of a stream may be different than that of the inlet temperature in the processes described in Figure 2.4 and Figure 2.5. The waste valorization products were adapted from the literature. Drying analyses were calculated theoretically and analyses for the other steps were carried out with the energy utilization values reported by the equipment manufacturers. Mass, energy and exergy balance equations were established to determine the CEnC, CExC, CCO2E in each process step of instant and ice tea production processes.

The cumulative degree of perfection (CDP) is defined as the ratio of the exergy of the products to the sum of the exergies of the input materials and non-renewable fuels [63]:

$$CDP = \frac{(mb)_{product}}{\sum(mCExC)_{\text{raw materials}} + \sum(mCExC)_{\text{fuels}}} \tag{2.5}$$

Renewability indicator is defined as:

$$I_r = \frac{(W_p - W_r)}{W_p} \tag{2.6}$$

where, Wp is the useful work obtained by the product, Wr is the restoration work. If the maximum work potential of the product is extracted via reversible process, then Wp equals to Xp [64, 65]. In the present study, electricity was the energy source and used to calculate cumulative exergy utilization and CO_2 emissions. CO_2 emission coefficient for the electric power utilization and CExC were taken as 0.14 kg/MJ and CExC 4.17 MJ/MJ, respectively [66].

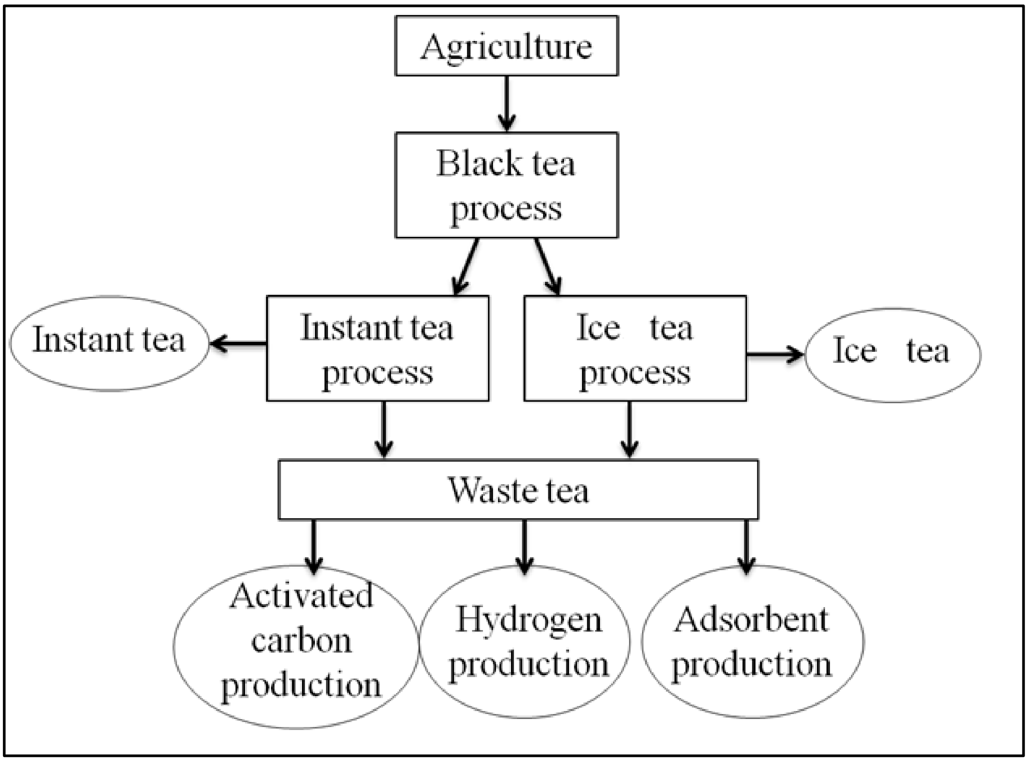

Figure 2.3. Valorization products and the byproducts of the black tea crop

2.2. EXPERIMENTAL ANALYSIS

2.2.1. Determination of Total Phenolic Content

The content of total phenolics was determined according to the procedure described by ISO 14502-2:2005, using the Folin−Ciocalteu phenol reagent [67]. Phenolics were extracted with 70 per cent methanol, and absorbance was read using a microplate reader (FLUOStar Omega, BMG Labtech, Ortenberg, Germany). The content of total phenolics was calculated from a standard curve using gallic acid as a standard and expressed as grams of gallic acid equivalents (GAE) per 100 g of instant tea. Details of the method used is given in Appendix A.

2.2.2. Determination of Oxygen Radical Absorbance Capacity (ORAC)

The antioxidant activity was determined according to the ORAC assay as described by Wu *et al.* [68]. Samples were extracted by acetone/water/acetic acid (70:29.5:0.5, v/v/v), and the analysis was performed using a microplate reader (FLUOStar Omega, BMG Labtech). ORAC values were calculated by using the trolox and sample concentration and the net area under the fluorescein decay curve (AUC). Data were expressed as micromoles of trolox equivalents (TE) per gram of instant tea. Details of the method used is given in Appendix A.

2.2.3. Determination of Phenolic and Alkaloid Compounds

Phenolic compounds were extracted and analyzed according to the HPLC method of Dou *et al.* [69] as outlined in detail by Serpen *et al.* [1] with some minor modifications. Chromatographic analyses were performed on a Shimadzu HPLC system (LC-20AD pump, SPDM20A DAD detector, SIL-20A HT autosampler, CTO-20AC column oven, DGU-20A5 degasser, and CMB-20A communications bus module, Shimadzu Corp., Kyoto, Japan). An Atlantis dC18 column (250 mm × 4.6 mm, 5 µm particles, Waters Corp.) was used to separate flavanols, alkaloids, and phenolic acids in instant tea extract. A linear gradient elution program with a mobile phase containing solvent A (acetonitrile) and solvent B (acetic acid/H_2O, 0.1:99.9, v/v) was used at a flow rate of 1 mL/min. The solvent gradient was programmed as follows: linear gradient elution from 10 to 20 per cent A (0−15 min), then linear gradient elution from 20 to 40 per cent A (15−25 min), and linear gradient elution from 40 to 10 per cent A (25−30 min). The quantitations of flavanols, alkaloids, and phenolic acids were based on calibration curves built for each of the compounds identified in instant teas. Data were expressed as milligrams per 100 g of instant tea. Details of the method used is given in Appendix A.

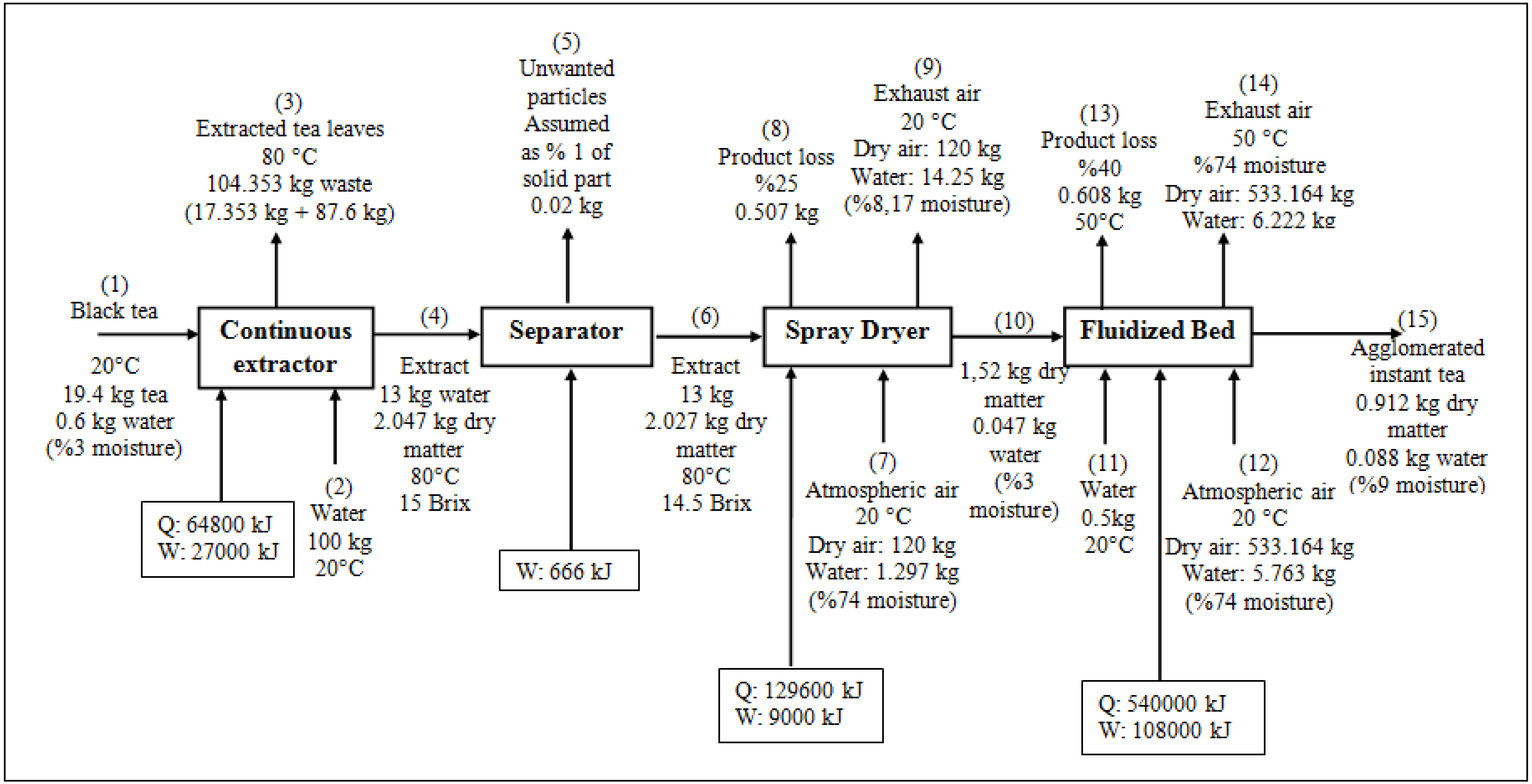

Figure 2.4. Flow diagram of the instant tea production process

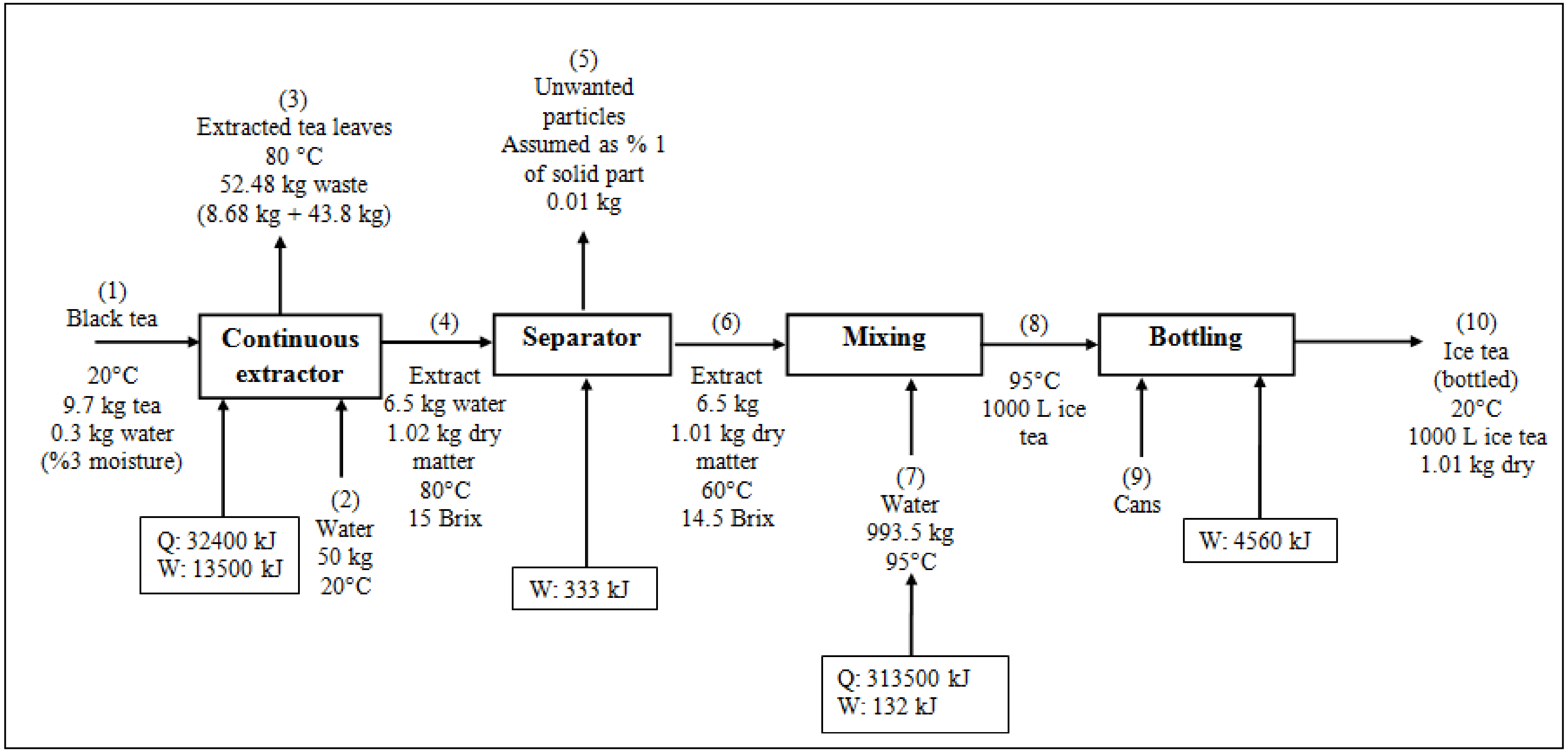

Figure 2.5. Flow diagram of the ice tea production process

3. RESULTS AND DISCUSSION

3.1. GROWTH AND TRANSPORTATION OF FRESH TEA LEAVES

Estimates of the energy and exergy utilization and the carbon dioxide emission associated with the agriculture of tea leaves are given in Table 3.1. The tea plant has about 100 years of lifespan, therefore energetic and exergetic requirements of the seed consumption are neglected. There is no irrigation because of the rainy climate of the Black Sea Region [70]. No chemicals (pesticides, etc.) is used in Turkey for growing tea [70] and the amounts of manure is 30 kg/ha for every 3 years and chemical fertilizers were given as 25 kg/ha, 30 kg/ha, and 15 kg/ha for nitrogenous, phosphorous and potassium fertilizer, respectively by Kaçar [70]. Helsel [71] reported the amounts of energy associated with the use of the chemical fertilizers as 78.2 MJ/kg for nitrogenous, 17.5 MJ/kg for phosphorus and 13.8 MJ/kg for potassium fertilizer, including production, packaging, transportation, and application. These data are used to calculate the energy utilization associated with the nitrogenous phosphorous and potassium fertilizer as 715 MJ/t, 192 MJ/t, and 75.7 MJ/t of black tea, respectively. The total energy utilization associated with the chemical fertilizers is 983 MJ/t of black tea. Since the energy utilization associated with the organic manure utilization is negligible (0.13 MJ/t black tea), it is not included in Table 3.1.

Table 3.1. Energy and exergy utilization and carbon dioxide emission during the agriculture of the fresh tea leaves.

	CEnC (MJ/t)	**CExC (MJ/t)**	**CCO_2E (kg/t)**
Chemical fertilizers	983	406	232
Nitrogenous	715	299	65.0
Phosphorous	192	82.3	29.6
Potassium	75.7	25.2	137
Diesel consumption for transportation and machine work (20 km)	84.8	78.5	1.4
Total	1,067	485	233

The CExC values of nitrogenous, phosphorus and potassium fertilizers are 32.7 MJ/kg [63], 7.5 MJ/kg [72], and 4.6 MJ/kg [73] respectively. This data leads to the calculation of exergy utilization associated with production of one ton of black tea, which is equivalent to 3,880 kg of fresh tea leaves [70], to be 299 MJ for nitrogenous, 82.3 MJ for phosphorus, and 25.2 MJ for potassium fertilizer production, implying that the total exergy consumed in association with fertilizer use is 406 MJ/t of black tea.

By using the modern factories energy consumption for chemical fertilizer production can be decreased. Kongshaug [74] and Anundskas [75] reported that for nitrogenous fertilizer 40 MJ/kg energy is utilized, which is approaching the theoretical minimum. According to Kongshaug [74] 2.71, 25, and 7.11 kg of CO_2 is emitted during production of one kg of phosphorus, potassium, and nitrogenous fertilizer, respectively. Using these estimates together with the amounts of each fertilizer used in the agriculture of fresh tea leaves as reported by Kaçar [70] yields that 232 kg CO_2 emitted/t of black tea.

Fresh tea leaves are transported with the diesel oil consuming trucks. Roy *et al.* [76] reported that 10 t capacity trucks consume 0.287 L/km of fuel, while traveling at 90 km/h speed. The fresh tea leaves are transported at 20 km of average distance from field to the plant and the trucks turn back empty. The density of diesel oil is about 0.832 kg/L, its energy equivalent is 57.5 MJ/kg [77] , CExC = 53.2 MJ/kg [63] and its carbon dioxide emission factor is 0.94 kg CO_2 /kg diesel oil [78]; by using these values the energy and exergy utilization and the carbon dioxide emission for transportation was calculated to be 84.8 MJ/t of black tea, 78.5 MJ/t of black tea and 1.4 kg CO_2 /t of black tea, respectively.

3.2. BLACK TEA PRODUCTION

The energy consumption data by the equipment (conveyor, fan, rolling and sorting machine and packaging and cardboard making machines) which may be employed in the black tea production plant were obtained from the web sites of the equipment manufacturers. The energy and exergy utilization for processing one ton black tea, which is the final product, were calculated from these data and given in Table 3.2. Electricity was chosen as the energy source to calculate exergy utilization and CO_2 emissions. Heating requirement in each stage of the process were calculated theoretically by referring to Table 3.3. The results represented in Table 3.2 and Table 3.3 are the minimum theoretical values, the calculations were carried out with the assumption of no heat loss to the surroundings. The stack loss to the surrounding was reported to be 40 per cent in the Asian Institute of

Technology report [51]. The exergy charts of the black tea production process are given in Figure 3.1.

Table 3.2. Energy and exergy utilization and CO_2 emission associated with the black tea production process.

Processing step and equipment details	**CEnC (MJ/t)**	**CExC (MJ/t)**	**CCO_2E (kg/t)**
Withering			
Fan (Steelsworth FA 102)	44.1	184	6.2
Conveyor (Heng Shun, China, model DT-75 belt conveyor)	64.8	270	9.1
Heater	3,101	12,931	434
Rolling			
Conveyor (Heng Shun, China, model DT-75 belt conveyor)	1.8	7.5	0.3
Rolling machine (Steelsworth Single and double action 46”)	234	975	32.7
Fermentation			
Fan (Steelsworth FA 102)	1.1	4.5	0.2
Conveyor (Heng Shun, China, model DT-75 belt conveyor)	5.4	22.5	0.8
Heater	26.1	109	3.7
Drying			
Fan (Steelsworth FA 102)	11.9	49.5	1.7
Conveyor (Heng Shun, China, model DT-75 belt conveyor)	5.4	22.5	0.8
Heater	5,360	22,351	750
Sorting			
Sorting machine (Arnott's tea sorter KTG, GK Tea Industrial C., India)	37.8	158	5.3
Conveyor (Heng Shun, China, model DT-75 belt conveyor)	43.2	180	6.1
Packaging into Kraft bags	5.4	22.5	0.8
Total	8,937	37,269	1,251

Table 3.3. Thermodynamic properties of streams and black tea production process steps

			Chemical composition (per cent)			Total mass flow (kg)	T (°C)	H (kJ)	S (kJ/K)	Ex (kJ)
			Dry Air	Water	Dry Tea					
Withering	In	Stream-1	0	75	25	3,880	20	313,438	-	106,097
		Stream-3	99	1	0	24,4054	32.5	14,966,759	53,033	488,686
		W-Conveyor						64,800		
	Out	Stream-4	0	65	35	2,771	21.5	236,878	-	8,959
		Stream-5	98	2	0	245,163	21.5	15,051,869	53,566	428,218
									Exergy Destruction =	222,405
HVAC unit for withering	In	Stream-2	99	1	0	244,054	20	11,865,797	42,675	215,622
		Q						310,0961		
		W-Fan						44,064		
	Out	Stream-3	99	1	0	244054	32,5	14,966,759	53,033	488,686
									Exergy Destruction =	2,542,072
Rolling	In	Stream-4	0	65	35	2,771	21.5	236,878	-	8,959
		W-Rolling						233,803		
	Out	Stream-6	0	65	35	2,771	35	385,310	-	22,895
									Exergy Destruction =	219,867
Fermentation	In	Stream-6	0	65	35	2,771	35	385,310	-	22,895
		Stream-10	99	1	0	5,992	20	317,818	1,139	6,876
		Stream-7	0	100	0	31	20	2,629	9	93
		W-Conveyor						5,400		
	Out	Stream-11	0	65	35	2,771	25	275,380	-	11,982
		Stream-12	98	2	0	6,024	25	427,995	1,513	14,875
									Exergy Destruction =	8,408

HVAC unit for fermentation	In	Stream-8	99	1	0	5,982	20	290,830	1,046	5,287
		Stream-9	0	100	0	11	20	893	3	32
		Q						26,095		
		W-Fan						1,080		
	Out	Stream-10	99	1	0	5,992	20	317,818	1,139	6,876
									Exergy Destruction =	23,835
Drying	In	Stream-11	0	65	35	2,771	25	275,364	-	11981
		Stream-13	99	1	0	65,799	100	8,559,188	27,671	1,005,056
		W-Conveyor						5,400		
	Out	Stream-14	0	3	97	1,000	40	143,542	-	11,939
		Stream-15	96	4	0	67,570	49	9,725,346	33,088	692,273
									Exergy Destruction =	316,861
HVAC unit for drying	In	Stream-12	99	1	0	65,799	20	3,199,131	11,505	58,153
		Q						5,360,056		
		W-Fan						11,880		
	Out	Stream-13	99	1	0	65,799	100	8,559,188	27,671	1,005,056
									Exergy Destruction =	30,752
Sorting	In	Stream-14	0	3	97	1,000	40	143,542	-	11,939
		W-Sorting						82,000		
	Out	Stream-16	0	3	97	1,000	20	71,775	-	3,488
									Exergy Destruction =	81,999

Black tea production starts with the arrival of fresh tea leaves to the plant and their conveying to withering step. Conveyor, used to convey fresh tea leaves, (Heng Shun, China, model DT-75 belt conveyor, capacity = 45-200 t/h) was calcalated to be utilizing an electric energy of 64.8 MJ/ t of black tea and the CExC was equal to 270 MJ/t of black tea. Fan (Steelsworth FA 102, Calcutta, India– Axial flow fan with a capacity of 25,500 CBM air flow), which was used to circulate air for 6 hours to remove the moisture from 3.88 tons of fresh tea leaves was reported to be utilizing an electric energy of 44.1 MJ/t of black tea and the CExC was equal to 184 MJ/t of black tea. To keep the temperature at 32 ^{o}C energy needed was 3,101 MJ/t of black tea and the CExC was equal to 12,931 MJ/t of black tea, when electricity was used as the energy source. Total energy and exergy utilized in the withering step was 3,210 MJ/t of black tea and 13,385 MJ/t of black tea with the emission of 449kg CO_2/t of black tea. Energy utilization in the withering step was reported as 1,656 MJ/t by Baruah *et al.* [52], 10,656 MJ/t and by de Silva [50]. In the Asian Institute of Technology report [51], theoretical minimum energy to remove moisture in withering step was reported to be 1.9 kWh, where as in practice energy utilization was between 4 -7 kWh, and the specific energy utilization was 4 - 10.4 kWh/kg, which can easily be converted to 6,840, 14,400-25,200, 14,400-374,400 MJ/t of black tea, respectively. In this report it was mentioned that the average was 1.8 kWh/kg (6,480 MJ/t of black tea). The energy requirement for withering was reported to be mainly in the form of electric power, constituting about 15 – 55 per cent of the total electrical energy utilization [51]. In our study, the heat energy required in the withering step (3,101MJ/t of black tea) was calculated based on the energy need for heating of the air, which was used to decrease moisture content of fresh tea from 75 per cent to 65 per cent. Our results are lower than those of the Asian Institute of Technology report [51] and de Silva [50], but higher than Baruah *et al.* [52]. The differences may be due to the initial moisture contents of the tea leaves, and the maximum inlet or exhaust air temperatures. In the present study exhaust air leaves the withering unit with maximum humidity and minimum temperature, so that the entire moisture removal capacity of the inlet air was used and there was also no heat loss to the surroundings.

The tea leaves are sent to the rolling step, after their moisture content decrease from 70 – 83 per cent to 58 – 67 per cent in withering. In the rolling step, it was calculated that the equipment (Steelsworth, China - single & double action 46"- 1150 mm with a capacity of

240 kg withered leaf/h) utilizes 234 MJ energy /t of black tea and 975 MJ exergy/ t of black tea with an emission of 32.7 kg CO_2/t of black tea. Jayah [79] reported the energy utilization in the rolling step as 720 MJ/t of black tea, whereas Baruah *et al.* [52] reported that the minimum and the maximum energy utilizations in this step as 360 - 720 MJ/t black tea. The Asian Institute of Technology report [51] states the specific energy utilization in the rolling step as 360-1,080 MJ/t of black tea. The energy requirement as calculated in our study was slightly lower than the ones reported in the literature; this may be due to the low energy requirement of the rolling machine employed. We assumed no loss in the system.

The rolled tea leaves are sent to the continuous fermentation stage. The tea leaves are oxidized by blowing air for 30 minutes over the tea leaves, while the leaves are moving on the belt conveyor (Heng Shun, model DT-75, China, capacity = 45-200 t/h, electric power requirement = 5.4 MJ/t black tea). In this stage of the production exergy utilized per ton of black tea was calculated as 22.5 MJ. Air was circulated in this process with the fan (Steelsworth axial flow fan, model FA 102, Calcutta, India, air flow capacity = 25,500 CBM, electric power requirement = 1.8 MJ/t black tea). Total energy and exergy utilized in the fermentation step was 32.6 MJ/t black tea and 135.8 MJ/t of black tea, respectively and the CO_2 emission was calculated as 4.6 kg CO_2/t of black tea. Exothermic oxidation reactions establish the aroma of black tea in the fermentation step. While carrying out this process temperature of the room must be less than 32°C. Liquid water is sprayed into to fermentation room to prevent the increase of the temperature.

The next step after fermentation is drying, in which the moisture content of tea becomes ~ 3 per cent [80]. Heat is used to remove water from the leaves. Energy utilization by the HVAC units, heater, fan and conveyors, and that of the drying step are given in Table 3.2. Theoretical amount of heat energy needed to remove water from the leaves was calculated to be 5,360 MJ/t of black tea, where CExC was 22,351 MJ/t of black tea and 750 kg CO_2 was emitted per ton of black tea. The energy utilization in the drying step was reported as 252 MJ/t by Baruah *et al.* [52] and 13,700 MJ/t heat energy with 252 MJ/t electrical energy by de Silva [50]. In the Asian Institute of Technology report [51], theoretical energy to remove moisture in drying step was stated as 10,440 MJ/t and the average is 15,768 MJ/t. The specific energy utilization rate range of the countries reported in the Asian Institute of Technology report [51] is 12,600 - 16,200 MJ/t. In our study, heat energy required in the drying step was 5,360 MJ/t of black tea, which was provided by air to reduce the moisture content of the fresh tea from 65 per cent to 3 per cent. Our results are lower than the ones reported by the Asian Institute of Technology [51] and de Silva [50], but higher than those of Baruah *et al.* [52]. The differences between the results of the present studies may be due to the differences in the operating moisture contents and the maximum inlet or exhaust air temperatures, also in present study energy requirement was made based on theoretical heat needed. Exergy efficiency of the withering process is reported to be highly sensitive to combination of the air and tea flow rates [8], confirming our argument about the differences among the present works. In the present study exhaust air leaves the drying unit with the maximum humidity and the minimum temperature, so all the heat capacity of inlet air was used and there was no heat loss to the surroundings.

Tea was sorted with Arnott's tea sorter (model KTG, GK Tea Industrial Corporation, West Bengal, India, capacity = 1000 kg/h, electric power requirement = 37.80 MJ/t). To have seven grades of black tea, black tea is conveyed from drying step to sorting and after sorting, seven grades of black tea are conveyed and packed into Kraft bags. When we consider all these steps the total energy and exergy requirement for sorting step was: CEnC: 86.4 MJ/t and CExC: 360.5 MJ/t, the CO_2 emission: 12.2 kg/t. Energy utilization in this stage was reported by de Silva [50] as 324 MJ/t of black tea, while Baruah *et al.* [52] reported that minimum and maximum energy utilization in sorting and packaging steps as 252 and 324 MJ/t of black tea, respectively. In the present study energy utilization by the sorting machine was provided by the equipment provider and it was lower than the ones reported in the literature. Sorting is the last step in the black tea production process (Figure 2.2).

Energy utilization by the HVAC units were calculated separately for each step. Due to the large size of the processing units, fans must be used efficiently to circulate the air. In practice, high – temperature exhaust air coming from the dryers may be fed to the withering or fermentation steps. Recycling the air in the same units is another option to decrease the energy needed by the HVAC units. Also, the inlet air temperature of a process may be increased by the exhaust air of another process.

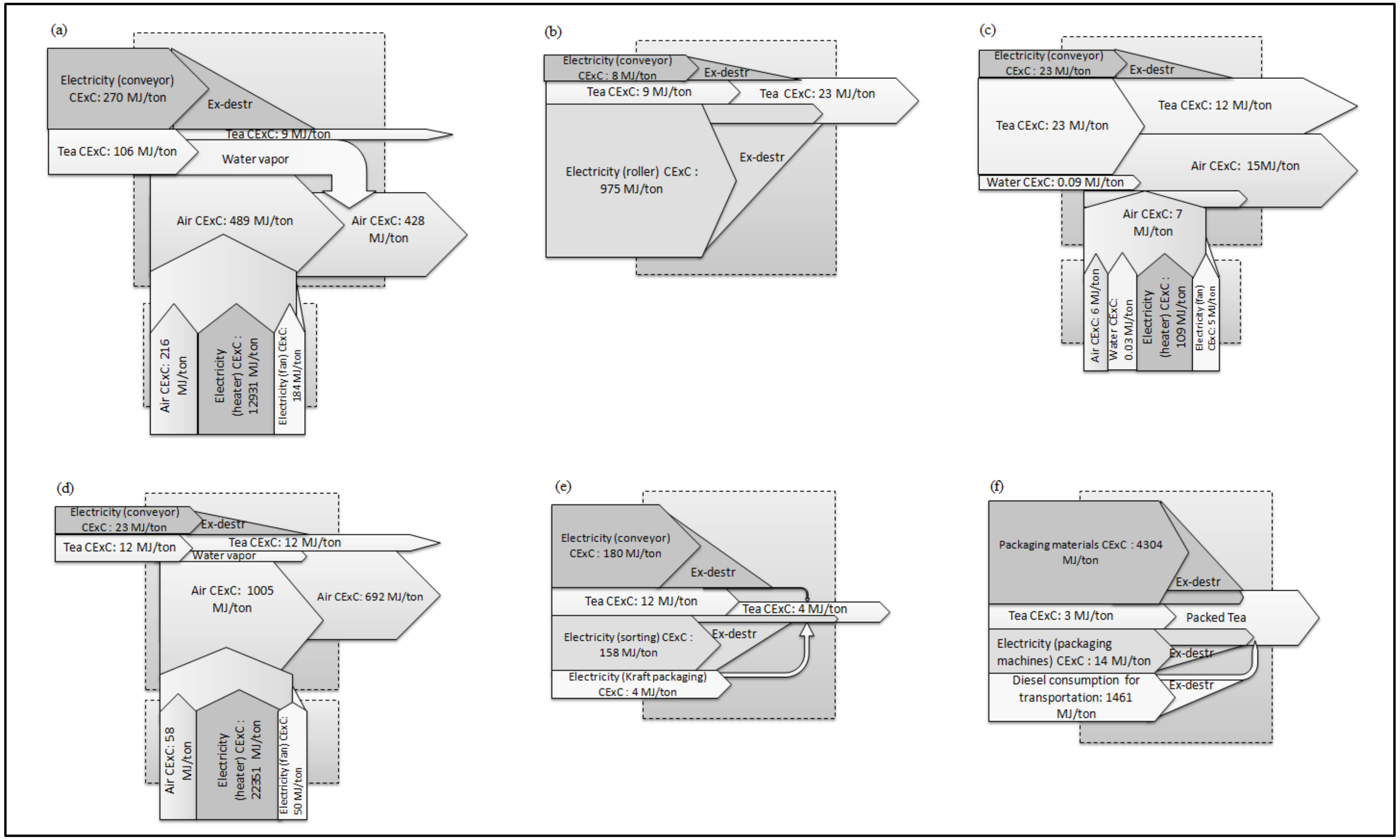

Figure 3.1. Exergy chart representing the exergy-content of the consumed resources and the tea itself during production of the black tea at the stages of (a) withering, (b) rolling, (c) fermentation, (d) drying, (e) sorting and (f) packaging

3.3. BLACK TEA PACKAGING

The calculations were carried out for packaging 500 gr tea in packages, e.g., the most common industrial practice in Turkey. The packaging materials needed for each 500 g tea package were 15 grams of virgin paper, 1.8 g hot melt glue, e.g., LDPE, and 4.32 g of PET holographic film. Twenty-four packages are placed in a carton made of 1.03 m^3 cardboard and 5 g of LDPE sticky tape and 1.35 g of liquefied PET glue.

The energy utilization to produce the raw materials of the black tea package polymers were collected from the literature as 4.8 MJ/kg for each of PET and LDPE [81]. The CExC and CCO_2E is reported to be 86.8 MJ/kg [82] and 4.8 kg/kg [81] for PET; 46.5 MJ/kg [82] and 2.1 kg/kg [83] for LDPE, respectively. With these values, energy need of the materials of the packaging process was calculated as 2,743 MJ/t black tea. Table 3.4 shows the energy and exergy utilization and CO_2 emission for the packaging and transporting the black tea. *Chow et al.* [84] stated that 0.75-1.25 MJ/m^2 energy is utilized for the cardboard making. If the average, 1.00 MJ/m^2, was used 12.6 MJ of energy was needed to produce the cardboard per one ton of black tea. CO_2 emission associated with the cardboard production was 1.8 kg CO_2/t black tea.

The energy required for packaging machine (Wenzhou Reador Machinery Co., Ltd Zhejiang, China – with a capacity of 40 packs/min) was 0.97 MJ/t of black tea and the associated CO_2 emission was 0.14 kg CO_2/t of black tea, while the CExC was 4.04 MJ/t of black tea. The energy requirement for carton printing and box making machine [Full servo carton making machine, Shanghai Liu Xiang General Equipment Co., Ltd, China – with a capacity of 250 cartons/min and 486 MJ (including dryer)] was 12.6 MJ/ t of black tea and the associated CO_2 emission was 1.8 kg CO_2/t of black tea, while the CExC was 52.5 MJ/t of black tea. When all were summed up the energy and exergy utilization of packaging step (including transportation to 1,150 km) were 2,743 MJ/t of black tea and 5,729 MJ/t of black tea, respectively. The CO_2 emission (248 kg CO_2/t of black tea) of packaging step is given in Table 3.4. Retail packages of tea are put into cartons first, and then the cartons are placed on recyclable pallets [85] and wrapped with HDPE. The cartons were palletized with Dalian Jialin (model JT-1200, China) palletizing machine (capacity = 20 cartons/min, power requirement = 9 kW).

Table 3.4. Energy and exergy utilization and carbon dioxide emission during retail marketing of black tea

	CEnC (MJ/t black tea)	**CExC (MJ/t black tea)**	**CCO_2E (kg/t black tea)**
Primary packaging materials			
Plastic bag (PET)	144	2,604	69.9
Hot-melt cola (LDPE)	17.3	167	7.6
Cardboard	75.3	28.7	2.0
Plastic band (LDPE)	48.0	465	21.0
Label for cardboard (PET)	13.0	234	6.3
Label for tea package (PET)	41.5	750	20.1
Packaging (machine)	1.0	4.0	0.1
Secondary packaging materials			
Cardboard for making the cartons	12.6	52.5	1.8
Palletizing materials			
HDPE and cardboard for palletizing (adapted from Özilgen [86], same as minced pistachios)	809	2,555	93
Palletizing equipment	2.3	9.5	0.3
Transportation			
Transportation for 1,150 km	1,579	1,461	25.8
Total	2,743	5,729	248

Figure 3.2 and Figure 3.3 show the CEnC and CExC, CCO_2E values for each step in the tea production processes, respectively. As can be seen in the figures, drying was the most energy and exergy utilizing step with 46 per cent and 52 per cent, respectively. The high CO_2 emission (46 per cent) in drying step was due to usage of heat energy to evaporate moisture from the tea leaves. Within the same scope, withering was the second most energy and exergy utilizing step (27 per cent, 31 per cent, respectively).

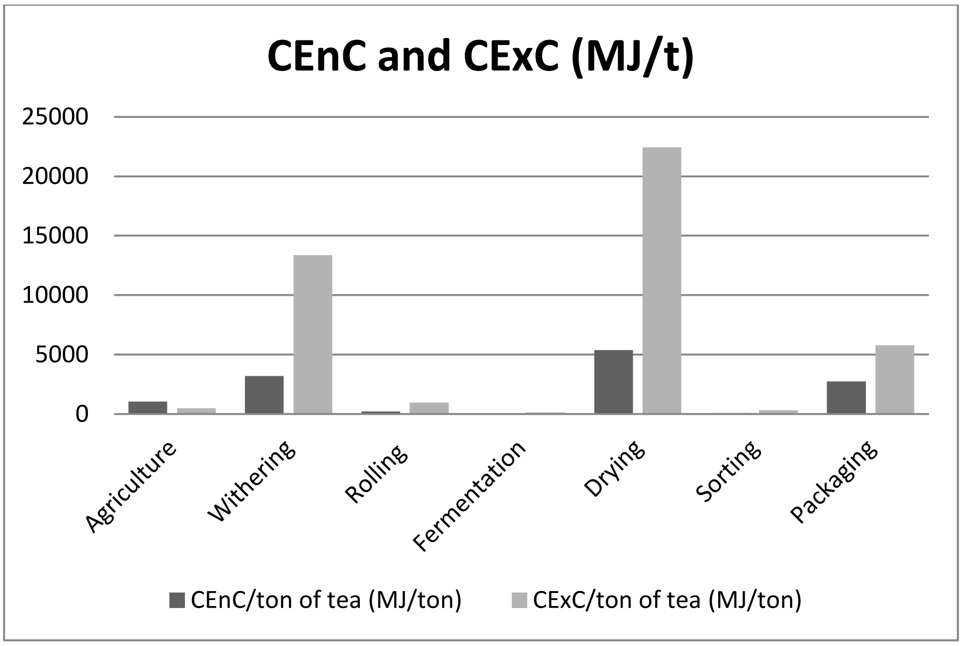

Figure 3.2. Comparison of energy and exergy utilization for each step to produce 1 ton of black tea in the tea plant

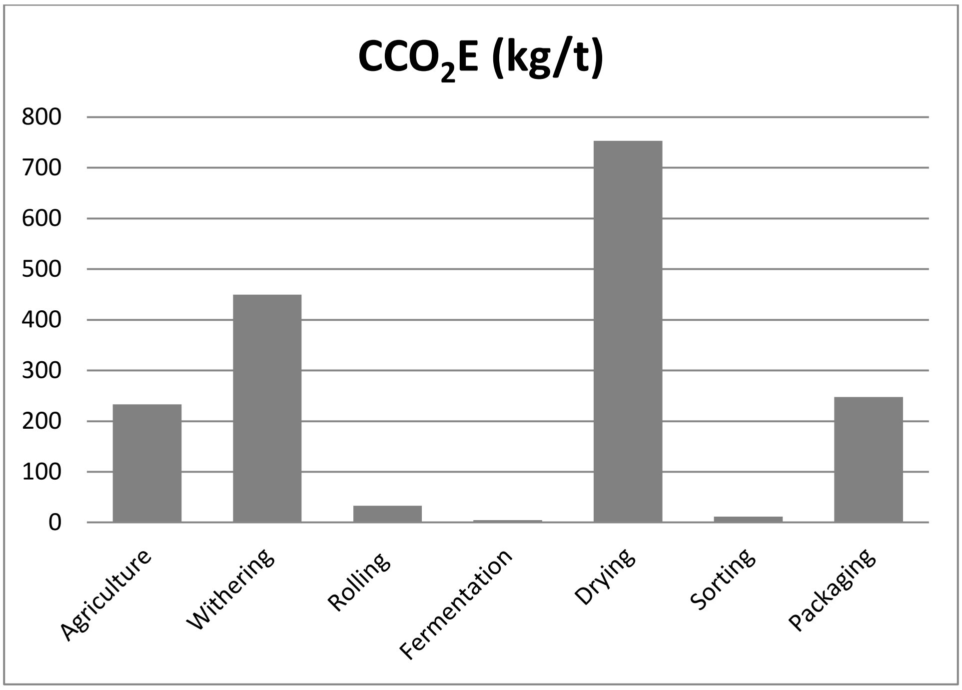

Figure 3.3. Comparison of CO_2 emissions for each step to produce 1 ton of black tea in the tea plant

3.4. BLACK TEA INDUSTRY IN TURKEY

Turkey is the fifth largest producer of tea and has its own production process for black tea [2]. Energy sources used in black tea production plants are electricity, coal, natural gas, and fuel oil, with descending order in usage, respectively. The utilization of energy source per kg of black tea is given in Table 3.5. By using these values energy utilization and CO_2 emissions per ton of black tea were calculated (Table 3.5). Our results indicate that the amount of the CO_2 emitted per ton of black tea may change dramatically depending on the energy source employed. Our results, as given in Table 3.5, were 27,442 MJ/t black tea, 19.499 MJ/t black tea, 1,495 MJ/t black tea and 9,649 MJ/t black tea for the fuel oil, natural gas, electricity and coal, respectively, and comparable with the energy utilization data reported by Baruah *et al.* [52] as 5,400 MJ/t and de Silva [50] as 25,652 MJ/t and the Asian Institute of Technology [51] as 18,288 - 24,480 MJ/t. Asian Institute of Technology [51] reported the CO_2 emission as 2.23 kg / kg tea produced in total and 2.15 kg CO_2 /kg tea in India.

Table 3.5. Energy utilization and CO_2 emission of Turkish tea industry

Energy source	**Utilization /kg black tea**	**Unit**	**CEnC (MJ/t black tea)**	**CCO_2E (kg/t black tea)**
Fuel oil	0.477	kg	27,442	1,551
Natural Gas	5.417	kWh	19,499	931
Electricity	0.415	kWh	1,495	167
Coal	0.768	kg	9,649	753

Eastern Black Sea region of Turkey, where tea is grown, is becoming an exclusively organic farming area [87]. No chemical fertilizers will be allowed under these circumstances. There are attempts in the region to replace the chemical fertilizers with their microbial counter parts. There are numerous studies in the literature, where extensive literature review is provided on this issue [86, 88]. The energy and exergy utilization and CO_2 emissions of black tea production with organic farming is given in Table 3.6.

Cumulative degree of perfection (CDP) is defined as the ratio of the exergy of the products to the sum of the exergies of the input materials and the exergies of the non-renewable fuels [63].

Table 3.6. Summary of energy and exergy utilization and carbon dioxide emission during production of the black tea without the use of the chemical fertilizers

	CEnC (MJ/t processed tea)	**CExC (MJ/t processed tea)**	**CCO_2E (kg/t processed tea)**
Agriculture (1000 kg of black tea produced from 3880 kg of fresh leaves)	0.13	1.95	0.02
Processing of the tea	8,937	37,269	1,251
Packaging of the tea	1,164	4,318	222
Transportation to the market	1,664	1,539	27
Total	11,765	43,128	1,500

The CDP of the packaged black tea was calculated as 0.061 in this study. Exergy efficiency is the ratio of the exergy of the product to the sum of the exergies of the raw materials and the fuels, regardless of whether the fuels are renewable or not. Therefore, exergy efficiency and the CDP of any process would be different. In the present study we did not have any renewable inputs, therefore the CDP of the process was the same as its exergy efficiency. The CDP is used to assess the degree of the renewability of a process, while the exergy efficiency is not. Özilgen and Sorgüven [30] reported the cumulative degree of perfection (CDP) for soybean, olive and sunflower oils production as 0.92, 0.98 and 2.36, respectively. Decreasing the diesel consumption with good agricultural practices and substituting with biodiesel from renewable resources would reported to decrease the cumulative exergy consumption, as a result, CDP of olive and soybean oil would rises to 1.6 and that of sunflower oil would be 2.9. Sorgüven and Özilgen [31] reported 0.036 cumulative degree of perfection for the strawberry-flavored yogurt, which rise up to 0.046, if renewable energy resources like hydropower and algal biodiesel are employed instead of fossil fuels. When we compare the CDP of the packaged black tea at the gate of the market with those of the vegetable oils and the flavored yogurt. The CDP of the black tea production process appears to be in the same order of magnitude with that of the flavored yogurt, but substantially lower than those of the vegetable oil production processes. This result may be attributed to utilization of no heating or phase change operations in the vegetable oil production process.

3.5. INSTANT TEA PRODUCTION

Instant tea production process was performed as described by Alasalvar *et al.* [13] and Kraujalytė *et al.* [48]. A schematic process diagram describing the agglomerated instant black tea production is presented in Figure 2.4. The extraction was performed in a pilot-scale continuous extractor (Niro Atomizer, AC-27, Soeborg, Denmark). The inlet temperature of water to the extractor was 80−85 °C, jacket temperature was 80−85 °C, tea and water feed rates were 12 and 42 L/h, respectively. The slope of the extractor was 3−5°. The extract was centrifuged (Westfelia, D-4740, North Rhine-Westphalia, Germany) at 17,000 g before feeding to the spray-dryer.

Cumulative energy and exergy utilization for processing one kg instant tea were calculated from user's manual of the equipment (Table 3.7). Exergy destruction in each step of the process was calculated with the data presented in Table 3.8 and presented in Figure 3.4.

Tea extract was produced with a continuous extractor, which was utilizing electric power of 92 MJ/ kg of instant tea, had CExC value of 383 MJ/ kg of instant tea. Carbon dioxide emission was 13 kg CO_2/kg of instant tea. Inlet water temperature was 80−85 °C, e.g., the serving temperature and the heaters were utilizing the highest energy in the extraction step. Good isolation of the extractor decreases the heat losses to the surroundings and lower the amounts of energy and exergy utilization per kg of the instant tea produced. The long start-up period of the extractor is among the causes lowering the extraction efficiencies. To lower the energy utilization and attain higher extract concentrations, the system must maintain longer steady state periods. The higher black tea leaves input to the extractor increases the duration that the extractor may be run under the steady state conditions. The higher efficiency attained in the extraction step also improves the efficiencies of the following steps. In this study, system was loaded with 20 kg of black tea leaves which was enough for the system to start working under steady state condition. It was calculated that the separator used to separate non-soluble particles was utilizing 0.7 MJ/kg of instant tea produced and had CExC value of 2.8 MJ/ kg of instant tea and causing emission of 0.1 kg CO_2/kg of instant tea. Centrifugation was the least energy utilizing step in instant tea production.

Table 3.7. Energy and exergy utilization and CO_2 emission associated with the instant tea production process

Processing step and equipment details	CEnC (MJ/kg)	CExC (MJ/kg)	CCO_2E (kg/kg)
Agriculture of tea	1.1	0.5	0.2
Process of tea into black tea	8.9	37.3	1.3
Extraction			
Pump + Screw carrier	27.0	113	3.8
Heaters	64.8	270	9.1
Separation			
Centrifuge	0.7	2.8	0.1
Spray Drying			
Pump	1.8	7.5	0.3
Fan	7.2	30.0	1.0
Heaters	130	540	18.1
Fluidized Bed			
Pump	9.0	37.5	1.3
Fan	99.0	413	13.9
Heaters	540	2,252	75.6
Packaging			
Single use plastic packs (PLA)	54.0	78.0	1.8
Primary packaging (cardboard)	229	87.1	6.2
Cardboard for making the cartons	254	96.8	6.9
Palletizing materials: HDPE and cardboard for palletizing (adapted from Özilgen, 2016, same as minced pistachios)	0.03	0.9	0.0
Single use plastic packaging machine (Anhuis Zengran Co., Ltd.China)	4.8	20.0	0.7
Cardboard making machine (Shanghai Liu Xiang, China)	0.02	0.1	0.0
Palletizing machine (Dalian Jialin Machine Manufacture Co., Ltd. China)	0.04	0.2	0.01
Total	1,431	3,987	140

Spray drying was performed in Minor Spray Dryer (Niro Atomizer, Denmark, Minor Spray Dryer), which had a centrifugal atomizer (inside diameter = 120 mm) and operated in a concurrent manner. The spray-dryer was operated at an inlet air temperature of 170−180 °C and outlet air temperature of 120−125 °C. The feed rate was 7.6 L/h. The operating conditions for spray dryer was optimized by sensory analysis and the results of instant tea powder was given in Kraujalytė *et al.* [48]. Spray dryer, used to evaporate water from the extract and calculated to be utilizing 139 MJ/ kg of instant tea of electric power and had

CExC of 578 MJ/kg of instant tea. The CO_2 emission was calculated as 19 kg CO_2/ kg of instant tea. In spray drying most of the energy was utilized for heating the inlet air. Efficiency of the drying process may be improved by decreasing the outlet air drying temperature and increasing the inlet air temperature and there is a great potential to recover the waste heat of the exhaust air [37, 41]. The energy and exergy efficiencies for fruit puree drying process were between 3.2 - 17.3 per cent and 0.7 - 4.1 per cent, respectively; and the exergetic efficiencies of the spray dryer and overall system were between 27.0-39.1 per cent and 26.7 - 32.9 per cent, respectively [41]. Exergoeconomic of the process showed that the inlet air temperature was the main operating parameter affecting the performance of the heater. In the same study, fan was reported as the least efficient system component subsequent to the atomizer [37].

Exergy of stream 9 (exhaust air of spray dryer) in Table 3.8 was high. Recycling of the exhaust air may help to reduce the energy utilization by the spray dryer. The amount of product loss in pilot scale spray dryer was another parameter that affects the efficiency. The amount of product lost is generally related with the design of the dryer, therefore, the product loss cannot be changed much by process optimization without changing the design of the dryer. During instant tea production process, as the concentration of the extract (which is the input of the spray dryer) increases, less amount of water will be evaporated and higher amounts of instant tea will be produced. This may decrease the energy and exergy utilization per kg of instant tea.

A fluidized bed dryer (GLATT, Procell Lab System, Weimar, Germany) was used for agglomeration of the instant black tea powder, with the inlet air flow rate of 105− 80 m3/h, at air temperature of 85 °C, exhaust air temperature of 45−50 °C, product temperature of 50−55 °C and the spraying pressure of 2.5 bar, with liquid flow 6.5 mL/min to 16 mL/min. The operating conditions for the fluidized bed dryer was studied by Alasalvar *et al*. [13] and the sensory evaluation of agglomerated instant tea was given in Kraujalytė *et al*. [48]. Also the compositional, nutritional, and functional characteristics of agglomerated instant tea from high-quality and low-quality black tea was studied by Alasalvar *et al*. [13].

Fluidized bed dryer, used to agglomerate instant tea powder, was calculated to be utilizing 648 MJ/kg of instant tea of electric power and had the CExC value of 2,703 MJ/kg of instant tea.The CO_2 emission was calculated as 91 kg CO_2/ kg of instant tea. Agglomeration was the most energy utilizing step in the instant tea production process,

Table 3.8. Thermodynamic properties of the streams and instant tea production process steps

			Chemical Composition (per cent)			Total mass flow rate (kg)	T (°C)	H (kJ)	S (kJ/K)	Ex (kJ)
			Dry Air	**Water**	**Dry Tea**					
Extraction	In	Stream-1	-	0.6	19.4	20	20	1,435	-	50
		Stream-2	-	100	-	100	20	8,392	29.7	297
		$W_{pump+Screw\ carrier}$						27,000		
		Q						64,800		
	Out	Stream-3	-	88	17	105	80	34,303	-	4,235
		Stream-4	-	13	2.1	15	80	4,940	-	610
									Exergy Destruction =	82,905
Centrifuge	In	Stream-4	-	13	2.1	15	60	3,704	-	357
		$W_{centrifuge}$						666		
	Out	Stream-5	-	-	0	0	40	143	-	0.2
		Stream-6	-	13	2	15	40	2,467	-	166
									Exergy Destruction =	857
Spray dryer	In	Stream-6	-	13	2	15	40	2,467	-	166
		Stream-7	120	1.3	-	121	20	2,415	8.5	86
		Q						129,600		
		$W_{pump+fan}$						9000		
	Out	Stream-8	-	-	0.5	0.5	80	144	-	18
		Stream-9	120	14	-	134	120	14,524	44	2,494
		Stream-10	-	0.05	1.5	1.6	80	450	-	55
									Exergy Destruction =	160,913

Fluidized Bed	In	Stream-10	-	0.05	1.5	1.6	40	225	-	15
		Stream-11	-	0.5	-	0.5	20	42	0.2	2
		Stream-12	533	5.8	-	539	20	10,729	38	380
		Q						540,000		
		$W_{pump+fan}$						108,000		
	Out	Stream-13	-	-	0.6	0.6	50	108	-	9
		Stream-14	533	6.2	-	539	50	26,834	90	2,207
		Stream-15	-	0.1	0.9	1	50	181	-	15
									Exergy Destruction =	562,575

e.g., 45 per cent of the entire process.

Özahi and Demir [39] and Nazghelichi *et al.* [89] reported that employing small particles, deep beds and high inlet air temperature in a fluidized bed drying process increases the energy utilization and exergy loss due to high rates of heat and mass transfer. Fluidized bed dryer may be used also in the withering and drying steps of the black tea production process [90]. Air velocity and temperature affects the drying rates. Recycling of the exhaust air may help to reduce the energy utilization of the fluidized bed dryer. The exergy of stream 14 (exhaust air of fluidized bed dryer) in Table 3.8 had very high values. In our study the main reason for the energy loss in agglomeration step was the high percentage of product loss. Due to the structure of powder tea (product of spray dryer, which was the feed of fluidized bed dryer) full loading of the system was not possible and aiming to produce agglomerated instant tea without using any drying aids or carrier materials, product loss in agglomeration step was high.

Instant tea is preferred for the convenience of the single-use packages. Our energy and exergy utilization and CO_2 emissions calculations regarding packaging was based on the production of the single-use packages. Sensory analysis has shown that the use of one gram of instant tea in 200 mL hot water provided the best taste [48]. A 0.5 g of packaging material was used in the calculations and 50 single-use packages were packed in a carton, then these cartons were packed in cardboards and pelletized. The amount of energy and exergy utilized to produce packaging material (including primary and secondary packaging), was 537 MJ/kg instant tea and 262 MJ/kg instant tea, respectively (Table 3.7). CO_2 emitted during production of the packaging material was calculated as 15 kg/ kg instant tea. With the addition of the electric power used for running the packaging machinery, the total energy and exergy utilization became 542 and 283 MJ/kg instant tea, respectively. The total CO_2 emission was 15.6 kg/ kg instant tea (Table 3.7). The cumulative energy and exergy utilization in production of single-use PLA packages, were reported as 54.0 MJ/kg [91] and 78.0 MJ/kg [92], respectively. Fifty of single-use packages are placed in one carton and 24 cartons are placed in a cardboard; 60 cardboards are placed on a pallet. The energy and exergy utilization and CO_2 emission for cardboard production were reported as 43.3 MJ/kg (calculated based on the data from Chow *et al.* [84]), 16.5 MJ/kg [93] and 1.17 kg/kg (calculated based on the data from Chow *et al.* [84]), respectively. The new high technology plastic pallets are 100 per cent recyclable and can make about 250 trips [85] therefore just the energy and exergy utilized in labeling of pallet and the CO_2 emission associated with pallet making is given in Table 3.7.

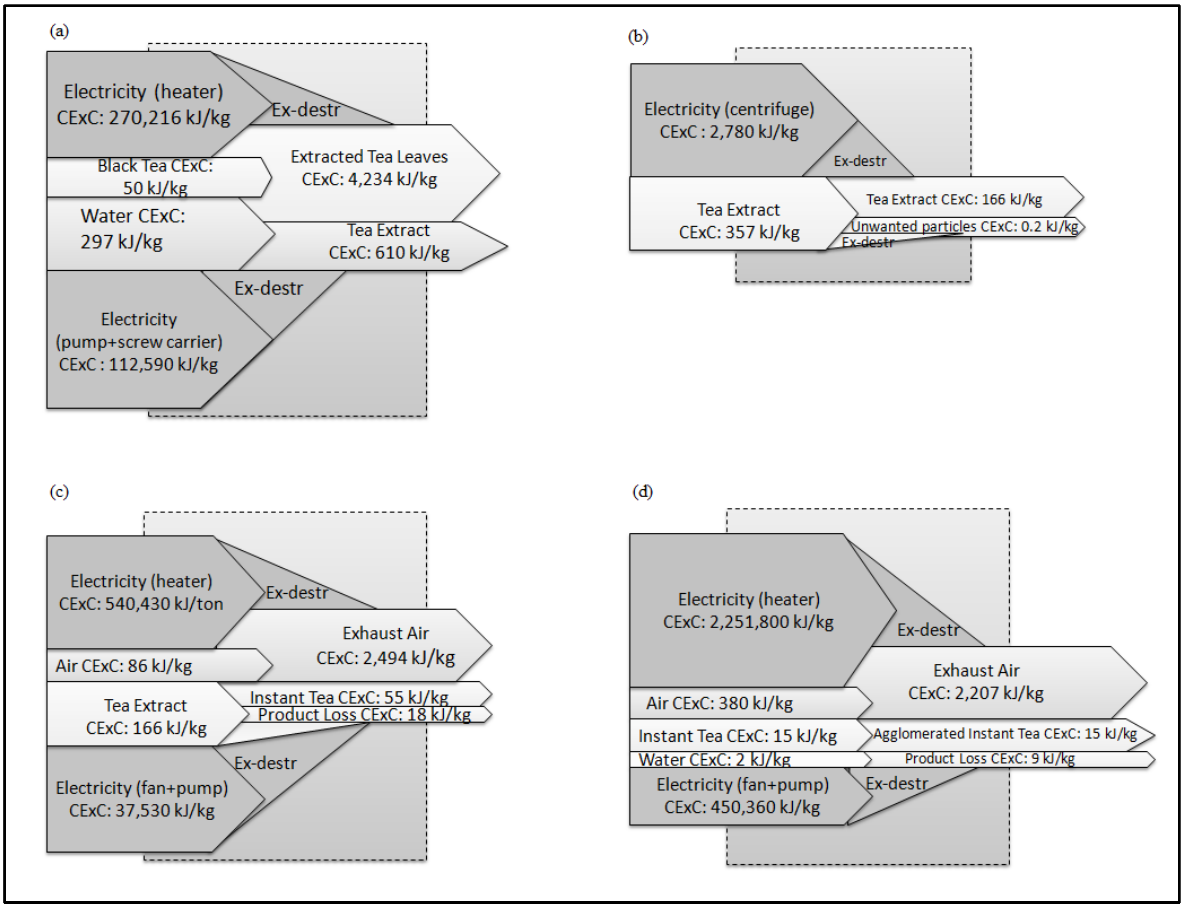

Figure 3.4. Exergy chart representing the exergy-content of the consumed resources and the tea itself during production of the instant tea at the stages of (a) extraction, (b) separation, (c) spray drying, (d) agglomeration

3.6. ICE TEA PRODUCTION

In our analysis, ice tea production was modified from the ice tea production and a schematic of the process used to produce the instant black tea powder is presented in Figure 2.5. Extraction and centrifugation of the ice tea was same as instant tea, after centrifugation tea extract is diluted with hot water and by hot filling technique, no extra pasteurization was used in bottling step. The cumulative energy and exergy utilization for processing 1000 L of ice tea, which was the final product, were calculated from the values given in user manual or from internet data and is given in Table 3.9. Exergy destruction in each step of the process was calculated with the data presented in Table 3.10 and is given Figure 3.5.

Aluminum cans, produced by using electric power only, were used for the packaging of the ice tea. The cumulative energy and exergy utilization and CO_2 emission values for the production of the aluminum cans were 191 MJ/kg, 188.51 MJ/kg and 18.66 kg/kg, respectively [94]. In 2007, the worldwide recycling rate of steel was 68 per cent [95]. Recycling the steel reduces the energy consumption by 75 per cent and the CO_2 emission by 80 per cent, when compared to steel making from virgin ore [95]. When we assume the same recycling values for the aluminum cans, we will end-up with 47.8 MJ/kg energy, 47.1 MJ/kg exergy utilization and 3.7 kg CO_2 emission per ton of aluminum produced. Cans were packed in cardboards and cardboards were pelletized for transportation. The most energy consuming step during the production of the ice tea was the production of the cans, 67 per cent of the total, followed by the cardboard production, and 21 per cent of the total. Heating of water to dilute the concentrate before filling the cans constitutes 8.8 per cent of the energy utilization of the entire process.

Table 3.9. Energy and exergy utilization and CO_2 emission associated with the ice tea production process

Processing step and equipment details	**CEnC (MJ/1000 L)**	**CExC (MJ/1000 L)**	**CCO_2E (kg/1000 L)**
Agriculture of tea	1.1	0.5	0.2
Process of tea into black tea	8.9	37.3	1.3
Extraction			
Pump + Screw carrier	13.5	56.3	1.9
Heaters	32.4	135	4.5
Separation			
Centrifuge	0.3	1.4	0.1
Mixing			
Heating of water	314	1307	43.9
Pump	0.1	0.6	0.02
Packaging			
Cans (Aluminum)	2,388	2,356	187
Coating cans (LDPE)	2.36	1.26	0.06
Cardboard for making the cartons	762	290	20.6
Palletizing materials: HDPE and cardboard for palletizing (adapted from Özilgen [86], same as minced pistachios)	3.2	86.0	0.5
Can making and filling machine (Anhuis Zengran Co., Ltd.China)	45.6	190	6.4
Cardboard making machine (Shanghai Liu Xiang, China)	0.3	1.2	0.04
Palletizing machine (Dalian Jialin Machine Manufacture Co., Ltd. China)	0.01	0.05	0.00
Total	3,571	4,464	267

Table 3.10**.** Thermodynamic properties of the streams and the steps of the ice tea production process

			Chemical Composition (kg)		Total mass (kg)	T (°C)	H (kJ)	S (kJ/K)	Ex (kJ)
			Water	**Dry Tea**					
Extraction	In	Stream-1	9.7	0.3	10	20	718	-	25
		Stream-2	50	-	50	20	4196	14.8	149
		$W_{pump+Screwcarrier}$					13500		
		Q					32400		
	Out	Stream-3	8.7	43.8	52.5	80	17153	-	2,117
		Stream-4	7.5	1.0	6.5	80	2469	-	305
								Exergy Destruction =	41,440
Centrifuge	In	Stream-4	6.5	1.02	7.5	60	1851	-	179
		$W_{centrifuge}$					333		
	Out	Stream-5	-	0.01	0.01	40	1.4	-	0.1
		Stream-6	6.5	1.01	7.5	40	1233	-	83
								Exergy Destruction =	429
Mixing	In	Stream-6	6.5	1.01	7.5	40	1233	-	83
		Stream-7	993.5	-	993.5	95	395,502	1242.3	56,362
		$Q_{to\ heat\ water}$					313500		
		Wpump					132		
	Out	Stream-8	1000	1.01	1000.01	95	398,433	-	56,779
								Exergy Destruction =	232,367
Bottling	In	Stream-8	1000	1.01	1000.01	95	398,433	-	56,779
		Stream-9			50 (Al cans)	20	879	-	31
		Wbottling					4560		
	Out	Stream-10	1000	1.01	1051.01	20	84,866	-	3,004
								Exergy Destruction =	53,806

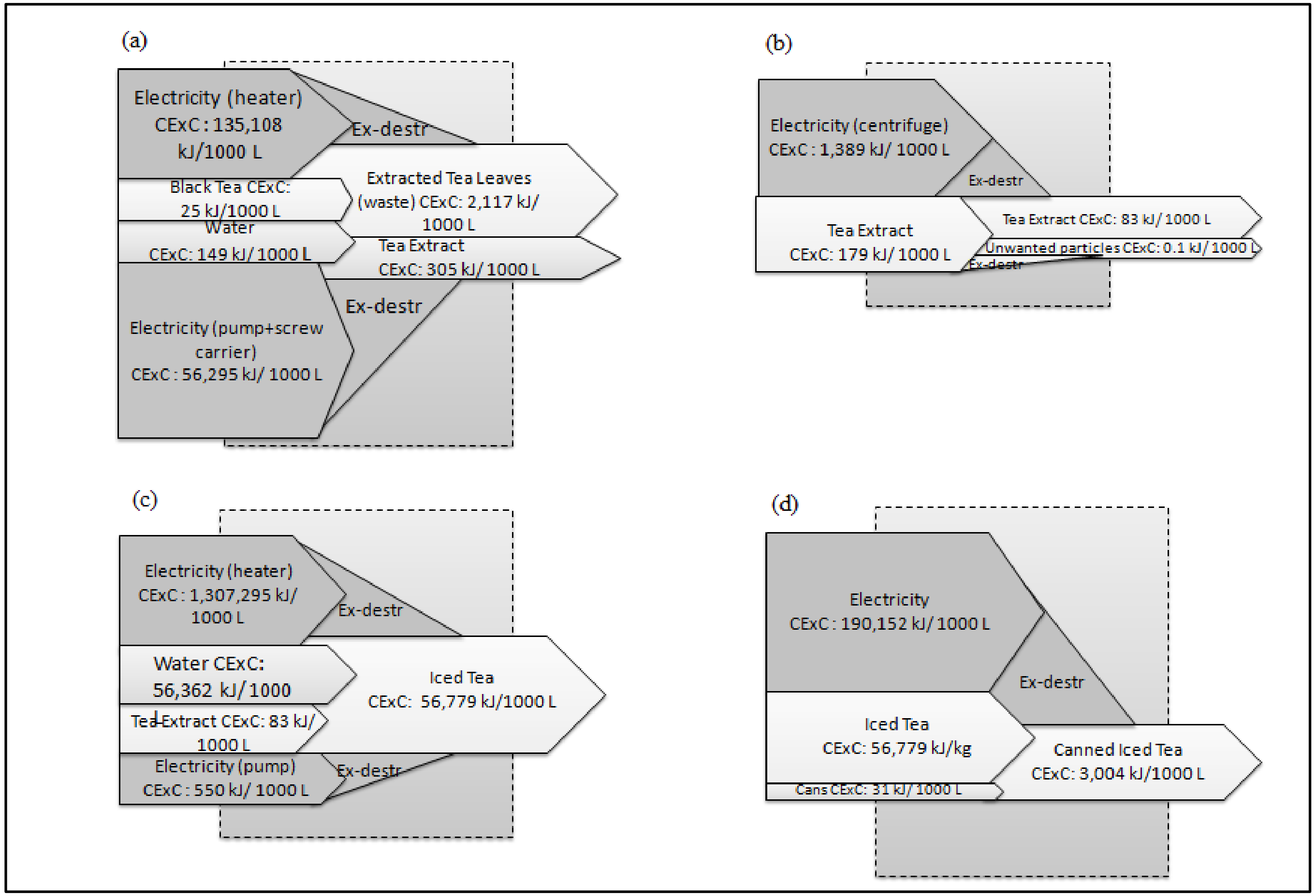

Figure 3.5. Exergy chart representing the exergy-content of the consumed resources and the tea itself during production of the ice tea at the stages of (a) extraction, (b) separation, (c) mixing (dilution), (d) bottling (canning)

3.7. VALORIZATION OF THE TEA WASTE

To use maximum potential of tea during production of the instant or ice tea, zero waste was aimed. In the literature, many options are described for the valorization of the waste tea [96, 97, 98]. In this study, only three of these options, e.g., production of activated carbon, adsorbent and hydrogen were assessed.

3.7.1. Production of Activated Carbon From Waste Tea

Auta and Hameed [54] studied producing activated carbon from waste tea by using potassium acetate. Where, waste tea was dried, ground and mixed with potassium acetate and dried again before loading to tubular reactor. The reactor was heated for 80 min to 800 °C with 100 cm^3/min of nitrogen flow. After activation, tea was washed and dried once more. Energy needed for drying was calculated theoretically and the rest of the equipment used in this process were chosen from internet and the energy, exergy utilization and CO_2 emissions were calculated from the data given by the supplier (Table 3.11). Instant or ice tea production waste was at 80 °C and had 83.4 per cent water and 16.6 per cent of tea leaf solids. Drying is the most energy utilizing step in production of activated carbon from waste tea, after the cumulative energy utilized for potassium acetate production (life cycle carbon footprint for potassium acetate was reported as 716 g CO_2 eq./kg by Liu and Shonnard [99]. By using the coefficients for CO_2 emission and CExC for electricity [66], CEnC and CExC values for potassium acetate production was estimated. Therefore, CEnC and CExC the values for the production of activated carbon from waste tea were calculated as 59.8 and 249.5 MJ/kg, respectively).

3.7.2. Production of Hydrogen From Waste Tea

Ayas and Esen [100] studied producing hydrogen from the waste tea by using potassium carbonate. In this process, waste tea was dried, ground and mixed with potassium carbonate and loaded to reactor, and then the reactor was heated for 15 min at 650 °C with 50 cm^3/min flow of air. Gas was collected in a collector. Energy needed for drying was calculated theoretically and the data regarding the rest of the equipment were obtained from the manufacturer specification sheets. Drying is the most energy utilizing step in production of activated carbon from waste tea after the cumulative energy utilized for potassium carbonate production, cumulative exergy extraction from the natural environment was reported as 53.79 MJ/kg by Dewulf *et al.* [101]. By using the coefficients for CO_2 emission and CExC for electricity [66], CEnC and CExC values for potassium acetate production was estimated. Therefore, CEnC and CExC the values for the production of hydrogen from waste tea were calculated as 17.8 and 74.3 MJ/kg, respectively (Table 3.11).

3.7.3. Production of Adsorbent From Waste Tea

Wan *et al.* [55] studied producing adsorbent from waste tea. Briefly, waste tea was dried and grinded. Energy needed for drying was calculated theoretically and the grinder used in this process was chosen from internet and the energy, exergy utilization and CO_2 emissions were calculated from the data given by the supplier. The energy, exergy and CO_2 emissions were given in Table 3.11.

Table 3.11. Thermodynamic indicators associated with producing the valorization products from the waste tea leaves

Method used	**Processing step and equipment details**	**CEnC (MJ/kg waste tea)**	**CExC (MJ/kg waste tea)**	**CCO_2E (kg/kg waste tea)**
Activated carbon production as described by Auta *et al.* (2011)	Pressing (Shangai Qlee Environmental Protection Equipment Co. Ltd. China)	0.02	0.10	0.00
	Drying	3.3	13.8	0.46
	Grinding (Juangyin Weiping Machinery Co. Ltd. China)	0.32	1.32	0.04
	Mixing (Jiangyin Baoli Machinery Co. Ltd. China)	0.03	0.12	0.00
	N_2 pump (CAN Gas Systems Company Limited. China)	0.01	0.04	0.00
	Potassium Acetate	52.3	218	7.3
	Reactor Heating	1.14	4.74	0.16
	Washing (Pump: Difful. China)	0.00	0.01	0.00
	Drying	2.65	11.07	0.37
	Total	59.8	250	8.4
Hydrogen production from waste as described by Ayas and Esen (2016)	Pressing (Shangai Qlee Environmental Protection Equipment Co. Ltd.. China)	0.02	0.10	0.00
	Drying	3.3	13.8	0.46
	Grinding (Juangyin Weiping Machinery Co. Ltd. China)	0.32	1.32	0.04
	Mixing (Jiangyin Baoli Machinery Co. Ltd. China)	0.03	0.12	0.00
	Air pump (Dongguan Quan Feng Environmental Protection Equipment Co. Ltd. China)	0.00	0.02	0.00
	Potassium Carbonate	13.2	55.1	1.85
	Reactor Heating	0.92	3.83	0.13
	Total	17.8	74.3	2.50
Adsorbent material production as described by Wan *et al.* (2014).	Pressing (Shangai Qlee Environmental Protection Equipment Co. Ltd. China)	0.02	0.10	0.00
	Drying	3.3	13.8	0.46
	Grinding (Juangyin Weiping Machinery Co. Ltd. China)	0.32	1.32	0.04
	Total	3.6	15.2	0.5

3.8. COMPARISON OF THE ENERGY AND EXERGY UTILIZATION DURING INSTANT, ICE, TURKISH STYLE BREWED AND BREWED TEA PRODUCTION

While brewing the Turkish style black tea, two pots - one placed on top of the other, are used. Water is boiled in the lower pot, tea is put in to the upper part and then brewed there with the addition of boiling water. About two grams of black tea is used per 200 mL of serving. Kraujalytė *et al.* [48], after performing sensory tests reported that having approximately one gram of instant tea in 200 mL hot water at 85 °C of serving temperature was the most preferred combination in Turkey. In our calculations, ice tea concentration was taken as 0.1 per cent (dry matter: water). Cumulative energy and exergy utilization and CO_2 emissions occurring in the production chain between agriculture and ready to drink Turkish style brewed tea, normal brewed tea, instant tea and ice tea production are given in Figure 3.6. Instant tea is the most energy and exergy utilizing product with 7,404 MJ/1,000 L of energy and 20,978 MJ/1,000 L of exergy utilization, respectively. Brewed tea is the least energy and exergy utilizing product, 362 MJ/1,000 L and 1,467 MJ/1,000 L respectively, which are about 5 per cent of those of instant tea. As boiling water and drying extract in the process were the most energy utilizing steps in the preparing instant tea and required the highest values. In our study transportation of final product to the market was not taken into consideration, but if the transportation of the final products would have taken into consideration, due to its density, instant tea utilization for transportation to the market would have lower values than black tea or ice tea.

Aside from the processing in the plant, the main energy consuming step is the boiling of water for instant, Turkish style brewed or brewed tea production. Azapagic *et al.* [5] reported that 85 per cent of the global warming potential of the tea is caused due to the way of its consumption, e.g., mainly boiling of water, when "*cradle to grave*" analyses are made.

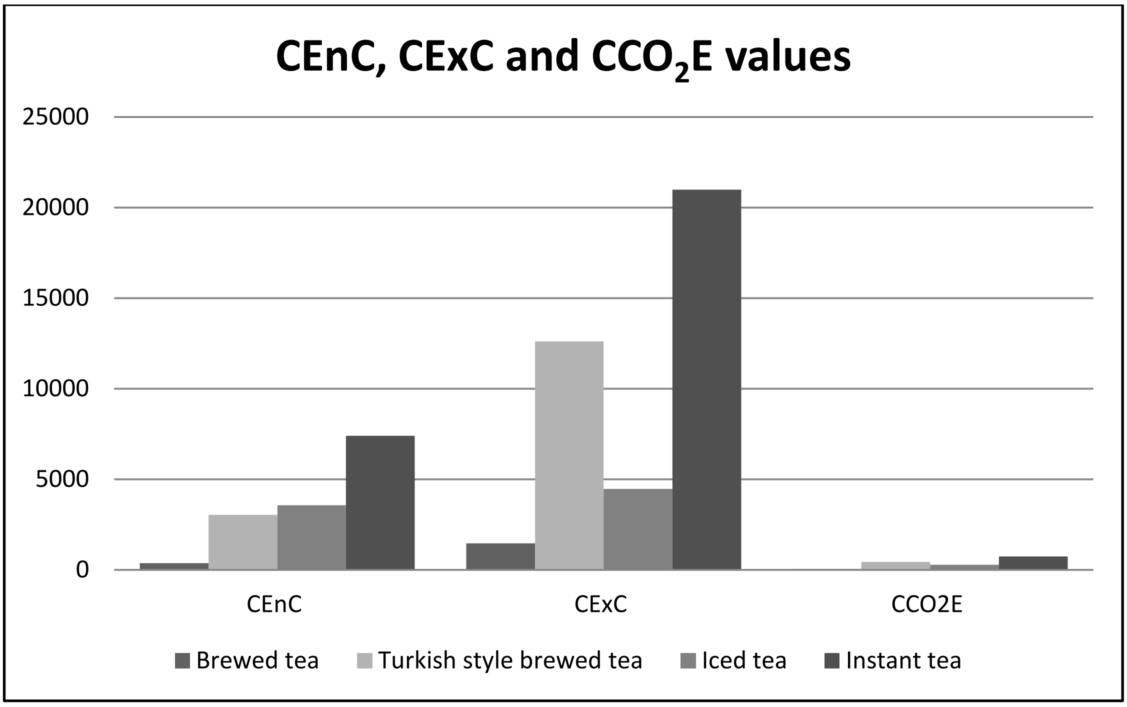

Figure 3.6. Energy and exergy utilization (MJ/1,000 L) and CO_2 emission (kg/1,000 L) associated with preparation of 1,000 L of Turkish style brewed tea, tea bag, instant tea and ice tea

Cichorowski *et al.* [49] analyzed the "*cradle to gate"* GHG emissions of the Darjeeling tea production and reported that the main reduction potential for the GHG emissions were at the water boiling step during preparation. Azapagic *et al.* [49], reported that the CO_2 equivalent of GHG emissions was 10.46 kg/kg dry tea in the factory to consumer chain in the UK. The CO_2 emissions calculated in our studies for the brewed (5.2 kg/ kg dry tea) and the Turkish style (10.8 kg/ kg dry tea) brewed tea were similar to those reported by Azagapic *et al.* [49].

3.9. CUMULATIVE DEGREE OF PERFECTION (CDP) AND ASSESSMENT OF THE RENEWABILITY INDICATOR

The CDP of the black tea, instant tea and ice tea with three different products produced from the waste are given in Table 3.12. Exergy efficiency is the ratio of the exergy of the product to the sum of the exergies of the raw materials and the fuels, regardless of whether the fuels are renewable or not. Therefore, exergy efficiency and the CDP of any process would be different. In the present study, however, we did not have any renewable inputs, therefore the CDP of the process was the same as its exergy efficiency.

Table 3.12**.** Cumulative degree of perfection (CDP) and renewability indicator of the black, instant and ice tea production and waste valorization processes

	CDP	**Renewability indicator**
Brewed black tea (1000 L)	0.425	-1.35
Instant tea (1000 L)	0.031	-31.30
Ice tea (1000 L)	0.000	-610,668
Instant tea + activated carbon	0.087	-10.53
Instant tea + hydrogen	0.035	-27.90
Instant tea + adsorbent material	0.172	-4.83
Ice tea + activated carbon	0.080	-11.47
Ice tea + hydrogen	0.005	-211
Ice tea + adsorbent material	0.178	-4.61

The waste of the instant and ice tea production processes were those of the extraction step for the preparation of 1,000 L of product, e.g., 85 and 8.5 kg of tea leaves, respectively and contained 83.7 per cent water and balance extracted solids. The CDP of 1,000 L of brewed black tea was 0.425, while the CDP of the packed black tea was 0.061 [14]. The difference was due to the exergy of hot water in the final product (brewed black tea). As the exergy of the product increases the CDP value increases. Brewed black tea had the highest CDP value, whereas ice tea had the lowest (Table 3.12). Among the waste valorization products, adsorbent material had the highest impact on CDP and hydrogen had the lowest. Using renewable resources, especially boiling the exact amount of water for black and instant tea and decreasing the effect of packaging material for ice tea may increase the CDP.

Özilgen and Sorgüven [30] reported the CDP values for soybean, olive and sunflower oil production as 0.92, 0.98 and 2.36, respectively. Decreasing the diesel consumption with good agricultural practices and substituting with biodiesel from renewable resources were reported to decrease the cumulative exergy consumption, as a result, CDP of olive and soybean oil would rise to 1.6 and that of the sunflower to 2.9.

Renewability indicators for products are given in Table 3.12. All the products, though to different extends, had negative renewability indicator values, implying that these processes are all nonrenewable. Ptansinski [65] argues that when $I_r < 0$ the process is nonrenewable and needs more restoration work than it produces.

The renewability indicator for ice tea was the minimum due to the use of 0.1 per cent of dry tea extract in the final product. Exergy of this product was very small, while exergy requirement of the process was high. Also, hot filling of ice tea and then cooling it to room temperature and not recovering its energy for heating any other streams is among the causes of the high exergy loss. Brewed tea had the maximum renewability indicator since it was not subject to further processing, which would increase the energy-exergy requirement of the process, and no waste.

As waste tea was further processed into valuable products, exergy associated with the useful products increased and the needed exergy to deactivate the wastes decreases, the renewability indicator became closer to zero and approached to renewability. Producing the adsorbent material from the waste tea had the highest impact on the renewability indicator. The main exergy requirement in further processing was caused by the use of potassium acetate or potassium carbonate. If those compounds were used as catalyst and recycled the renewability indicator would increase. The second most exergy consuming step was the drying of the waste. If waste tea can be used by skipping the drying step the renewability indicator would be higher. When only the waste valorization process is taken into account, producing the adsorbent material from the waste would had the highest renewability indicator value of 0.56. Whereas, producing the activated carbon from the waste had negative renewability indicator value of -6.30. These results show that producing activated carbon from the waste tea is not a renewable process, due to the high CExC value of the potassium acetate used in the process. Ptansinski [65] presented a review of the values of the renewability indicator (I_r) in the studies of ethanol production from corn. In this review the renewability indicator values were negative implying that all of these processes were nonrenewable.

3.10. CHEMICAL COMPOSITION/ EXPERIMENTAL RESULTS

3.10.1. Total Phenolics and Antioxidant Activities

Total phenolic content and antioxidant activity (ORAC method) were measured for seven grades of black tea and instant tea produced from low- and high-quality black tea (Table 3.13 and Table 3.14). Total phenol contents ranged from 7.52 to 8.29 g of GAE/100 g, being lowest in grade 6 and highest in grade 1. With respect to antioxidant activities, a large variation in ORAC values was observed among all grades of black tea (ranging from 777 μmol of TE/g in grade 7 to 1,210 μmol of TE/g in grade 3). The ORAC values for high-quality black tea (grades 1−3) showed significantly higher ($p < 0.05$) values compared to the low-quality black teas (grades 4−7), with some exceptions.Total phenolic contents varied between 17.82 g of GAE/100 g in low-grade instant tea and 17.35 GAE/100 g in high grade instant tea. No significant differences ($p > 0.05$) in total phenolic, ORAC contents between low and high-quality instant teas were observed. Instant tea has been reported to have high polyphenol content, and the corresponding value was 19.63 per cent [6].

3.10.2. Phenolic and Alkaloid Compounds

Six major flavanols (catechin, epicatechin, epicatechin gallate, epigallocatechin, epigallocatechin gallate, and gallocatechin) and one phenolic acid (gallic acid) were identified in seven grades of black tea and low- and high-quality instant teas (Table 3.13 and Table 3.14). Some variations ($p < 0.05$) in phenolics were noted among the seven grades of black tea, with some exceptions. Despite the fact that there was no clear trend, high-quality black teas (grades 1−3) had a tendency to have higher flavanols and alkoloids, than low-quality black teas (grades 4−7). The variations of phenolic constituents could be attributed to the varying leaf quality and the different plucking intervals in each shooting period [1]. As expected, concentrations of phenolics detected in instant teas were much higher than those reported in seven grades of black tea [1]. This was due to the concentration of instant tea.

Hakim *et al*. [102] analyzed 40 tea samples (representing the most typical preparation techniques of hot, ice, and sun tea) using HPLC for total flavonoids, catechins, theaflavin, thearubigins, caffeine, and gallic acid. In black tea, the highest concentrations of flavonoids were found in brewed hot tea (ranging from 541 to 692 μg/mL), whereas the lowest concentrations were for instant tea preparations (ranging from 91 to 100 μg/mL). They concluded that tea concentration, brewing time, and beverage temperature had major influences on flavonoid concentrations.

The content of gallic acid in instant teas (Table 3.14) were almost 7-fold higher than those of black tea (Table 3.13) reported by Serpen *et al.* [1] in seven grades of black tea. The concentration and composition of phenolic acids in tea products depend not only on differences in processing but also tea plant cultivars and agricultural conditions [103]. Gallic acid has been reported in instant black tea at varying concentrations [102, 104].

Table 3.13. Total phenolic content (grams of GAE per 100 g), antioxidant activities (micromoles of TE per gram) and phenolic and alkaloid contents of black tea grades produced by Çaykur*

	grade - 1	**grade - 2**	**grade - 3**	**grade - 4**	**grade - 5**	**grade - 6**	**grade - 7**
total phenolics	8.29 ± 0.15^{a}	8.18 ± 0.20^{a}	8.14 ± 0.55^{a}	7.75 ± 0.12^{ab}	7.79 ± 0.37^{ab}	7.52 ± 0.12^{b}	8.23 ± 0.35^{a}
ORAC	1173 ± 57^{ab}	1075 ± 136^{abc}	1210 ± 98^{a}	983 ± 33^{c}	1051 ± 152^{bc}	795 ± 56^{d}	777 ± 106^{d}
flavanols							
catechin	89.6 ± 5.6^{ab}	98.3 ± 1.8^{a}	86.1 ± 2.7^{b}	90.3 ± 1.6^{ab}	93.9 ± 2.2^{ab}	75.1 ± 3.4^{c}	59.3 ± 4.0^{d}
epicatechin	83.9 ± 7.0^{a}	78.8 ± 6.2^{ab}	70.2 ± 5.9^{bc}	66.5 ± 1.8^{bc}	69.6 ± 2.9^{bc}	61.9 ± 1.1^{c}	62.6 ± 0.8^{c}
epicatechin gallate	103 ± 7^{ab}	115 ± 6^{a}	100 ± 5^{ab}	93.7 ± 4.9^{b}	102 ± 6.3^{ab}	89.5 ± 6.3^{b}	99.3 ± 1.6^{ab}
epigallocatechin	1214 ± 18^{a}	1141 ± 52^{ab}	1065 ± 34^{b}	1091 ± 59^{ab}	1042 ± 68^{b}	1038 ± 55^{b}	1127 ± 29^{ab}
epigallocatechin gallate	111 ± 2^{d}	155 ± 3^{a}	122 ± 2^{c}	105 ± 4^{de}	131 ± 3^{b}	102 ± 2^{e}	108 ± 3^{de}
gallocatechin	650 ± 38^{a}	624 ± 7^{a}	524 ± 13^{b}	506 ± 13^{bc}	524 ± 26^{b}	467 ± 11^{c}	530 ± 11^{b}
phenolic acids							
gallic acid	96.8 ± 9.3^{a}	110 ± 11^{a}	100 ± 9^{a}	99.0 ± 6.9^{a}	105 ± 10^{a}	100 ± 8^{a}	116 ± 10^{a}
alkaloids							
caffeine	1695 ± 21^{b}	1806 ± 5^{a}	1626 ± 6^{bc}	1596 ± 37^{cd}	1624 ± 41^{bc}	1525 ± 28^{d}	1689 ± 27^{b}

* Data are expressed as the mean ± SD ($n = 3$) on a fresh weight basis. Means followed by the same letter, within a row, are not significantly different ($p > 0.05$).

Table 3.14. Total phenolic content (grams of GAE per 100 g), antioxidant activities (micromoles of TE per gram) and phenolic and alkaloid contents of low- and high-quality of instant teas*

	Instant tea produced from	
	low quality	**high quality**
total phenolics	17.82 ± 0.68[a]	17.35 ± 0.60[a]
ORAC	1603 ± 311[a]	1968 ± 9[a]
flavanols		
catechin	288 ± 3[a]	316 ± 3[b]
epicatechin	889 ± 7[a]	524 ± 8[b]
epicatechin gallate	428 ± 7[a]	315 ± 5[b]
epigallocatechin	3460 ± 26[a]	2004 ± 13[b]
epigallocatechin gallate	176 ± 3[a]	173 ± 3[a]
gallocatechin	506 ± 2[a]	397 ± 3[b]
phenolic acids		
gallic acid	751 ± 6[a]	697 ± 5[b]
alkaloids		
caffeine	4398 ± 34[a]	3964 ± 26[b]

* Data are expressed as the mean ± SD (n = 3) on a fresh weight basis. Means followed by the same letter, within a row, are not significantly different ($p > 0.05$).

4. CONCLUSIONS

4.1. BLACK TEA

Energy and exergy utilization, carbon dioxide emission and exergy destruction is calculated for the "*orchard to the retail market"* industrial production of the black tea in Turkey. Energy and exergy utilization was 12,748 and 43,532 MJ/t of black tea produced, being consistent with the results given in the literature. The total amount of the CO_2 emission in the entire process was 1,732 kg/t of black tea. The largest amounts of energy and exergy were used in the drying, withering and packaging stages of the processes, respectively. HVAC units employed in withering were causing the largest exergy destruction, 2,542 MJ/t, followed by the exergy destruction by the drying unit employed, e.g. 318 MJ/t.

In the entire process, 70 per cent of the total energy and 86 per cent of the total exergy utilization was allocated to the processing of the tea, which also accounted for 72 per cent of the total amount of the carbon dioxide emission. Drying process utilizes 42 per cent of the total energy and 52 per cent of the total exergy allocation and accounts for 44 per cent of the total CO_2 emission. Using energy efficient modern techniques may help reducing the energy utilization and selection the fuel used in drying step affects the CO_2 emissions. Using renewable energy, circulating the exhaust gas and optimizing the inlet and outlet temperatures are the other factors that may help to reduce energy utilization and CO_2 emissions in drying step. Also recycling and isolation are the most important topics to use the energy of the stream efficiently. Due to the large size of the process units, fans must be positioned carefully to circulate air efficiently in the unit. Also using the exhaust gas of a process as an inlet stream of another process may decrease the energy utilization.

Energy utilization of drying and withering steps are followed by packaging step, due to the usage of high amount of packaging material and the long distance of transportation (from plant to market). By choosing the correct packaging material and transportation route the energy utilization may be decreased.

Although agriculture appears as the least energy demanding step, applying fertilizer management programs, providing fertilizers from the energy efficient chemical plants and using them based on soil analysis the energy cost and the CO_2 emission may be reduced. Also by providing information to the consumers about energy cost and the CO_2 emission associated with each product may convince the producers to use cleaner energy sources.

The HVAC units appear to be the most energy and exergy utilizing units in the process, therefore they appear to be the perfect candidate for attempts of the energy savings. Wang *et al.* [105] has suggested a power saving strategy via reducing the total pressure applied by the primary air fan of a coal – fired air fan, and estimated the possibility of 15 per cent energy savings. Applying such an optimization scheme may also reduce exergy destruction and energy utilization in the black tea production facilities.

4.2. INSTANT AND ICE TEA

Energy and exergy utilization, carbon dioxide emission and exergy destruction were calculated for the pilot scale production of the instant tea and ice tea. Calculations were also performed for packaging of the instant and ice tea and further processing of the waste into value added products. Energy and exergy utilization in the chain extending from agriculture to packaging was 1,431 and 3,987 MJ/kg of instant tea and 3,571 and 4,464 MJ/kg of ice tea, respectively. The total amount of the CO_2 emission in the entire process was 140 kg/ kg of instant tea and 267 kg/ kg of ice tea.

Instant tea, ice tea, Turkish style brewed tea and normal brewed tea were compared for their energy and exergy utilization and CO_2 emissions. Instant tea preparation was the most energy and exergy utilizing process when compared with ice tea, Turkish style brewed tea and brewed tea. Reducing the amount of the water boiled to prepare instant tea, Turkish style brewed tea or brewed tea may reduce the energy and exergy utilization substantially. Drying was the second highest energy utilizing step in all the processes after boiling of water. So, depending on the equipment used, circulating the exhaust gases and optimizing the inlet and outlet temperatures are the most important factors that may help to reduce energy utilization and CO_2 emissions in the drying step. Decreasing the loss of the product and using the optimum production capacity of the equipment in processing may improve the efficiencies. Using renewable energy, recycling the waste heat and insulating the process stream lines are among the other important aspects to be considered to increase the stream efficiently. Increasing the concentration of the extract may help to evaporate smaller amounts of water and lead to utilization of less energy and exergy.

Renewability indicator for whole process, including further processing of the waste into valorization products had negative renewability indicator values, meaning that these processes were not renewable. Although the valorization of waste was renewable, it was not large enough to make the entire process renewable. Using less energy, renewable or reusable materials like catalyst may improve the renewability of these processes.

4.3. EXPERIMENTAL RESULTS

The present work suggests that that seven gardes of (high- and low-quality) black teas and high- and low-quality black teas should not be distinguished on the basis of their phenolic contents and antioxidant activity and some variations, albeit to different extents, were observed between the low- and high-quality black tea and instant teas. Despite the fact that low-quality black tea had a tendency to have lower values as compared to that of their high-quality counterparts, no significant differences ($p > 0.05$) existed in most instances. Therefore, the combination of nutritional compounds together with functional characteristics renders synergistic effects that provide the characteristic quality of each grade of black tea and instant tea.

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APPENDIX A: EXPERIMENTAL PROCEDURES

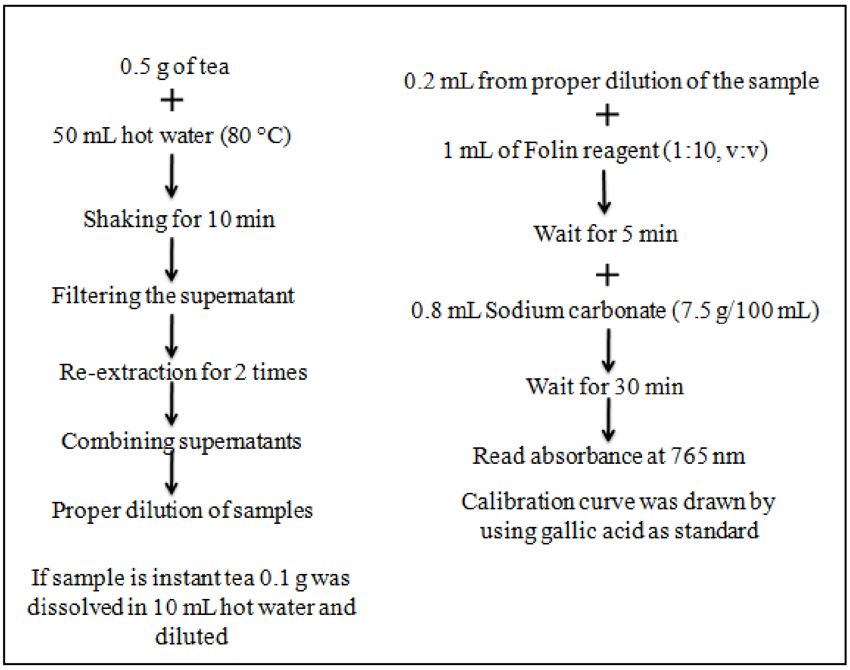

Figure A.1. Flow diagram for total phenolics analysis

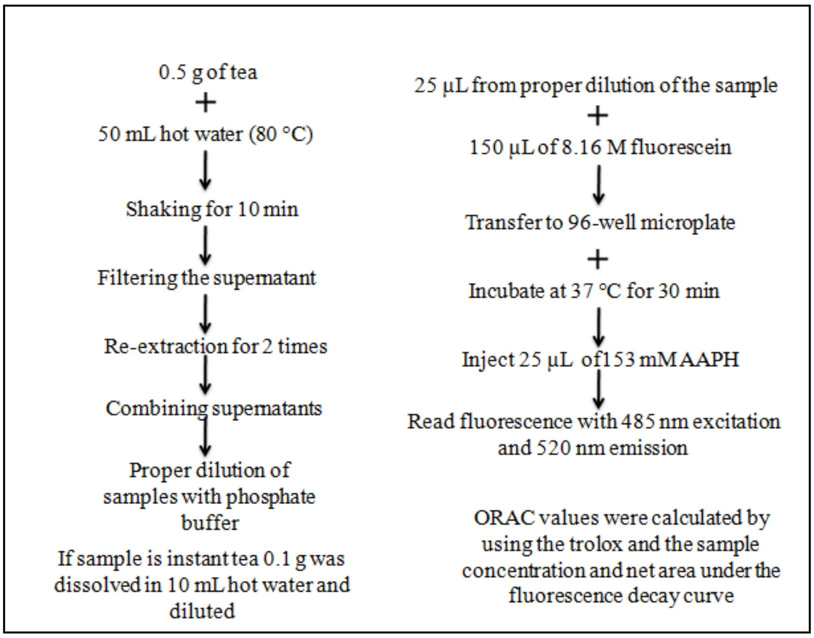

Figure A.2. Flow diagram for total antioxidant activity (ORAC) analysis

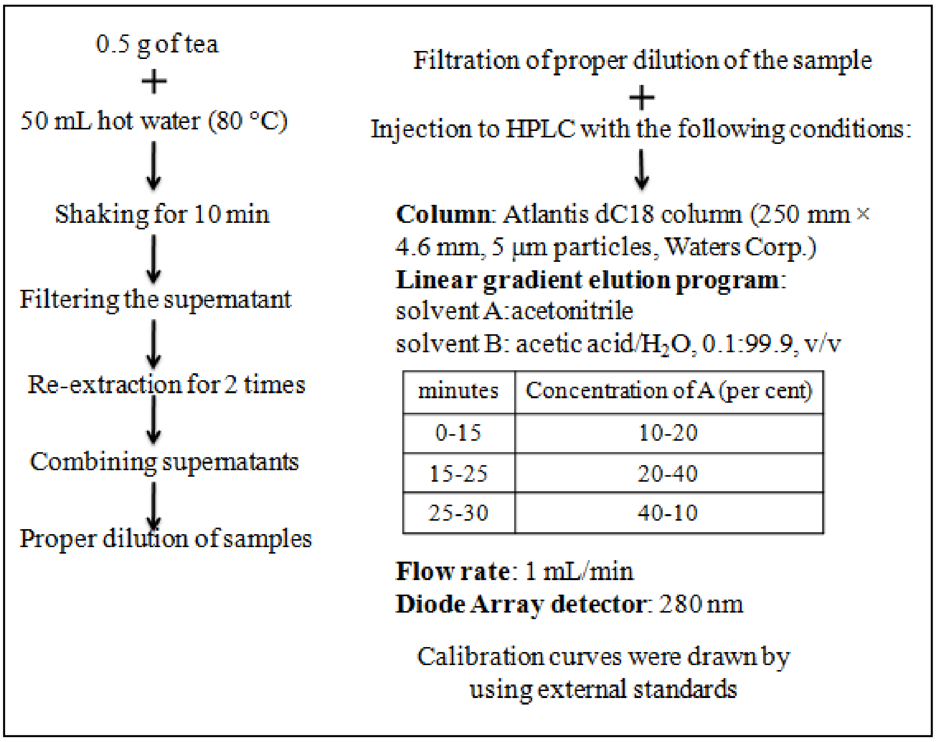

Figure A.3. Flow diagram for phenolics analysis

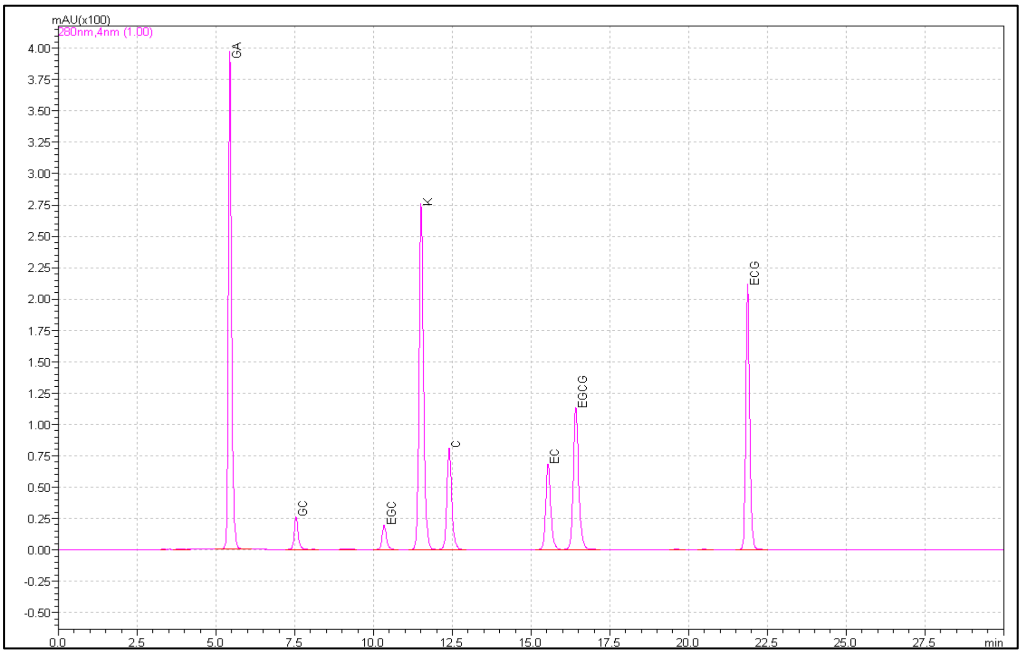

Figure A.4. Chromatogram for phenolics standards

APPENDIX B: CALCULATIONS

Table B.1. Calculations for agriculture step for black tea

	kg fertilizer /decare	fresh tea t/decare	kg fertilizer/t fresh tea	kg fertilizer /t black tea	CEnC-for fertilizer production (MJ/kg fertilizer)	CExC-for fertilizer production (MJ/kg fertilizer)	CCO_2E (kg/kg)	CEnC-for fertilizer used (MJ/kg black tea)	CExC-for fertilizer used (MJ/kg black tea)	CCO_2E (kg/t black tea)
Organic manure	1.0	0.9	1.1	0.4	0.4	5.3	0.0	0.1	1.9	0.0
Nitrogenous	25.0	0.9	28.2	9.1	78.2	32.7	7.1	714.9	298.9	65.0
Phosphorous	30.0	0.9	33.9	11.0	17.5	7.5	2.7	192.0	82.3	29.6
Potassium	15.0	0.9	16.9	5.5	13.8	4.6	25.0	75.7	25.2	137.1

All the calculations in Appendix B were based on the examples in Özilgen and Sorgüven (2016) [106]:

kg fertilizer/t fresh tea = (kg fertilizer /decare) / (fresh tea t/decare)

t black tea = (t fresh tea)/1000 x 323.8 (B.2)

kg fertilizer /t black tea = (kg fertilizer/t fresh tea) /1000 x 323.8 (B.3)

CEnC-for fertilizer used (MJ/kg black tea) = CEnC-for fertilizer production (MJ/kg fertilizer) x kg fertilizer /t black (B.4)

CExC-for fertilizer used (MJ/kg black tea) = CExC-for fertilizer production (MJ/kg fertilizer) x kg fertilizer /t black (B.5)

CCO_2E (kg/t black tea) = CCO_2E (kg/kg) x kg fertilizer /t black tea (B.6)

Table B.2. Calculations for transportation of black tea

	diesel consumption (kg)	black tea transported (t)	kg diesel/t black tea	CEnC for diesel (MJ/kg)	CExC for diesel (MJ/kg)	CCO_2E for diesel (kg/kg)	CEnC- (MJ/t black tea)	CExC- (MJ/t black tea)	CCO_2E- (kg CO_2/t black tea)
20 km -for fresh tea transportation	4.78	3.24	1.47	57.5	53.2	0.94	84.81	78.46	1.39
1150 km -for black tea transportation	274.60	10.00	27.46	57.5	53.2	0.94	1578.96	1460.88	25.81

kg diesel/t black tea = diesel consumption (kg) x black tea transported (t)

CEnC- (MJ/t black tea) = CEnC for diesel (MJ/kg) x kg diesel/t black tea (B.8)

CExC- (MJ/t black tea) = CExC for diesel (MJ/kg) x kg diesel/t black tea (B.9)

CCO_2E- (kg CO_2/t black tea) = CCO_2E for diesel (kg/kg) x kg diesel/t black tea (B.10)

Table B.3. Enthalpy and exergy calculations of the streams for black tea production

			m (kg)					m (kg)			ENTHALPY		ENTROPY		EXERGY	
	No		dry air	H_2O	Ø (kg/kg dry air)	per cent moisture	air (kg)	dry tea	H_2O	T (C)	h (kJ/kg)	H (kJ)	s (kJ/kg.K)	S (kJ/K)	Ex (kJ/kg)	EX (kJ)
WITHERING	1	air	241290	2764	0.01146	78.0	244054			20.0	49	11865797	0.177	42675	0.89	215622
	2	air	241290	2764	0.01146	37.3	244054			32.5	62	14966759	0.220	53033	2.03	488686
	3	air	241290	2764	0.01605	98.9	245163			21.5	62	15051869	0.222	53566	1.77	428218
	4	tea				0.75	3880	970	2910	20.0		313438				106097
		dry tea				0.75	3880	970	2910	20.0	71	69258			2.49	2419
		water				0.75	3880	970	2910	20.0	84	244180	0.177		35.63	103677
	5	tea				0.65	2771	970	1801	21.5		236878				8959
		dry tea				0.65	2771	970	1801	21.5	77	74452			2.87	2786
		water				0.65	2771	970	1801	21.5	90	162426	0.318		3.43	6172
FERMENTATION	6	air	5914	67.74	0.01146	78.0	5982			20	49	290830	0.177	1046	0.89	5287
	17	H_2O		10.65			11			20	84	893	0.296	3	2.97	32
	7	air	5914	78.39	0.01325	90.0	5992			20	54	317818	0.193	1139	1.16	6876
	18	H_2O	5914	31.33						20	84	2629	0.296	9	2.97	93
	8	air	5914	110	0.01855	92.2	6024			25	72	427995	0.256	1513	2.52	14875
	9	tea				0.65	2771	970	1801	35		385310				22895
		dry tea				0.65	2771	970	1801	35	125	121202			7.38	7163
		water				0.65	2771	970	1801	35	147	264109	0.505		8.73	15732
	10	tea				0.65	2771	970	1801	25		275364				11981
		dry tea				0.65	2771	970	1801	25	89	86573			3.85	3737
		water				0.65	2771	970	1801	25	105	188791	0.367		4.58	8244
DRYING	11	air	65054	745	0.01146	78.0	65799			20	49	3199131	0.177	11505	0.89	58153
	12	air	65054	745	0.01146	1.8	65799			100	132	8559188	0.425	27671	15.45	100505

	13	air	65054	2516	0.03868	50.2	67570			49	149	9725346	0.509	33088	10.64	692273
	14	tea				0.65	2771	970	1801	25		275364				11981
		dry tea				0.65	2771	970	1801	25	89	86573			3.85	3737
		water				0.65	2771	970	1801	25	105	188791	0.367		4.58	8244
	15	tea				0.03	1000	970	30	40		143542				11939
		dry tea				0.03	1000	970	30	40	143	138516			9.54	9254
		water				0.03	1000	970	30	40	168	5026	0.286		89.51	2685
SORTING	16	tea				0.03		970	30	20		71775				3488
		dry tea				0.03		970	30	20	71	69258			2.49	2419
		water				0.03		970	30	20	84	2517	0.177		35.63	1069

Ø (kg/kg dry air) and per cent moisture values were determined by using CYTSoft Psychrometric Calculator 1.0 Demo program.

h and s values were taken from Çengel and Boles (2006) [107] and H and S were calculated as follows:

$$H = m \times h$$
$$S = m \times s \qquad \text{(B.12)}$$

For air and water exergy was calculated as follows (for which, h and s values were taken from Çengel and Boles (2006) [107] :

$$Ex = h - T_0 x s \qquad \text{(B.13)}$$

For black tea, c_p was assumed as 3.57kJ/kg.K and exergy was calculated as follows [108]:

$$Ex = c_p\, xT - T_0 \times c_p \times \ln((T_0+T)/T_0))$$
$$EX = m \times Ex \qquad \text{(B.15)}$$

Table B.4. Cumulative energy, exergy and CO_2 calculations for each equipment in black tea production process

	Energy utilization (kW=kJ/s)	Conversion factor for 1 t black tea	Working time for 1 t black tea (s)	Energy utilization for 1 t black tea (MJ/t)	CEnC- for electricity (MJ/MJ)	CExC- for electricity (MJ/MJ)	CCO_2E- for electricity (kg/MJ)	CEnC- for black tea (MJ/t)	CExC- for black tea (MJ/t)	CCO_2E- for black tea (kg/t)
conveyor	3	1	300	0.90	1	4.17	0.14	0.90	3.75	0.13
withering			21600	0.00				3209.83	13385	449
fan	1.5	1.36	21600	44.06	1	4.17	0.14	44.06	183.75	6.17
heater	3100961		21600	3101	1	4.17	0.14	3101	12931	434.1
conveyor	3	1	21600	64.80	1	4.17	0.14	64.80	270.22	9.07
rolling										
roller	11.25	11.55	1800	233.8	1	4.17	0.14	233.80	975	32.73
conveyor	3	1	600	1.80	1	4.17	0.14	1.80	7.51	0.25
fermentation			1800	0.00				33	136	5
fan	1.5	0.4	1800	1.08	1	4.17	0.14	1.08	4.50	0.15
heater	26095		1800	26.09	1	4.17	0.14	26.09	108.8	3.65
conveyor	3	1	1800	5.40	1	4.17	0.14	5.40	22.52	0.76
drying			1800	0.00				5377	22423	753
fan	1.5	4.4	1800	11.88	1	4.17	0.14	11.88	49.54	1.66
heater	5360056		1800	5360	1	4.17	0.14	5360	22351	750.4
conveyor	3	1	1800	5.40	1	4.17	0.14	5.40	22.52	0.76
sorting										
sorter	1.5	1	3600	5.40	1	4.17	0.14	37.80	157.63	5.29

Conversion factor for 1 t black tea is the coefficient that capacities of the equipment were multiplied to produce 1 t of black tea.

$$\text{Energy utilization for 1 t black tea} = \text{Energy utilization (kW=kJ/s)} \times \text{Conversion factor for 1 t black tea} \times \text{Working time for 1 t black tea (s)} / 1000 \tag{B.16}$$

$$\text{CEnC- (MJ/t black tea)} = \text{CEnC for electricity (MJ/MJ)} \times \text{Energy utilization for 1 t black tea (MJ/t)} \tag{B.17}$$

$$\text{CExC- (MJ/t black tea)} = \text{CExC for electricity (MJ/MJ)} \times \text{Energy utilization for 1 t black tea (MJ/t)} \tag{B.18}$$

$$\text{CCO}_2\text{E- (kg CO}_2\text{/t black tea)} = \text{CCO}_2\text{E for electricity (kg/ MJ)} \times \text{Energy utilization for 1 t black tea (MJ/t)} \tag{B.19}$$

Table B.5. Calculations for packaging materials for black tea

	Amount used for 500 g capacity packs	Units	CEnC- for packaging material (MJ/kg)	CExC- for packaging material (MJ/kg)	CCO_2E - for packaging material (kg/kg)	number of packages used to pack 1 t of black tea in 500 gr capacity packs	Amount of packages used to pack 1 t of black tea in 500 gr capacity packs (kg packaging material/t black tea)	CEnC- for black tea (MJ/t)	CExC- for black tea (MJ/t)	CCO_2E- for black tea (kg/t)
primary package (PET)	15	gr	4.8	86.8	2.33	2000	30	144.0	2604.0	69.9
hot melt kola (LDPE)	1.8	gr	4.8	46.5	2.1	2000	3.6	17.28	167.4	7.56
cardboard	0.00038	m^2 (d:55kg/m^3)	43.3	16.5	1.17	2000		75.33	28.71	2.04
plastic band (LDPE)	5	gr	4.8	46.5	2.1	2000	10	48	465	21
cardboard label (PET)	1.35	gr	4.8	86.8	2.33	2000	2.7	13.0	234.4	6.3
halogram label (PET)	4.32	gr	4.8	86.8	2.33	2000	8.64	41.5	750.0	20.1

number of packages used to pack 1 t of black tea in 500 gr capacity packs = 1 t/500 g = 1000 kg/0.5 kg = 2000 (B.20)

Amount of packages used to pack 1 t of black tea in 500 gr capacity packs (kg packaging material/t black tea) = Amount used for 500 g capacity packs x 2000 (B.21)

CEnC- for black tea (MJ/t black tea) = CEnC for packaging material (MJ/kg) x Amount of packages used to pack 1 t of black tea in 500 gr capacity packs (kg packaging material/t black tea) (MJ/t) (B.22)

CExC- for black tea (MJ/t black tea) = CExC for packaging material (MJ/kg) x Amount of packages used to pack 1 t of black tea in 500 gr capacity packs (kg packaging material/t black tea) (MJ/t) (B.23)

CCO_2E- for black tea (kg CO_2/t black tea) = CCO_2E for packaging material (kg/ kg) x Amount of packages used to pack 1 t of black tea in 500 gr capacity packs (kg packaging material/t black tea) tea (MJ/t) (B.24)

Table B.6. Calculations for packaging machines for black tea

	Energy utilization (kW=kJ/s)	**Capacity**	**CEnC- for electricity (MJ/MJ)**	**CExC- for electricity (MJ/MJ)**	**CCO_2E- for electricity (kg/MJ)**	**CEnC- for black tea (MJ/t)**	**CExC- for black tea (MJ/t)**	**CCO_2E- for black tea (kg/t)**
Packaging machine	48.5	250 packs/min	1	4.17	0.14	0.97	4.04	0.14
Cardboard making machine	3.5	1 t/h	1	4.17	0.14	12.60	52.54	1.76

CEnC- (MJ/t black tea) = CEnC for electricity (MJ/MJ) x Energy utilization for 1 t black tea (MJ/t) (B.25)

CExC- (MJ/t black tea) = CExC for electricity (MJ/MJ) x Energy utilization for 1 t black tea (MJ/t) (B.26)

CCO_2E- (kg CO_2/t black tea) = CCO_2E for electricity (kg/ MJ) x Energy utilization for 1 t black tea (MJ/t) (B.27)

Table B.7. Amount of energy sources used by Çaykur

	Amount used for 1 kg fresh tea	**Amount used for 1 kg black tea**	**Amount used for 1 t black tea**
Fuel oil (kg)	0,123	0,477	477
Natural gas (kWh)	1,396	5,417	5417
Electricity (kWh)	0,107	0,415	415
Coal (kg)	0,198	0,768	768

In conversion of fresh tea to black tea, 1000 kg black tea was assumed to be produced from 3880 kg fresh tea

Amount used for 1 kg black tea = Amount used for 1 kg fresh tea x 3880 kg fresh tea / 1000 kg fresh tea (B.28)

Table B.8. Cumulative energy and CO_2 calculations for each energy source used by Çaykur

	Amount used for 1 t black tea	**CCO_2E- for the source**	**CEnC/t of tea (MJ/t)**	**CCO_2E (kg/t)**
Fuel oil	477 (kg)	0,94 (kg/kg)	27442	2
Natural gas	5417 (kWh)	0,06 (kg/MJ)	19499	931
Electricity	415 (kWh)	0,14 (kg/MJ)	1495	167
Coal	768 (kg)	0,078 (kg/MJ)	9649	753

CEnC- (of tea (MJ/t) = Amount used for 1 t black tea (kg/t or kWh/t) x CEnC for energy source (MJ/kg or MJ/kWh) (B.29)

CCO_2E- (kg CO_2/t black tea) = CCO_2E for energy source x CCO_2E for energy source (B.30)

Table B.9. Enthalpy and exergy calculations of the streams for instant tea production

			m (kg)					m (kg)			ENTHALPY		ENTROPY		EXERGY	
	No		dry air	H2O	Ø (kg/kg dry air)	per cent moisture	specific volume (m3/kg)	dry tea	H_2O	T (°C)	h (kJ/kg)	H (kJ)	s (kJ/kg.K)	S (kJ/K)	Ex (kJ/kg)	EX (kJ)
EXTRACTION	1	black tea	0	0	0	0	0	19.4	0.6	20	-	1435.51	-	-		50.17
		dry tea	0	0	0	0	0	19.4	0	20	71.40	1385.16	-	-	2.49	48.39
		water	0	0	0	0	0	0	0.6	20	83.92	50.35	0.30	0.18	2.97	1.78
	2	water	0	0	0	0	0	0	100	20	83.92	8391.50	0.30	29.65	2.97	297.05
	3	extracted tea	0	0	0	0	0	17.353	88	80	-	34302.91	-	-		4234.48
		tea leaves	0	0	0	0	0	17.350	0	80	285.60	4955.16	-	-	35.13	609.49
		water	0	0	0	0	0	0	88	80	335.02	29347.75	1.08	94.22	41.38	3624.99
	4	extract	0	0	0	0	0	2.047	13	80	-	4939.88	-	-		609.86
		dry matter	0	0	0	0	0	2.047	0	80	285.60	584.62	-	-	35.13	71.91
		water	0	0	0	0	0	0	13	80	335.02	4355.26	1.08	13.98	41.38	537.96
CENTRIFUGE	4	extract	0	0	0	0	0	2.047	13	60	-	3703.81	-	-		357.17
		dry matter	0		0	0	0	2.047	0	60	214.20	438.47	-	-	20.57	42.11
		water	0	0	0	0	0	0	13	60	251.18	3265.34	0.83	10.81	24.24	315.06
	5	unwanted	0	0	0	0	0	0.02	0	40	142.80	2.86	-	-	9.54	0.19
	6	s.extract	0	0	0	0	0	2.027	13	40	-	2467.35	-	-		165.78
		dry matter	0	0	0	0	0	2.027	0	40	142.80	289.46	-	-	9.54	19.34

		water	0	0	0	0	0	0	13	40	167.53	2177.89	0.57	7.44	11.26	146.44
SPRAY DRYER	6	s.extract	0	0	0	0	0	2.027	13	40	-	2467.35	-	-		165.78
		dry matter	0	0	0	0	0	2.027	0	40	142.80	289.46	-	-	9.54	19.34
		water	0	0	0	0	0	0	13	40	167.53	2177.89	0.57	7.44	11.26	146.44
	7	air	120	1.297	0.010809	74	0.844018	0	0	20	20.12	2414.80	0.07	8.53	0.71	85.61
	8	Product loss	0	0	0	0	0	0.507	0	80	285.60	144.73	-	-	35.13	17.80
	9	exhaust air	120	14.25	0.118751	8.17		0	0	120	121.04	14524.30	0.37	44.07	20.78	2493.78
	10	tea powder	0	0	0	0	0	1.52	0.047	80	-	449.86	-	-		55.34
		dry matter	0	0	0	0	0	1.52	0	80	285.60	434.11	-	-	35.13	53.40
		water	0	0	0	0	0	0	0.047	80	335.02	15.75	1.08	0.05	41.38	1.94
FLUİDİZED BED	10	tea powder	0	0	0	0	0	1.52	0.047	40	-	224.93	-	-		15.03
		dry matter	0	0	0	0	0	1.52	0	40	142.80	217.06	-	-	9.54	14.50
		water	0	0	0	0	0	0	0.047	40	167.53	7.87	0.57	0.03	11.26	0.53
	11	water	0	0	0	0	0	0	0.500	20	83.92	41.96	0.30	0.15	2.97	1.49
	12	air	533.164	5.763	0.010809	74	0.844018	0	0	20	20.12	10729.06	0.07	37.91	0.71	380.37
	13	Product loss	0	0	0	0	0	0.608	0	50	178.50	108.53	-	-	14.59	8.87
	14	exhaust air	533.164	6.222	0.01167			0	0	50	50.33	26834.19	0.17	90.21	4.14	2206.49
	15	Agglomerated	0	0	0	0	0	0.912	0.088	50	-	181.21	-	-		14.82
		dry matter	0	0	0	0	0	0.912	0	50	178.50	162.79	-	-	14.59	13.31
		water	0	0	0	0	0	0	0.088	50	209.34	18.42	0.70	0.06	17.20	1.51

Ø (kg/kg dry air) and per cent moisture values were determined by using CYTSoft Psychrometric Calculator 1.0 Demo program.

h and s values were taken from Çengel and Boles (2006) [107] and H and S were calculated as follows:

$$H = m \times h$$
$$S = m \times s \quad \text{(B.12)}$$

For air and water exergy was calculated as follows (for which, h and s values were taken from Çengel and Boles (2006) [107] :

$$Ex = h - T_0 x s \quad \text{(B.13)}$$

For black tea, c_p was assumed as 3.57kJ/kg.K and exergy was calculated as follows [108]:

$$Ex = c_p \, x(T-T_0) \, x \, c_p \, x \, \ln((T_0+T)/T_0))$$
$$EX = m \, x \, Ex \qquad (B.15)$$

Table B.10. Cumulative energy, exergy and CO_2 calculations for each equipment in instant tea production process

		Energy utilization (kW=kJ/s)	**Working time (h)**	**Energy utilization for 1 kg black tea (MJ/kg)**	**CEnC- for electricity (MJ/MJ)**	**CExC- for electricity (MJ/MJ)**	**CCO_2E- for electricity (kg/MJ)**	**CEnC- for instant tea (MJ/kg)**	**CExC- for instant tea (MJ/kg)**	**CCO2E- for instant tea (MJ/kg)**
extraction	pump+screw carrier	5	1.5	27.00	1	4.17	0.14	27.00	112.59	3.78
	heaters	12	1.5	64.80	1	4.17	0.14	64.80	270.22	9.07
	Total							91.80	382.81	12.85
separation	centrifuge	0.37	0.5	0.67	1	4.17	0.14	0.67	2.78	0.09
spray dryer	pump	0.5	1	1.80	1	4.17	0.14	1.80	7.51	0.25
	fan	2	1	7.20	1	4.17	0.14	7.20	30.02	1.01
	heaters	36	1	129.60	1	4.17	0.14	129.60	540.43	18.14
	Total							138.60	577.96	19.40
fluidized bed	pump	0.5	5	9.00	1	4.17	0.14	9.00	37.53	1.26
	fan	5.5	5	99.00	1	4.17	0.14	99.00	412.83	13.86
	heaters	30	5	540.00	1	4.17	0.14	540.00	2251.80	75.60
	Total							648.00	2702.16	90.72

Energy utilization for 1 kg instant tea = Energy utilization (kW=kJ/s) x Working time for 1 kg instant tea (h/t) x 3600 (s/h) / 1000 (B.31)

CEnC- (MJ/ kg instant tea) = CEnC for electricity (MJ/MJ) x Energy utilization for 1 kg instant tea (MJ/t) (B.32)

CExC- (MJ/ kg instant tea) = CExC for electricity (MJ/MJ) x Energy utilization for 1 kg instant tea (MJ/t) (B.33)

CCO_2E- (kg CO_2/ kg instant tea) = CCO_2E for electricity (kg/ MJ) x Energy utilization for 1 kg instant tea (MJ/t) (B.34)

Table B.11. Calculations for packaging materials for instant tea

	Amount used for single packs (kg)	**CEnC- for packaging material (MJ/kg)**	**CExC- for packaging material (MJ/kg)**	**CCO_2E - for packaging material (kg/kg)**	**Amount used for 1 kg instant tea (kg)**	**CEnC- for instant tea (MJ/kg)**	**CExC- for instant tea (MJ/kg)**	**CCO_2E- for instant tea (MJ/kg)**
Single packs (PLA)	0.0005	54	78	1.8	1	54.0	78.0	1.8
Cardboard for 50 single packs	0.132	43.3	16.5	1.17	5.28	228.62	87.12	6.18
cardboard	3.52	43.3	16.5	1.17	5.9	254.03	96.80	6.86
Palletizing material (HDPE)		3.2	86	0.45	0.010	0.032	0.860	0.005

Amount used for 1 kg instant tea (kg) = Amount used for single packs (kg)/ Amount of instant tea per pack (kg) x 1000 kg (B.35)

CEnC- for instant tea (MJ/kg instant tea) = CEnC for packaging material (MJ/kg) x Amount used (kg/kg instant tea) (B.36)

CExC- for instant tea (MJ/ kg instant tea) = CExC for packaging material (MJ/kg) x Amount used for (kg/kg instant tea) (B.37)

CCO_2E - for instant tea (MJ/ kg instant tea) = CCO_2E for packaging material (MJ/kg) x Amount used (kg/kg instant) (B.38)

TableB.12. Calculations for packaging machines for instant tea

	Energy utilization (kJ)	**Capacity**	**CEnC- for electricity (MJ/MJ)**	**CExC- for electricity (MJ/MJ)**	**CCO_2E- for electricity (kg/MJ)**	**Working time for 1 kg instant (s)**	**CEnC- for instant tea (MJ/kg)**	**CExC- for instant tea (MJ/kg)**	**CCO_2E- for instant tea (kg/kg)**
Packaging machine	1.2 kW	30 packs/min	1	4.17	0.14	4000			
Cardboard making machine	48.5 kW	250 packs/min	1	4.17	0.14	0.4008	0.97	4.04	0.14
Palletizing equipment	3.5 kW	25 pallet/min	1	4.17	0.14	4.008	12.60	52.54	1.76

CEnC- (MJ/kg instant tea) = CEnC for electricity (MJ/MJ) x Energy utilization (MJ/kg instant tea) (B.39)

CExC- (MJ/ kg instant tea) = CExC for electricity (MJ/MJ) x Energy utilization (MJ/kg instant tea) (B.40)

CCO_2E- (kg CO_2/ kg instant tea) = CCO_2E for electricity (kg/ MJ) x Energy utilization (MJ/kg instant tea) (B.41)

Table.B.13. Cumulative energy, exergy and CO_2 calculations for preparation of 1000 L instant tea

	CEnC (MJ/kg)	**CExC (MJ/kg)**	**CCO_2E (kg/kg)**
Process values for 1 kg instant tea	1430.6	3986.5	140.3
Process values for 5 kg instant tea	7153.0	19932.3	701.4
Preparation values	250.8	1045.8	35.1
Total	7403.8	20978.1	736.5

Process values for 1 kg instant tea is the summation of all CEnC, CExC and CCO_2E values in Table 3.7. For 5 kg the results were multiplied by 5. For the calculation of preparation values, 1000 L of water must be heated to 85 °C from 25°C so:

$$Q = m \times c \times \Delta T \quad (B.42)$$

$$\text{CExC- (MJ/1000 L instant tea)} = \text{CExC for electricity (MJ/MJ)} \times Q \text{ (MJ/1000 L)} \quad (B.43)$$

$$CCO_2E\text{- (kg } CO_2\text{/1000 L instant tea)} = CCO_2E \text{ for electricity (kg/ MJ)} \times Q \text{ (MJ/1000 L)} \quad (B.44)$$

Table.B.14. Cumulative energy, exergy and CO_2 calculations for preparation of 1000 L Turkish style brewed tea

	CEnC (MJ/kg)	**CExC (MJ/kg)**	**CCO_2E (kg/kg)**
Process values for 1 kg black tea	11.2	42.1	1.7
Process values for 10 kg black tea	111.6	420.8	17.0
Preparation values	647.9	2701.7	90.7
Total	759.5	3122.5	107.7

Process values for 1 kg black tea is the summation of all CEnC, CExC and CCO_2E values in Table 3.1, Table 3.2 and Table 3.4. For 10 kg, the results were multiplied by 10. For the calculation of preparation values ,1000 L of water must be heated to 100 °C from 25°C and kept at that temperature for 15 min so:

$$Q = m \times c \times \Delta T + m \times c \times \Delta T \quad (B.45)$$

$$CExC\text{- (MJ/1000 L black tea)} = CExC \text{ for electricity (MJ/MJ)} \times Q \text{ (MJ/1000 L)} \quad (B.46)$$

$$CCO_2E\text{- (kg } CO_2\text{/1000 L black tea)} = CCO_2E \text{ for electricity (kg/ MJ)} \times Q \text{ (MJ/1000 L)} \quad (B.47)$$

Table.B.15. Cumulative energy, exergy and CO_2 calculations for preparation of 1000 L brewed tea

	CEnC (MJ/kg)	**CExC (MJ/kg)**	**CCO_2E (kg/kg)**
Process values for 1 kg black tea	11.2	42.1	1.7
Process values for 10 kg black tea	111.6	420.8	17.0
Preparation values	250.8	1045.8	35.1
Total	362.4	1466.6	52.1

Process values for 1 kg black tea is the summation of all CEnC, CExC and CCO_2E values divided into 1000 in Table 3.1, Table 3.2 and Table 3.4. For 10 kg, the results were multiplied by 10. For the calculation of preparation values, 1000 L of water must be heated to 85 °C from 25°C so:

$$Q = m \times c \times \Delta T \quad (B.42)$$

$$CExC\text{- (MJ/1000 L black tea)} = CExC \text{ for electricity (MJ/MJ)} \times Q \text{ (MJ/1000 L)} \quad (B.46)$$

$$CCO_2E\text{- (kg } CO_2\text{/1000 L black tea)} = CCO_2E \text{ for electricity (kg/ MJ)} \times Q \text{ (MJ/1000 L)} \quad (B.47)$$

Table.B.16. Cumulative energy, exergy and CO_2 calculations for preparation of 1000 L ice tea

	CEnC (MJ/kg)	**CExC (MJ/kg)**	**CCO_2E (kg/kg)**
Process values for 1000 Lice tea	3568.5	4462.6	265.9
Total	3568.5	4462.6	265.9

Process values for 1000 L ice tea is the summation of all CEnC, CExC and CCO_2E values in Table 3.9.

Table B.17. Cumulative energy, exergy and CO_2 calculations for each equipment in ice tea production process

		Energy utilization (kW=kJ/s)	**Working time for 1000 L ice tea (h)**	**Energy utilization for 1000 L ice tea (MJ/1000L)**	**CEnC- for electricity (MJ/MJ)**	**CExC- for electricity (MJ/MJ)**	**CCO_2E- for electricity (kg/MJ)**	**CEnC- for ice tea (MJ/1000L)**	**CEcC- for ice tea (MJ/1000L)**	**CCO2E- for ice tea (MJ/1000L)**
extraction	pump+helezon	5	0.75	13.50	1	4.17	0.14	13.50	56.3	1.89
	heaters	12	0.75	32.40	1	4.17	0.14	32.40	135.1	4.54
	Total							45.90	191.4	6.43
separation	centrifuge	0.37	0.25	0.33	1	4.17	0.14	0.33	1.389	0.05
dilution	heating of water			313.5	1	4.17	0.14	313.5	1307.3	43.9
	pump	2.2	0.02	0.13	1	4.17	0.14	0.13	0.550	0.02
	Total							313.6	1307.8	43.91
bottling	bottling machine	3.8	3.33	45.60	1	4.17	0.14	45.60	190.1	6.38
	Total							45.60	190.1	6.38
secondary packaging	cardboard machine	48.5	0.0017	0.2910	1	4.17	0.14	0.29	1.21	0.04
	pelletizing machine	10	0.000347	0.0125	1	4.17	0.14	0.01	0.05	0.00
	Total							0.30	1.27	0.04

Energy utilization for 1000 L ice tea = Energy utilization (kW) x Working time for 1 t black tea (h/t) x 3600 (s/h) / 1000 (B.48)

CEnC- (MJ/1000 L ice tea) = CEnC for electricity (MJ/MJ) x Energy utilization for ice tea (MJ/1000 L) (B.49)

CExC- (MJ/1000 L ice tea) = CExC for electricity (MJ/MJ) x Energy utilization for ice tea (MJ/1000 L) (B.50)

CCO_2E- (kg CO_2/1000 L black tea) = CCO_2E for electricity (kg/ MJ) x Energy utilization for ice tea (MJ/1000 L) (B.51)

Table B.18. Calculations for packaging materials for ice tea

	Amount used (kg)	CEnC- for packaging material (MJ/kg)	CExC- for packaging material (MJ/kg)	CO_2E - for packaging material (kg/kg)	Amount of packages used to pack 1000 L ice tea (kg packaging material/1000 L ice tea)	CEnC- for ice tea (MJ/1000L)	CExC- for ice tea (MJ/1000L)	CCO_2E- for ice tea (MJ/1000L)
Can (Aluminum)	0.01	191	188.51	18.66	50	9550.0	9425.5	933.0
Can when recycled		47.75	47.1275	3.732		2387.5	2356.4	186.6
Can coating (LDPE)	5.43E-6	87	46.5	2.1	0.02713	2.36	1.26	0.06
Cardboard	0.704	43.3	16.5	1.17	17.6	762.08	290.40	20.59
Palletizing material		3.2	86	0.45	1.000	3.200	86.000	0.450

Amount of packages used to pack 1000 L ice tea (kg packaging material/1000 L ice tea) = Amount used for single bottle (kg)/ number of ice tea bottle for 1000 L (B.52)

CEnC- for ice tea (MJ/1000 L ice tea) = CEnC for packaging material (MJ/kg) x Amount used for 1000 L ice tea (kg/1000 L ice tea) (B.53)

CExC- for ice tea (MJ/1000 L ice tea) = CExC for packaging material (MJ/kg) x Amount used for 1000 L ice tea (kg/1000 L ice tea) (B.54)

CCO_2E - for ice tea (MJ/1000 L ice tea) = CCO_2E for packaging material (MJ/kg) x Amount used for 1 kg instant tea (kg/1000 L ice tea) (B.55)

Table B.19. Enthalpy and exergy calculations of the streams for ice tea production

				m (kg)			ENTHALPY		ENTROPY		EXERGY	
	No			dry tea	H_2O	T (C)	h (kJ/kg)	H (kJ)	s (kJ/kg.K)	S (kJ/K)	Ex (kJ/kg)	EX (kJ)
EXTRACTION	1	black tea	10.00	9.7	0.3	20	-	717.8	-	-		25.1
		dry tea	9.70	9.7	0.0	20	71.400	692.6	-	-	2.494	24.2
		water	0.30	0.0	0.3	20	83.915	25.2	0.297	0.1	2.971	0.9
	2	water	50.00	0.0	50.0	20	83.915	4195.8	0.297	14.8	2.971	148.5
	3	extracted tea leaves	52.48	8.7	43.8	80	-	17152.9	-	-		2117.4
		tea leaves	8.68	8.7	0.0	80	285.600	2479.0	-	-	35.129	304.9
		water	43.80	0.0	43.8	80	335.020	14673.9	1.076	47.1	41.381	1812.5
	4	extract	7.52	1.0	6.5	80	-	2468.9	-	-		304.8
		dry matter	1.02	1.0	0.0	80	285.600	291.3	-	-	35.129	35.8
		water	6.50	0.0	6.5	80	335.020	2177.6	1.076	7.0	41.381	269.0
CENTRIFUGE	4	extract	7.52	1.0	6.5	60	-	1851.2	-	-		178.5
		dry matter	1.02	1.0	0.0	60	214.200	218.5	-	-	20.574	21.0
		water	6.50	0.0	6.5	60	251.180	1632.7	0.831	5.4	24.235	157.5
	5	unwanted particles	0.01	0.0	0.0	40	142.800	1.4	-	-	9.540	0.1
	6	s.extract	7.51	1.0	6.5	40	-	1233.2	-	-		82.9
		dry matter	1.01	1.0	0.0	40	142.800	144.2	-	-	9.540	9.6
		water	6.50	0.0	6.5	40	167.530	1088.9	0.572	3.7	11.265	73.2
MIXING	6	s.extract	7.51	1.0	6.5	40	-	1233.2	-	-		82.9
		dry matter	1.01	1.0	0.0	40	142.800	144.2	-	-	9.540	9.6

		water	6.50	0.0	6.5	40	167.530	1088.9	0.572	3.7	11.265	73.2
	7	Water	993.50	0.0	993.5	95	398.090	395502.4	1.250	1242.3	56.731	56362.0
	8	ice tea	1001.01	1.0	1000.0	95	-	398432.5	-	-		56779.4
		dry matter	1.01	1.0	0.0	95	339.150	342.5	-	-	48.121	48.6
		water	1000.00	0.0	1000.0	95	398.090	398090.0	1.250	1250.4	56.731	56730.8
BOTTLING	8	tea powder	1001.01	1.0	1000.0	95	-	398432.5	-	-		56779.4
		dry matter	1.01	1.0	0.0	95	339.150	342.5	-	-	48.121	48.6
		water	1000.00	0.0	1000.0	95	398.090	398090.0	1.250	1250.4	56.731	56730.8
	9	Cans	50.00	0.0	0.0	20	17.574	878.7	-	-	0.614	30.7
	10	Bottled iced tea	1051.01	1.0	1000.0	20	-	84865.8	-	-		3003.7
		dry matter	1.01	1.0	0.0	20	71.400	72.1	-	-	2.494	2.5
		water	1000.00	0.0	1000.0	20	83.915	83915.0	0.297	296.5	2.971	2970.5
		cans	50			20	17.574	878.7	-	-	0.614	30.7

Ø (kg/kg dry air) and per cent moisture values were determined by using CYTSoft Psychrometric Calculator 1.0 Demo program.

h and s values were taken from Çengel and Boles (2006) [107] and H and S were calculated as follows:

$$H = m \times h$$
$$S = m \times s \qquad (B.12)$$

For air and water exergy was calculated as follows (for which, h and s values were taken from Çengel and Boles (2006) [107] :

$$Ex = h - T_0 x s \qquad (B.13)$$

For black tea, c_p was assumed as 3.57kJ/kg.K and exergy was calculated as follows [108]:

$$Ex = c_p\ x(T-T_0)\ x\ c_p\ x\ \ln((T_0+T)/T_0)$$
$$EX = m \times Ex \qquad (B.15)$$

Table B.20. Calculations of exergy destruction for ice tea process

Processes	Q (kJ)	W (kJ)	Ex_{in}-Ex_{out}	1-T/(T+273)	Ex Destroyed	ΔQ (out -in)	mass balance (kg)	H balance (in-out) kJ
extraction	32400	0	-2249	0.932	41440	14708	0.0	31192
pump	0	13500						
centrifuge	0	333	96	0.820	428.6	-616	0.0	949.6
mixing			-335	0.742	232367	1670	0.0	311935
pump		132						
water heating	313500							
bottling		4560	53806	0.932	53806	-312688	0.0	318127

Q and W values were calculated by energy utilization og the equipment (given in the user manual or internet), for water heating it is the theoretical heat needed.

Ex_{in}-Ex_{out} = exergy of the streams entering to the process step – exergy of the streams leaving the process step

$$\text{Ex destroyed} = (Ex_{in}-Ex_{out}) + (1-T/(T+273))*Q + W \quad \text{(B.57)}$$

$$\Delta Q = Q_{out} - Q_{in} \quad \text{(B.58)}$$

Mass balance = mass of the streams entering to the process step – mass of the streams leaving the process step (B.59)

H balance = enthalpy of the streams entering to the process step – enthalpy of the streams leaving the process step (B.60)

Table B.21. Cumulative energy, exergy and CO_2 calculations for each equipment in waste tea valorization process

		Energy utilization (kW=kJ/s)	**Working time for 1 kg waste tea (h)**	**Energy utilization for 1 kg waste tea (MJ/kg)**	**CEnC- for electricity (MJ/MJ)**	**CExC- for electricity (MJ/MJ)**	**CCO_2E- for electricity (kg/MJ)**	**CEnC- for waste tea (MJ/kg)**	**CExC- for waste tea (MJ/kg)**	**CCO_2E- for waste tea (MJ/kg)**
1. activated carbon (M. Auta. B.H. Hameed)	press machine	0.55	0.01	0.02	1	4.17	0.14	0.02	0.10	0.00
	drying			3.31	1	4.17	0.14	3.31	13.82	0.46
	grinding	7.5	0.01	0.32	1	4.17	0.14	0.32	1.32	0.04
	mixing	4.0	0.00	0.03	1	4.17	0.14	0.03	0.12	0.00
	drying	-			1	4.17	0.14	0.00	0.00	0.00
	N_2 pump	0.2	0.01	0.01	1	4.17	0.14	0.01	0.04	0.00
	potassium acetate							52.3	218.3	7.33
	Reactor heating			1.14	1	4.17	0.14	1.14	4.74	0.16
	washing (pump)	2.2	0.00	0.00	1	4.17	0.14	0.00	0.01	0.00
	Drying			0.00	1	4.17	0.14	2.65	11.07	0.37
	Total			0.00				59.79	249.53	8.38
Hydrogen Production (Nezihe Ayas. Tugce Esen)	press machine	0.55	0.01	0.02	1	4.17	0.14	0.02	0.10	0.00
	drying		3.31	0.00	1	4.17	0.14	3.31	13.82	0.46
	grinding	7.5	0.01	0.32	1	4.17	0.14	0.32	1.32	0.04
	mixing	4.0	0.00	0.03	1	4.17	0.14	0.03	0.12	0.00
	air pump	0.37	0.00	0.00	1	4.17	0.14	0.00	0.02	0.00
	K_2CO_3- Potassium			0.00				13.2	55.1	1.85
	reactor heating			0.00	1	4.17	0.14	0.92	3.83	0.13
	Total			0.00				17.8	74.3	2.5
3. Lead adsorption (Shunli Wan.Zhaozhao Ma. et al)	press machine	0.55	0.01	0.02	1	4.17	0.14	0.02	0.10	0.00
	drying			3.31	1	4.17	0.14	3.3	13.8	0.46
	grinding	7.5	0.01	0.32	1	4.17	0.14	0.32	1.32	0.04
	Total							3.7	15.2	0.5

Energy utilization for 1 kg waste tea = Energy utilization (kW=kJ/s) x Working time for 1 t waste tea (h/t) x 3600 (s/h) / 1000 (B.61)

CEnC- (MJ/kg waste tea) = CEnC for electricity (MJ/MJ) x Energy utilization for waste tea (MJ/kg) (B.62)

CExC- (MJ/ kg waste tea) = CExC for electricity (MJ/MJ) x Energy utilization for waste tea (MJ/ kg) (B.63)

CCO_2E- (kg CO_2/ kg waste tea) = CCO_2E for electricity (kg/ MJ) x Energy utilization for waste tea (MJ/ kg) (B.64)

Table B.22. Exergy calculations for the product and the processes for preparation 1000 L of tea

							product		**process**		
	m (kg)		**ENTHALPY**		**ENTROPY**		**EXERGY**		**EXERGY**		
	H_2O	**T(°C)**	**h (kJ/kg)**	**H (kJ)**	**s (kJ/kg.K)**	**S (kJ/K)**	**Ex (kJ/kg)**	**Ex (kJ)**	**Ex (MJ/kg)**	**Ex (MJ)**	**Ex (MJ/1000L tea)**
water	1000	100	2256	2256400	6.05	6047	605.57	605569		1045.84	
black tea (dry)	10	100					3.49	34.88	37.76	377.60	1423.44
instant tea (dry)	5	100					14.82	74.10	3703	18516	19562.64
ice tea								2.52	1538.41	1538.41	1538.41

h and s values were taken from Çengel and Boles (2006) [107] and H and S were calculated as follows:

$$H = m \times h$$

$$S = m \times s \quad (B.12)$$

For water exergy was calculated as follows (for which, h and s values were taken from Çengel and Boles (2006) [107] :

$$Ex = h - T_0 \times s \quad (B.13)$$

For black tea, c_p was assumed as 3.57kJ/kg.K and exergy was calculated as follows [108]:

$$Ex = c_p \times (T - T_0) \times c_p \times \ln((T_0 + T)/T_0)$$

$$EX = m \times Ex \quad (B.15)$$

Table B.23.Amount of wastes produced for black, instant and ice tea processes

	Total kg	**Tea leaves (kg)**	**water (kg)**
Waste from black tea process	0	0	0
Waste from instant tea process	525	87	438.00
Waste from ice tea process	52.48	8.68	43.80

Table B.24.Calculations of CDP and renewability indicator for value added products from tea waste

	Exergy of the product (kJ/kg)	**Exergy of the process (MJ/kg waste tea)**	**CDP**	**Renewability Indicator**
activated carbon	34.19	249.53	0.14	-6.30
hydrogen	118.05	72.53	1.63	0.39
adsorbent material	34.19	14.94	2.29	0.56

$$CDP = \frac{(mb)_{product}}{\sum (mCExC)_{\text{raw materials}} + \sum (mCExC)_{\text{fuels}}} \text{ = Exergy of the product/ Exergy of the process} \quad (2.5)$$

$$I_r = \frac{(W_p - W_r)}{W_p} \text{ = (Exergy of the product-Exergy of the process) / Exergy of the product} \quad (2.6)$$

Table B.25.Calculations of CDP and renewability indicator for whole processes

	m (kg)	**EXERGY (MJ/kg)**		**CDP**	**Renewability Indicator**
		product	**process**		
Black tea	1010	606	1423	0.425	-1.35
Instant tea	1100	606	19563	0.031	-31.30
Iced tea	1010	0	1538	0.000	-610667.54
Instant tea					
Activated carbon	87	2974	21709	0.14	-6.30
Hydrogen	0.62	73	45	1.63	0.39
Adsorbent material	87	2974	1300	2.29	0.56
Activated carbon+Instant tea		3580	41272	0.087	-10.53
Hydrogen+Instant tea		679	19607	0.035	-27.90
Adsorbent material+Instant tea		3580	20863	0.172	-4.83
Ice tea					
Activated carbon	8.7	297	2171	0.14	-6.30
Hydrogen	0.06	7	4	1.63	0.39
Adsorbent material	8.7	297	130	2.29	0.56
Activated carbon+Ice tea		297	3709	0.080	-11.47
Hydrogen+Ice tea		7	1543	0.005	-210.52
Adsorbent material+Ice tea		297	1668	0.178	-4.61