THERMODYNAMIC ANALYSIS ON ENERGY-EXERGY REQUIREMENT AND EFFICIENCY OF SEROGROUP C ANTIGEN PRODUCTION, *"FARM TO FORK"* BREAD PRODUCTION AND SOURDOUGH LEAVENING

by
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ABSTRACT

THERMODYNAMIC ANALYSIS ON ENERGY-EXERGY REQUIREMENT AND EFFICIENCY OF SEROGROUP C ANTIGEN PRODUCTION, *"FARM TO FORK"* BREAD PRODUCTION AND SOURDOUGH LEAVENING

Efficient use of food and energy sources has gained great importance with increasing population, the increase of greenhouse gases and global warming. Hence, the yield of food and chemical processes with low energy consumption is intended to provide the energy efficient production systems.

In context of this thesis; three biochemical processes were studied by kinetic and thermodynamic models. Thermodynamic models are investigated by first and second laws of thermodynamics. In the first study; kinetic and thermodynamic models are developed to relate substrate consumption, serogroup C antigen production and growth rate of *Neisseria meningitidis*, a meningitides causing bacterium for three cases: the uncontrolled; pH controlled and dissolved oxygen controlled cultivation. The model shows that maximum antigen production, minimum energy consumption, minimum entropy generation and exergy loss are obtained under stress conditions that *N. meningitidis* are exposed to. As the second study; energy and exergy efficiencies of the wheat and rye bread and hamburger bun making processes are assessed based on data from Turkey and Germany. Energy and exergy consumption, the cumulative degree of perfection (CDP) and CExC in each step in production of these various breads were calculated. Agriculture is the most significant step in bread production affecting all following steps. Hamburger bun production requires the maximum energy utilization due to the higher weight loss in baking. The rye bread production process requires the minimum energy utilization due to the lower energy input in the agriculture and higher efficiency in the flour production. The maximum exergy destructions occur during the milling and the baking steps. In the third study; the leavening process in sourdough is investigated in presence of various ratios of *Saccharomyces cerevisiae* and *Lactobacillus plantarum* in different temperatures in order to find out the maximum carbon dioxide production, expansion work and dough volume increase with optimum energy and exergy utilization.

ÖZET

SEROGRUP C ANTİJEN ÜRETİMİ, *"ÇİFTLİKTEN ÇATALA"* EKMEK ÜRETİMİ VE EKŞİ HAMUR MAYALANMASININ ENERJİ-EKSERJİ GEREKSİNİMİ VE VERİMİNİN TERMODİNAMİK ANALİZİ

Artan popülasyon, sera gazlarının artması ve küresel ısınma ile gıda ve enerji kaynaklarının verimli kullanımı önem kazanmıştır. Bu yüzden, düşük enerji tüketimi ile gerçekleşen yüksek verimli gıda ve kimyasal proseslerin uygulanması hedeflenmektedir.

Tez kapsamında üç biyokimyasal proses, kinetik ve termodinamik modellerle çalışılmıştır. Thermodinamik modeller, Termodinamik'in birinci ve ikinci kanunlarına göre incelenmiştir. Birinci çalışmada; kinetik ve termodinamik modeller, substrat tüketimi, serogrup C antijen üretimi ve menenjit hastalığına sebep olan *Neisseria meningitidis* bakterisinin büyüme hızı arasındaki ilişkiyi üç farklı koşulda incelemek için kullanılmıştır: kontrolsüz koşullar, pH kontrollü koşul ve çözünmüş oksijen kontrollü koşul. *N. meningitidis* bakterisinin stres koşulları altında maksimum antijen üretiminin yanında minimum enerji tüketimi, minimum entropi üretimi ve minimum ekserji kaybını da sağladığı tespit edilmiştir. Ikinci çalışmada; buğday, çavdar ve hamburger ekmeği üretiminde enerji ve ekserji verimleri Türkiye ve Almanya için bulunan bilgilere göre hesaplanmıştır. Enerji ve ekserji tüketimleri, CDP ve CExC değerleri ekmek çeşitlerinin üretimindeki her aşama için hesaplanmıştır. Tarım diğer tüm aşamaları etkileyen en önemli aşamadır. Hamburger ekmeği üretimi üretimi pişirmedeki en fazla ağırlık kaybı sebebiyle maksimum enerji tüketimine sebep olmaktadır. Tarımda en düşük enerji tüketimi ve un üretiminde en fazla verim sebebiyle; çavdar ekmeği üretimi en düşük enerji tüketimine sahiptir. Maksimum ekserji yıkımı öğütme ve pişirme aşamalarında olmaktadır. Üçüncü çalışmada; ekşi hamurdaki mayalanma prosesinde maksimum karbondioksit üretimi, genişleme işi ve hamur hacmindeki artış ile optimum enerji ve ekserji tüketimini bulmak için, *Saccromyces cerevisiae* mayası ve *Lactobacillus plantarum* bakterisinin farklı oranlarının farklı sıcaklıklarda kullanılmasının etkisi kinetik ve termodinamik modellerle incelenmiştir.

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LIST OF SYMBOLS/ABBREVIATIONS

C	Consumption (mol)
CCO_2E	Cumulative carbon dioxide emission (kg/ton or kg/ha)
CDP	Cumulative degree of perfection
CEnC	Cumulative energy consumption (MJ/ton or MJ/ha)
CExC	Cumulative exergy consumption (MJ/ton or MJ/ha)
ch	Chemical
D	Dead state of microorganisms
e	Element
ex	Molar exergy (kJ/mol)
G	Gibbs free energy (kJ/mol)
Gen	Generation
H	Molar enthalpy (kJ/mol)
i	Element, atomic group or molecular group
in	Input
k	Rate Coefficient
K	Heat source index
L	Lactic acid concentration
m	Maintenance
max	Maximum
N	Molar mass flow (mol)
n	Number of the elements atomic groups in molecules
o	Standard
out	Output
p	Pressure (kPa)
P	Product formation
Q	Heat (kJ/mol)
R	Universal gas constant (J/mol K)
S	Molar entropy (kJ/mol K)
SE	Standard error (g/L)
T	Temperature (K)
t	Time

U	Universal
V	Dough volume
W	Work (kJ)
X	Biomass concentration (mol)
Y	Yield
α	Luedeking - Piret constant
B	Luedeking - Piret constant
Δ	Gibbs energy, enthalpy and entropy increment of an atomic group (kJ)
μ	Initial specific growth rate (1/h)
Φ	Constant
0	Restricted dead state

1. INTRODUCTION

Recent environmental issues such as climate change and global warming and have been caused by the human behavior and lead to the release of some greenhouse gases, especially carbon dioxide [1]. Therefore, the use of energy sources and energy efficiency are among the current topics of the world and "Sustainable Development" is stated to provide the current necessities of the world by leaving the necessary resources to of following generations. Thermodynamically, an important aspect of sustainable development is the minimization of irreversibilities caused by the use of non-renewables [2]. The improvement of efficiency is a significant step in sustainability that will promote the efficient use of nonrenewable resources and make the human focused to develop renewable materials and energy, which are currently expensive and difficult to obtain [3].

Fermentation and microbial processes have an important place in the industry. Process efficiency and economical use of biosources build up the core of the energy saving steps.

Microbial growth is a systemically progressing biochemical process that describes the increase in cell number. It involves the biosynthesis of macromolecules for cell structure and energy supply by the uptake of nutrients. Living cells have a complex cell structure including carbon, hydrogen, oxygen, nitrogen, sulphur, phosphorus, magnesium, potassium, and a number of trace elements (Mn^{2+}, Cu^{2+}, Fe^{3+}, Zn^{2+}, *etc*.) [4]. The industrial products of microbial growth by engineering yeast and bacteria have been a crucial target to maximize the production yield, titer and productivity of desired substances. Mathematical models have been used to design and optimize biological and biochemical processes for higher product yields, utilization of non-natural substrates and modifications in strains for product tolerance [5]. Modeling is a fundamental step in process development to predict the behavior of a system. A model is used to investigate the variables of a system and to correlate parameters of biological, chemical and physical properties of the processes in order to plan the experimental design; and to interpret experimental results [6].

Kinetics investigates the rate and mechanism of physical, chemical and biological processes. Microbial kinetics contains growth, death, product formation, environmental factors and biological effects. The microbial processes are analyzed by stoichiometric relationships as consistent with mass and energy conversation [7]. New computational

kinetic models have been developed for cellular metabolism [8]. Many chemical, physical, biological and food processes have been studied both kinetically and thermodynamically. Thermodynamic modeling comprises the enthalpy, entropy and exergy variations [9].

The first law of thermodynamics explains the conversation of energy. It represents that energy can neither be created nor destroyed, yet transformed into another form of energy. The first law does not differ between the different modes of energy transfer.

The second law of thermodynamics states this distinction by entropy definition, which provides an insight into the irreversibility intrinsic to a process and helps to specify the energy losses and ensures the chance to minimize energy loss. Second law phrases that each transfer of energy causes the increase in entropy of the universe. A part of the energy in most energy conversion systems is released as heat because of the irreversibilities [10].

In most energy conversion systems, a part of the energy, which is lost due to irreversibility, is later released to the environment as heat [10]. Living organisms must maintain a state of high organization [11], therefore increase of the entropy accumulation implies increasing disorder in the system [12], which is associated with aging [12-21]. When the amount of heat, which is released to the environment as a result of irreversibility, is divided to temperature; the associated entropy generation may be calculated. Hershey (1974) [22] and Hershey and Wang (1980) [23] calculated the human lifespan entropy in terms of the metabolic heat generation divided by body temperature. Their work led to the definition of the concepts like entropic-age, expected lifespan and senile death. Silva and Annamalai [18,19] related the concept of the lifespan entropy and related it with the physical activity level of the people and the composition of their diet. Demetrius et al. (2009) [20] draw attention to the point that body size is a fundamental indication of an organism, which regulates metabolism rate transforming the resource energy into biological work, therefore the metabolic rate and showed that the lifespan entropy is related with the lifespan, and the body size. Balmer (1982) [14] based on Prigogine and Wiame's (1946) [13] argument states that the "organisms have evolved over the years to minimize entropy generation". The biological systems have a limited capacity of generating entropy. When the total entropy generation of a living being reaches a certain limit, which is referred as the "lifespan entropy", it dies. In the previous studies lifespan entropy was related to the nutrient consumption [19] and heat loss [15,16,18] from the body. The increase of the cellular entropy is related with aging in the literature [17,21] and occurs due to changing

energy state of the biomolecules. The increase in cellular entropy causes the inactivation or malfunction of biomolecules. The functions of molecules are regulated by genetically induced repair and replacement processes but the balance of this regulation shifts toward inactivation and malfunctioning [17]. The incidents which result in the increase of the cellular entropy during aging is hypothesized [24], and its indications are evidenced in the literature [25, 26], but the attempts for quantifying the lifespan entropy is yet very limited [18, 19, 27].

Exergy is stated as the useful work potential and defined as depending on the second law of thermodynamics. The maximum work of a system may generate is the exergy of a system in thermal, mechanical and chemical equilibrium with its surroundings via reversible processes. In other words, exergy is the maximum energy amount that can be obtained from a system without violating the laws of thermodynamics.

The cumulative exergy consumption (CExC) is the summation of all exergy resources consumed in stages of production processes. The CExC is calculated as total consumption of exergy depending on the process flow steps such as raw materials, transportation, work, and heat transfer for production. The cumulative degree of perfection (CDP) is calculated as dividing the chemical exergy of the product by the sum of the exergies of all the raw materials and the fuel consumed during production.

In the last decade, a high number of studies are performed associated with exergetic analysis of the biological systems [28-36], particularly to assess the exergy utilization of biochemical systems and to correlate kinetic models with thermodynamic parameters to evaluate the processes by energy utilization, exergy analysis and carbon dioxide emissions [37, 12]. Karakaya and Ozilgen (2011) [38] calculated the energy utilization and carbon dioxide emissions during the production of fresh, peeled, diced, and juiced tomatoes including the energy utilization for production of raw and packaging materials, transportation, and waste management with 189.4 kg/ton carbon dioxide emission. Sorguven and Ozilgen (2012) [39] investigated the effect of food production processes on the environment by energy - exergy utilization and carbon dioxide emission, then analyzed strawberry-flavored yogurt production. The study begins with agriculture and lasts with the transportation of products to the market. Ozilgen and Sorguven (2011) [40] assessed the energy utilization and carbon dioxide emission calculations for three different vegetable oils production. The exergy utilization, energy utilization and carbon dioxide emission

calculations were performed for the all steps of the production of sunflower, olive and soybean oil. The results of this study targeted to help to evaluate exergy and energy utilization and carbon dioxide emission associated with one ton of product.

In this concept, the study is composed of three parts: i) kinetic and thermodynamic analysis of serogroup C antigen production by *Neisseria meningitidis*; ii) thermodynamic analysis of "farm to fork" wheat bread and rye bread production in Turkey and Germany; iii) kinetic and thermodynamic analysis of sourdough bread fermentation by *Saccharomyces cerevisiae* and *Lactobacillus plantarum*.

1.1. SEROGROUP C ANTIGEN PRODUCTION BY *NEISSERIA MENINGITIDIS*

Meningitis is the disease caused by the infection of meninges which is the membrane covering the brain and spinal cord. A gram negative bacterium *Neisseria meningitidis* leads to the infection [41] and it has a polysaccharide capsule [42, 43]. When *N. meningitidis* goes into the bloodstream, crosses the blood-brain barrier, and reaches the cerebrospinal fluid, causes meningitis [44]. The capsular polysaccharide antigen chains and their alternative light chain partners are the agents causing the disease [45]. *N. meningitidis* is characterized immunologically by serogrouping with respect to its capsular polysaccharides [46]. The capsules of serogroup C meningococci are composed of homopolymers of n-acetylneuraminic acid linked through alpha 2, 9 linkages [45]. The polymer of n-acetylneuraminic acid is referred to as the serogroup C polysaccharide antigen [47]. Among the thirteen serogroups of *N. meningitidis*, serogroup C is one of the most common causes of meningococcus infections [48, 43].

The mechanism of the serogroup C antigen production reaction constitutes the backbone of the thermodynamic analysis. In microbial metabolism n-acetylneuraminic acid is synthesized through a complex process in the cells: first glucose enters into the glycolysis pathway, and then converted to glucose-6-phosphate and then to fructose-6-phosphate [49]. Fructose-6-phosphate reacts with L-glutamine, whose precursor is L-glutamic acid, to form glucosamine-6-phosphate [50, 51]. Next, glucosamine-6-phosphate enters into the hexosamine pathway to form a mannose derivative n-acetyl-D-mannosamine, which goes into the sialic acid biosynthetic pathway to produce n-acetylneuraminic acid [52, 53]. It could be realized that even if glucose and glutamic acid do not contribute directly into the

reaction to produce antigen, they are converted into another isomer forms in the same mole numbers of reactants in the antigen production and consequently n-acetylneuraminic acid and water molecules are produced. In respiration, net 30 ATP is produced [54] and the antigen production reaction can be written as below due to the equal mole numbers with the reactants in the antigen production pathway in a representative way. Therefore, the reactions of *N. meningitidis* could be simplified as given in Figure 1.1 and Figure 1.2.

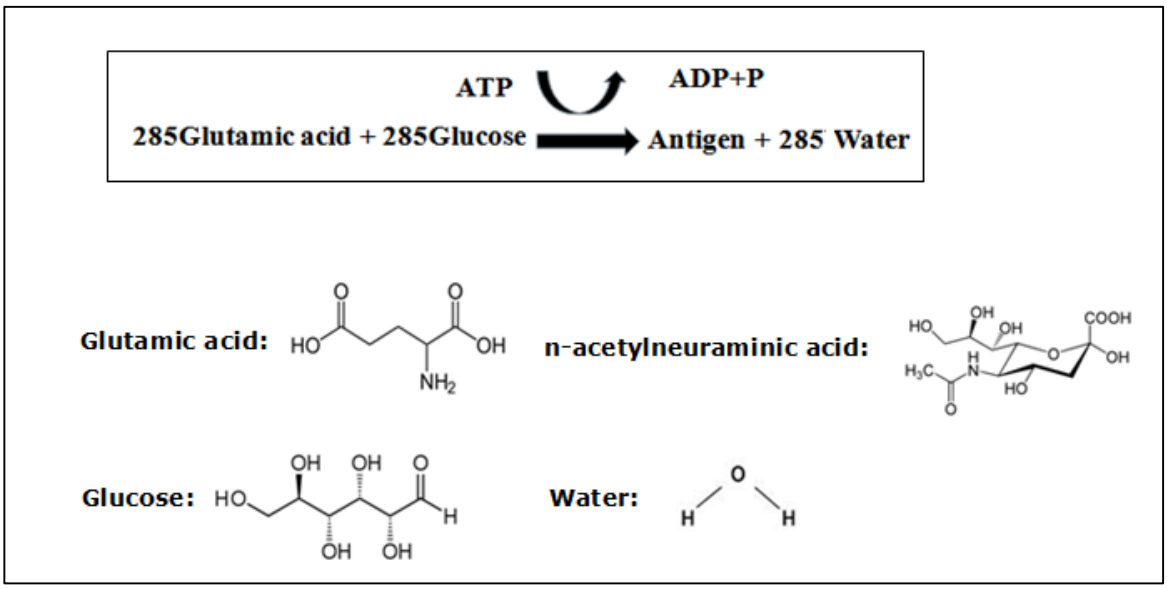

Figure 1.1. Reaction of serogroup C antigen production

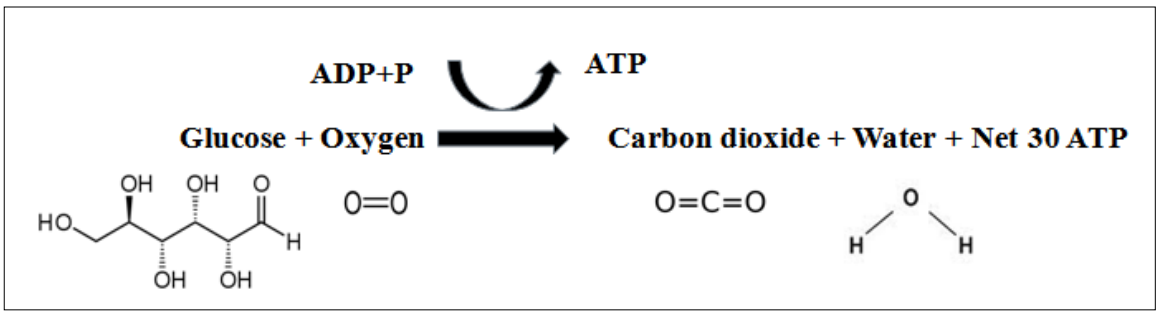

Figure 1.2. Cellular respiration

Vaccine production is important against meningitides but it is not a definite treatment. Serogroup C bacteria are important for the development of vaccines. Hence, optimum conditions to cultivate these bacteria and to produce antigen are among the studies that target the vaccine production. Fitting and Scherp (1952) [55] made a study about the

glucose and maltose consumption of *N. meningitidis*. Also, the growth of microorganisms, the rate of oxygen consumption and carbon dioxide production are affected with respect to the carbohydrate substrate due to the change in metabolic pathways [55].

Joshi et al. (2009) [56] reports that the production of polysaccharide capsules is related to growth in the bacteria population up to the twelfth hour of cultivation. After exponential phase; polysaccharide production proceeds without growth of bacteria in the stationary phase which means that there is not growth-associated production in stationary phase. Commonly, large scale cultivation of *N. meningitidis* is provided in three media: Frantz medium, Modified Frantz medium (with the replacement of glucose by glycerol), Catlin 6 medium (a synthetic medium with glucose) [56].

Henriques et al. (2006) [57] has a study that gathers lots of variations to optimize process conditions to obtain maximum polysaccharide production by using response surface methodology. In this study, Frantz medium was used and it was suggested that the glucose consumption and polysaccharide formation is observed clearly in exponential phase of microbial growth.

Baruque-Ramos et al. (2005) [58] studied a vaccine from serogroup C polysaccharide antigen from *N. meningitidis*. The study was carried out by controlling the dissolved oxygen at 10%, pH at 6.5 and without dissolved oxygen and pH controls in order to enhance the final polyssaccharide antigen concentration. Kinetic and thermodynamic modeling of this study forms the first part of this thesis.

1.2. *"FARM TO FORK"* BREAD PRODUCTION

Bread is the main food for centuries which is cooked by baking in the oven [59]. Bread is composed of flour, water, yeast and salt, as well as a variety of other ingredients.

Flour basically consists of starch and gluten, water, fat, vitamins, minerals and enzymes. Starch is a polysaccharide comprised of glucose molecules linked to each other. Gluten is a protein which possesses the abilities to deform, stretch, recover shape and trap gases is very crucial in bread and all fermented products [60]. Various methods have been used for bread making by manipulating the gluten structure of the dough [61].

Starch is degraded into the glucose molecules when attacked by α-amylase enzyme naturally found in flour structure. The yeast which the yeast feeds as shown in Equation 1.1.

$$C_6H_{12}O_6 + 6O_2 \xrightarrow{yeast} 6CO_2 + 6H_2O + energy \quad (1.1)$$

glucose + oxygen → carbon dioxide + water

The energy release provides the yeast to grow, and the carbon dioxide causes the dough expansion. The kneading of the dough ensures the evenly distributed of equal size of bubble production throughout the dough. In the presence of insufficient oxygen, the yeast catalyzes the following reaction and leads to ethanol evaporation in Equation 1.2:

$$C_6H_{12}O_6 \xrightarrow{yeast} 2C_2H_5OH + 6CO_2 \quad (1.2)$$

glucose → ethanol (alcohol) + carbon dioxide

Whole wheat bread, rye-bread, bran bread, toast bread, oat bread, whole grain bread and wheat germ bread are mostly consumed bread types in Turkey [62]. Bread is a significant part of German cuisine and most popular breads of Germany are rye-wheat, toast bread, whole-grain, wheat-rye, white bread, multigrain, usually wheat-rye-oats with sesame or linseed, rye, sunflower seeds in dark rye bread, pumpkin seeds in dark rye bread and roasted onions in light wheat-rye bread [63].

The breadmaking processes are comprised of mainly six steps: agriculture of grains, flour production, dough preparation and baking, cooling, packaging and the transportation of breads to the market.

In the food and most other industries, studies on the energy accounting and efficiency began in the late 1970s, and the pioneering outcomes became available in the early 1980s [64]. Modern chemical fertilizer factories reduced the energy consumption and succeeded to approach to the theoretical minimum at the end of the 1990s [65, 66], in 2006 Ramirez et *al* [67] reported that the energy efficiency improved approximately 1 percent every year in the Dutch food industry, from 2006 to 2010.

The energy utilization for Taiwanese food industry with respect to gross domestic production exhibited a continuous decrease [68]. Energy utilization for the food production usually consists a sizeable fraction of the total energy utilization in a country, e.g., towards the end of the first decade of the 21st century 20 % of the total energy use was allocated to the food sector in Sweden [69]. The electricity consumption is high due to cold stages including freezing, cooling and refrigeration; natural gas is consumed for mostly drying and cooking and 5-15% of energy utilization is wasted [70]. Because of the very high cost of the energy utilization, e.g., American bakery industry pays more than $ 870 million annually for the energy [71], there is rigorous research in the food industry to find ways to reduce the energy utilization [72, 73].

1.3. SOURDOUGH LEAVENING BY *SACCHAROMYCES CEREVISIAE AND LACTOBACILLUS PLANTARUM*

Sourdough is made of a mixture of flour and water that is fermented using yeast and lactic acid bacteria which are aerotolerant and especially important for rye bread production. In addition to flour and water, some extra ingredients may be added such as sugar or enzymes to boost the microflora. In recent studies sourdough is referred to as a “complex ecosystem in which lactic acid bacteria and yeast interact together and with the ingredients depending on the process parameters [74-77].

Pepe et al (2004) [78] isolated thirty *Lactobacillus* (L.) *plantarum* strains from natural sourdoughs and they provided identification by 16S rDNA sequencing and biochemical tests. They classified them based on technological properties, such as amylase, protease, phytase and antirobe activities. The microflora of sourdough consists of stable associations of lactobacilli and yeasts, in particular due to metabolic interactions [79]. *Lactobacillus sanfransicensis, Lactobacillus reuteri, Lactobacillus rossiae, Lactobacillus delbrueckii ssp., Lactobacillus casei, Lactobacillus plantarum, Lactobacillus brevis, Lactobacillus alimentarius, Lactobacillus fermentum* are mostly isolated bacteria from Italian sourdoughs and *Saccharomyces cerevisiae, Saccharomyces exiguus and Candida holmii are* mostly found in sourdough [80]. *Kazachstania exigua* (maltose-negative, acid-tolerant) and *Lb. sanfranciscensis* (maltose-positive), *Candida humilis* (maltose-negative, acid-tolerant) and *Lb. sanfranciscensis*, *Kazachstania barnettii* (maltose-negative) and *Lb. sanfranciscensis*,

S. cerevisiae (maltose-positive) and *Lb. plantarum* (prefers glucose and fructose), and unique combination of *S. cerevisiae, Candida milleri* and *Lb. sanfranciscensis* are examples of stable yeast-lactic acid bacteria associations [75]. Pulvirenti et al (2004) [81] reported that the dominant species in home-made sourdoughs can differ from each other. The method of sourdough rebuilding exerts a strong selective pressure on the yeasts present, thereby determining the dominance of one species over others. This selection process is analogous to the competition that occurs in an ecosystem. In addition to *S. cerevisiae, C. humilis, C. milleri, Issatchenkia orientalis* and *S. exiguus* are among the competing yeast species in sourdough ecosystem [81]. The composition and function of sourdough microorganisms eventually determine the bread quality [76].

Sourdough does not have a homogeneous medium. There are a lot of microenvironments in the same batch of sourdough. Chemical and physical properties of each microenvironment may be substantially different than the others. In a typical sourdough bread making process, dough is fermented in two stages. After the initial yeast addition, kneading and proofing, e.g., microbial growth, the dough it is kneaded for the second time, e.g., the microorganisms are dispersed once more to obtain a more uniform microbial growth [82]. This two-stage may help to obtain a uniform structure, from the bread making point of view, but the final population of the ecological system would be different.

Wheat doughs fermented by *Lactobacillus* types undergo microstructural variations due to both fermentation and mechanical properties.

Assessment of the microstructural changes that occur in wheat doughs during fermentation due to the *Lactobacillus* type. Colin-Orozco (2014) [83] added an inoculum to wheat doughs and made observations by Scanning Electron Microscope to determine the fractal dimension (FD_{SDBC}) and entropy. They have found that *Lactobacillus plantarum* and *Lactobacillus sanfranciscensis* reduced extensibility by 40 and 42%, respectively, while dough yield decreased by more than 85%. The results enable the chance to select the necessary bacteria type for the sough preparation and to understand the changes formed in the dough structurally and mechanically in fermentation process [83].

2. METHODOLOGY

Kinetic models were developed to obtain continuous mathematical relations between microbial biomass, other substracts and products. The evaluation of the thermodynamic properties of the cells and substances are based on their chemical structures, and then these properties are combined with enthalpy, entropy and exergy balances for thermodynamic analyses.

2.1. SEROGROUP C ANTIGEN PRODUCTION BY *NEISSERIA MENINGITIDIS*

The serogroup C antigen production of *N. meningitidis* is assessed thermodynamically to investigate the maximum antigen production and energy efficiency simultaneously. A kinetic model is developed to obtain continuous mathematical relations between cell, antigen and substrate concentrations at any moment of the process. The evaluation of the thermodynamic properties of the cell, antigen, and the substrate is based on their chemical structures, and then these properties are combined with the entropy and the exergy balances to assess the exergetic efficiency of microbial growth and antigen production processes.

2.1.1. Experimental Data

Experimental data published by Baruque-Ramos et al., (2005) [58] for serogroup C antigen production by *N. meningitidis* in the Franz medium under three different conditions: i) while controlling the dissolved oxygen concentration at 10%, ii) by maintaining pH at 6.5, and iii) without dissolved oxygen and pH controls.

2.1.2. Assumptions For Thermodynamical Modeling

The assumptions for the thermodynamical modeling of the antigen production by *N. meningitidis* are as below:

- The serogroup C antigen production was in the Frantz medium with limited glucose content in a closed system. The data employed here did not include any glucose addition during the course of microbial growth. Glutamic acid was in the medium since it is needed for the antigen synthesis.
- The temperature for the growth was 35ºC as a stress condition to increase the antigen production; pH was about 6.5.
- Aerobic conditions prevailed during the experimental study. The respiration and the antigen production were the main reactions.

2.1.3. System Boundary

Baruque-Ramos et. al [58] used a 13 liter reactor for the cultivation of *N. meningitidis*. The system boundary to be examined was chosen as 1 liter of the reactor in the study. Contribution of the impeller work and initial microbial concentration on the energy, entropy and exergy balances were neglected due to their small magnitude.

2.1.4. Kinetic Modeling

Kinetic models were developed to obtain continuous mathematical functions to relate the substrate (glucose) consumption and the product formation with the microbial population, and with time. The growth rate of *N. meningitidis* is simulated with the logistic equation:

$$\frac{dx}{dt} = \mu x\left(1 - \frac{x}{x_{max}}\right) \tag{2.1}$$

The logistic growth model assumes that the growth of the systems propagates until an upper limit, x_{max}, is attained; meanwhile, the growth rate decreases gradually, producing the characteristic S-shape curve [84]. The polysaccharide production is reported to be growth associated [56]; but its continuation in the stationary phase, when there is no bacterial growth, suggests an additional non-growth-associated production [85], therefore, the rate of antigen production is simulated with the Luedeking-Piret model:

$$\frac{dP}{dt} = \alpha x + \beta \frac{dx}{dt} \tag{2.2}$$

where the first term αx implies that the product is formed in proportion with the size of the microbial population, and the next term, $\beta(dx/dt)$, represents the additional product formation rate in proportion with the growth rate. The dimensionless constants α and β were obtained to minimize the sum of the square difference between the data and the model. The substrate consumption was considered as the sum of substrate consumption for growth, product formation and maintenance:

$$-\frac{dS}{dt} = \left(\frac{1}{Y}\frac{dx}{dt}\right) + \left(\frac{1}{Y_p}\frac{dP}{dt}\right) + k_m x \tag{2.3}$$

where Y is the growth yield (biomass/substrate consumed), Y_p is the product formation yield (product formed/substrate consumed) and k_m is the maintenance coefficient [84].

2.1.5. Thermodynamic Analysis

The following equations represent the first and second law of thermodynamics for the control volume.

Mass balance:

$$\left(\sum N\right)_{in} - \left(\sum N\right)_{out} = 0 \tag{2.4}$$

Energy balance:

$$\left(\sum NH\right)_{out} - \left(\sum NH\right)_{in} = Q - W \tag{2.5}$$

Entropy and exergy are not conserved quantities like mass and energy. Hence, internal and external irreversibilities cause entropy generation and exergy destruction.

Entropy balance:

$$\left(\sum Ns\right)_{out} - \left(\sum Ns\right)_{in} - \sum \frac{Q}{T} = \Delta S_{gen} \tag{2.6}$$

Exergy balance:

$$\left(\sum Nex\right)_{in} - \left(\sum Nex\right)_{in} + \sum Q\left(1 - \frac{T_O}{T}\right) - W = X_{destroyed} \tag{2.7}$$

The work introduced by the impeller for stirring the medium was small when divided into the volume of the fermentation medium stirred, therefore W=0 is substituted in Equations (2.5) and (2.7). The enthalpy of formation at 298 K, specific heat capacity, specific molar entropy and the standard chemical exergy data are tabulated in Table 2.1. The enthalpy of formation data at 298 K is used with the specific heat capacities of the reactants and the products (Table 2.1) to calculate the enthalpy of formations at 308 K.

Table 2.1. Molecular weight and thermodynamical data of the compounds

Chemical compound	**MW (g/mol)**	**ΔH_{f298K}^{0} (kJ/mol)**	**C_p (kJ/mol K)**	**ΔH_{f308K}^{o} (kJ/mol)**	**S^o (kJ/mol K)**	**X^o (kJ/mol)**
Glucose	180 [86]	-1274.5 [89]	0.226 [86]	-1272.2	0.209 [86]	2955 [96]
Oxygen	32 [86]	0 [90]	2.94×10^{-2} [94]	0.294	0.205 [94]	3.97 [94]
Glutamic acid	147.13 [86]	-1003.3 [86]	0.175 [86]	-1001.6	0.188 [86]	2393.2 [97]
Water	18 [86]	-285.8 [91]	7.53×10^{-2} [94]	-285.0	9.1×10^{-3} [95]	0.9 [97]
Carbon dioxide	44 [86]	-394.0 [91]	3.71×10^{-2} [94]	-393.6	0.215 [94]	19.48 [94]
Antigen	8.8×10^{4} [87]	-4.7×10^{5} [92]	115 [95]	-4.7×10^{5}	242 [95]	1.6×10^{6} [98]
Biomass	95 [88]	-512.6 [93]	0.135 [95]	-511.3	0.138 [93]	2037.1 [98]

The exergetic efficiency for antigen is investigated by the rate of the standard chemical exergy of antigen and the sum of standard chemical exergy of reactants. The exergetic efficiency of the antigen production is calculated from:

$$Exergetic\ efficiency\ of\ antigen\ production = \frac{ex}{\sum ex^{o}_{reactants}} \times 100 \quad (2.8)$$

The exergetic efficiency of the microbial growth is calculated as:

$$Exergetic\ efficiency\ of\ microbial\ growth = \frac{ex^{o}_{biomass}}{\sum ex^{o}_{reactants}} \times 100 \quad (2.9)$$

The rate of heat release per unit mass for antigen production to total heat release per unit mass is:

$$\frac{Q_{antigen}}{Q_{total}} \times 100 \quad (2.10)$$

2.1.6. Estimation of Thermodynamic Properties of N-Acetylneuraminic Acid and Biomass

Group contribution method is employed to estimate heat of formation and Gibbs free energy of n-acetylneuraminic acid and its polymer serogroup C polysaccharide antigen [92]. Molecular weight and thermodynamical data of the compounds are given in Table 2.1. First-order groups of n-acetylneuraminic acid and their contributions are listed in Table 2.2.

The specific heat capacity of n-acetylneuraminic acid at 308 K is estimated with Hurst and Herrison's modification of Kopp's rule [95]:

$$C_{pS} = \sum_{i=1}^{n} N_i \Delta_{Ei} \quad (2.11)$$

where C_{pS} is the specific heat capacity of the solid compound at 298 K (J/mol K), n is the number of the elements contributing to the formation of the compound, N_i is the number of the atoms of each element contributing to the compound, and Δ_{Ei} is the elemental specific

heat. Constants employed to estimate the specific heat capacity, specific molar entropy and standard chemical exergy of n-acetylneuraminic and the biomass are given in Table 2.3.

Table 2.2. First-order groups of n-acetylneuraminic acid and their contributions

Group	**Occurrence**	G^o **(kJ/mol)**	H^o **(kJ/mol)**
CH_3CO	1	-120.667	-180.604
COOH	1	-337.090	-389.931
OH	5	-144.051	-178.360
–O–	1	-114.062	-137.353
NH (cyclic)	1	72.540	23.138
-CH (cyclic)	3	6.107	-12.464
$-CH_2$ (cyclic)	1	13.287	-18.575
C (cyclic)	2	-0.193	-2.098
		$\sum G^o$= -1188.1 kJ/mol	$\sum H^o$= -1634.6 kJ/mol

Table 2.3. Specific heat capacity, absolute entropy and standard chemical exergy estimations

Molecule	$S^r_{element\ i}$ **[95]**	$n_{m,NA}$	$n_{m,biomass}$	X_{chne} **(kJ/mol) [98]**	**atom**	ΔE_i **(J/atom K) [95]**
C	5.74	11	3.85	410.25	C	10.89
H_2	130.57	9.5	6.69/2	236.10	H	7.56
O_2	205.04	4.5	1.78/2	3.97	O	13.42
N_2	191.50	0.5	0.5	0.72	N	18.74

n_e = number of atoms in the unit carbon formula, for hydrogen, oxygen and nitrogen, $n_m=n_e/2$

Enthalpy of formation of the antigen at 308 K is calculated from:

$$H_{308\,K}=H^o+C_p\Delta T \tag{2.12}$$

Then, the standard molar entropy of formation may be estimated from [95]:

$$\Delta G^{\circ}_{fT}=\Delta H^{\circ}_{fT}-T\Delta S^{\circ}_{fT} \tag{2.13}$$

where $\Delta G_{fT}°$ is Gibbs energy formation at T (kJ/mol), $\Delta H_{fT}°$ is the enthalpy of formation at T (kJ/mol) and $\Delta S_{fT}°$ is the standard molar entropy of formation at T (kJ/mol K). The absolute entropy of n-acetylneuraminic acid may be calculated from:

$$\Delta S^{\circ}_{f298}=S^{\circ}_{compound}-\sum_{i=1}^{n} N_i S^{r}_{element\ i} \tag{2.14}$$

where $\Delta S_{f298}°$ is the standard molar entropy of formation at 298 K and 1 atm (J/mol K), $S°_{compound}$ is the ideal gas absolute entropy of the compound at 298 and 1 atm (J/mol K) and n is the number of different elements contained in the compound, N_i is the moles of element i contained in one mole of compound and $S^{r}_{\text{element } i}$ is the absolute entropy of element i in its standard state at 298 K and 1 atm (J/mol K). The values of $S^{r}_{element\ i}$ are listed in Table 2.3. The standard chemical exergy of the n-acetylneuraminic acid is calculated from the exergy of a reversible formation reaction by following the same procedure as Szargut et al., (2005) [99]:

$$ex_{ch} = \Delta G_f + \sum_{e} n_e\, ex_{ch,e} \tag{2.15}$$

where X_{ch} is the standard chemical exergy of the compound, ΔG_f is the Gibbs energy of formation, n_e is the number of moles of the element e and $X_{ch,e}$ standard chemical exergy of the element.

The standard molar entropy of formation and standard molar entropy of biomass are calculated with the same procedure as Battley (1999) [93]:

$$\Delta S^{\circ}_{f}=-0.813\sum S^{\circ}_{atoms} \tag{2.16}$$

$$S^{\circ}_{biomass}=0.187\sum S^{\circ}_{atoms} \tag{2.17}$$

The bacterial composition was described by Rittman and McCarty (2001) [88] as $C_{3.85}H_{6.69}O_{1.78}N$.

2.2. *"FARM TO FORK"* BREAD PRODUCTION

Energy utilization is accompanied by the emission of the greenhouse gases [100, 101, 40]. Therefore, any improvement in the energy and exergy efficiency pertinent to their production will not only reduce the energy budget only, but also decrease the environmental cost.

The first law of thermodynamics, namely energy balance, is used mostly while assessing the energy efficiency of a plant or process. However, energy balances do not provide information about the potential work lost in the energy transformation processes [102]. Exergy analysis may be used to pinpoint the irreversibilities in a process and reduce them to improve efficiency. At the dead state mechanical, thermal and chemical equilibria prevail between the system and the environment. The widespread of the use of the exergy method has led to attempts towards cutting down on energy cost, conservation of the limited energy resources and reduction of the environmental damage. These methodologies have been applied to many industrial systems such as sugarcane bagasse gasification [103], malt drink [104], and vegetable oil [40], flavored yogurt [39] production.

The CDP values increase if the non-renewable resources are replaced with the renewable resources in a process. The CDP of bottled vegetable oil production was recently reported to be 0.92 for soybean and 0.98 olive oils, whereas the CDP of the sunflower oil is 2.36. The decrease in diesel consumption, good agricultural applications and supply of biodiesel from the renewable resources would reduce the cumulative exergy and fossil consumption, resulting in the CDP of the olive and the soybean oils rise to 1.6 and that of sunflower oil to 2.9 [40]. Sorgüven and Özilgen [39] reported 0.036 cumulative degree of perfection for the strawberry-flavored yogurt, which rises up to 0.046 if renewable energy resources like hydropower and algal biodiesel are employed instead of fossil fuels. The low value of the CDP observed in the flavored yogurt production process may be attributed to the lesser

amount of the renewable energy employment in its production, when compared those of the oils.

2.2.1. System Boundaries

Processes occurring within the system boundaries include agriculture of wheat and rye, flour production (cleaning and milling), dough preparation, dividing, fermentation, baking, cooling, slicing, packaging and the transportation of breads to the market. Accordingly, thermodynamic analysis for the wheat and rye bread and hamburger bun making processes in Turkey and Germany were performed in detail by performing the energy and exergy balances and carbon dioxide emission, starting with the cultivation of the ingredients in the farm, and ending with the transfer of the final product to the market. The overall bread production system with its boundary, inputs and outputs is presented in Figure 2.1.

Nonrenewable chemicals are consumed for fertilizers and pesticides and the environmental costs for these raw materials are paid attention. Electricity provided for all processes is generated from fossil fuel. The energy or exergy consumed due to human labor is not accounted for, because it is not possible to collect representative data. Transportation of the goods is taken into account: the product delivery trucks are considered to be making one-way trip only. Heavy-duty trucks have the capacity of 10 tons and traveling with the velocity of 90 km/h. The total distance for transportation was assumed to be 550 km. Information related to the energy utilization and the processing rates of the equipments are taken from the manufacturer websites. Data about the agriculture of wheat and rye are taken from the literature to study energy and exergy utilization and carbon dioxide emission. Lal [105] stated that the carbon dioxide emission of the diesel oil is 0.94 kg CO_2/kg of diesel oil. Inputs and outputs of the wheat and rye agriculture in Turkey and Germany are compiled from the literature as given in Table 2.4 and their mass balances are given in Figures 2.2-2.5.

Equipment used for bread making and energy utilization in each stage of the wheat bread, rye bread and hamburger bun making processes are given in Table 2.5.

Table 2.4. Inputs and outputs of the wheat and rye agriculture in Turkey and Germany

	Agriculture of wheat in Turkey	Agriculture of wheat in Germany	Agriculture of rye in Turkey	Agriculture of wheat in Germany
Inputs				
Diesel oil (L/ha)	165.6 [106]	165.6 [106]	124.3 [111]	124.3 [111]
Nitrogen fertilizer (kg/ha)	101.88 107]	145 [108]	40 [109]	98 [110]
Phosphorus fertilizer (kg/ha)	72.2 [107]	37 [108]	50 [109]	24 [110]
Potassium fertilizer (kg/ha)	-	41 [108]	-	44 [110]
Herbicide (kg/ha)	1.12 [112]	1.12 [112]	1.12 [112]	1.12 [112]
Insecticide (kg/ha)	0.56 [113]	0.56 [113]	0.56 [113]	0.56 [113]
Fungicide (kg/ha)	1.69 [114]	1.69 [114]	1.69 [114]	1.69 [114]
Seed (kg/ha)	227.7 [107]	227.7 [107]	200 [107]	200 [107]
Irrigation water (kg/ha)	1195 [115]	6350 [115]	1982 [115]	4731 [115]
Transportation (L diesel /km)	0.287 [116]	0.287 [116]	0.287 [116]	0.287 [117]
Outputs				
Grain (kg/ha)	2388.5 [107]	7980 [118]	2590 [119]	5960 [118]
Straw (kg/ha)	223.6 [107]	3990 [118]	1295 [119]	2980 [118]

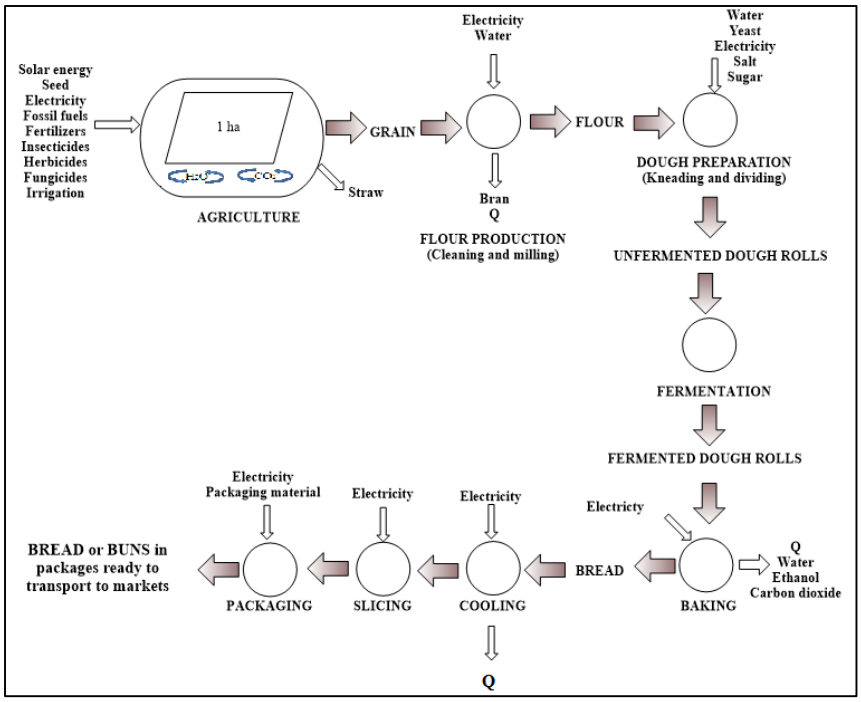

Figure 2.1. The overall bread production system with its boundary, inputs and outputs

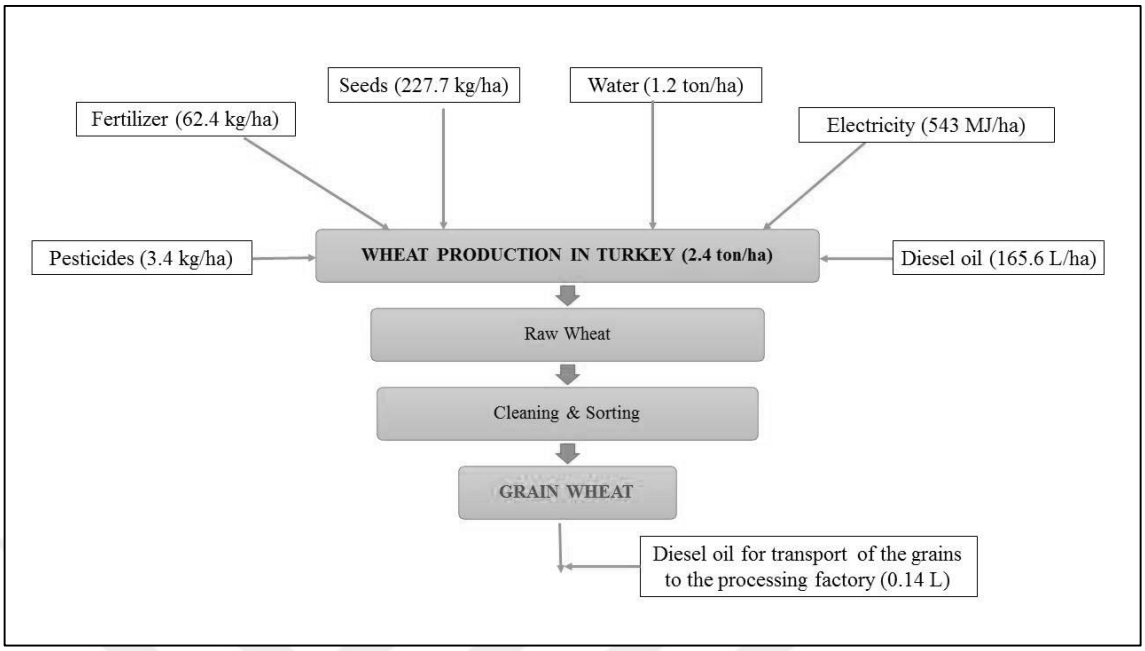

Figure 2.2. Mass balance of the wheat agriculture in Turkey

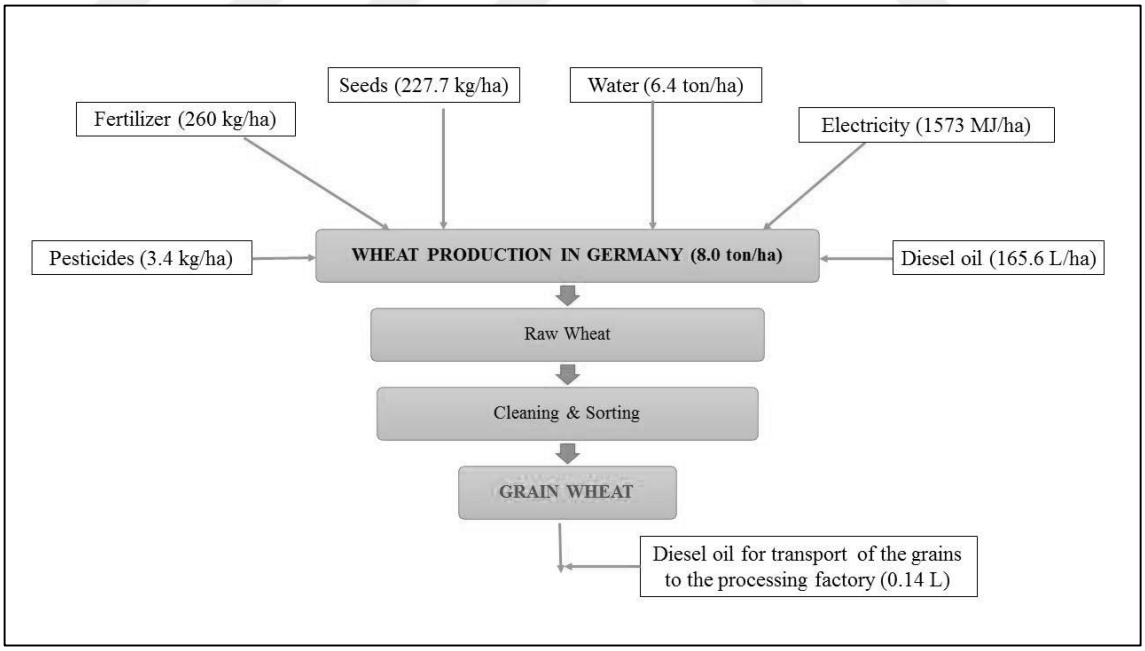

Figure 2.3. Mass balance of the wheat agriculture in Germany

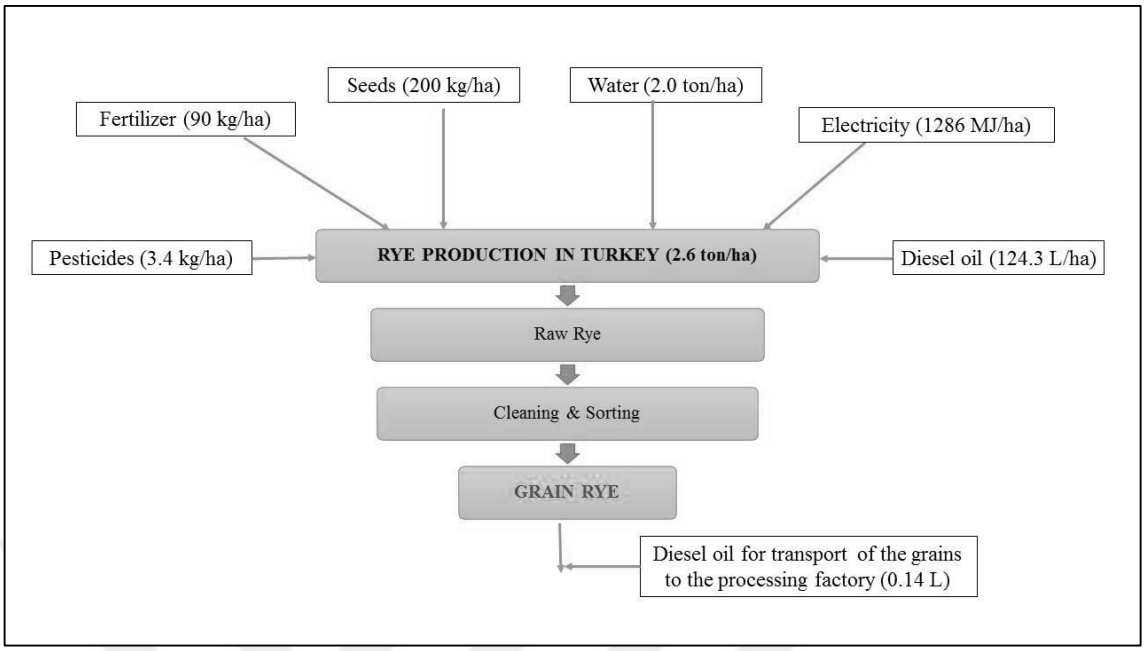

Figure 2.4. Mass balance of the rye agriculture in Turkey

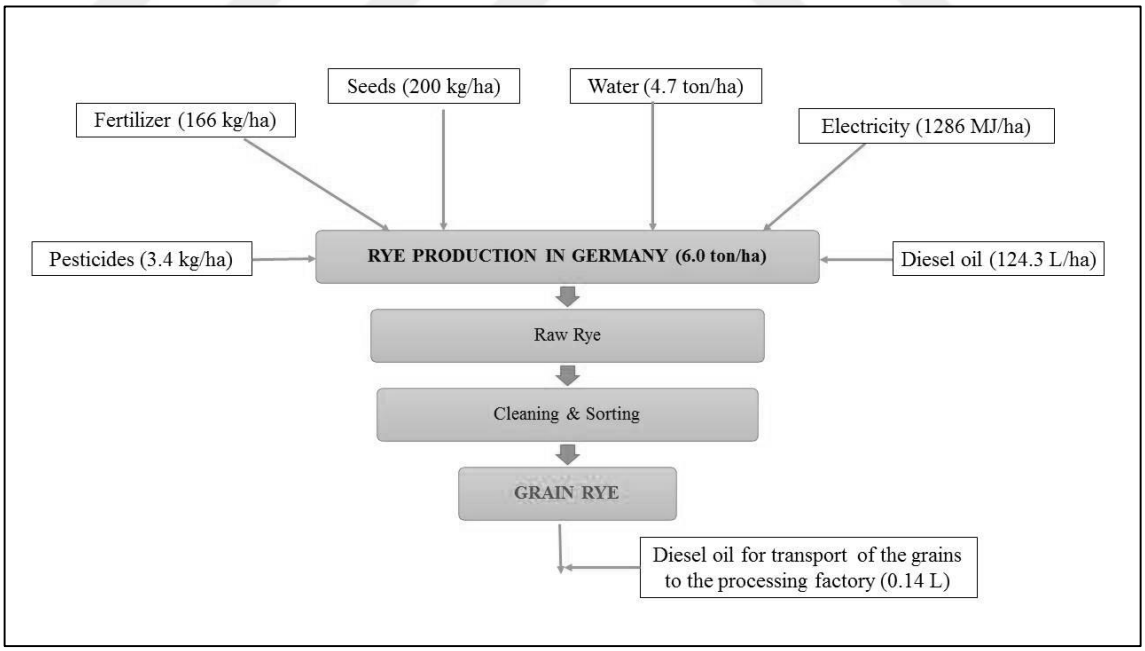

Figure 2.5. Mass balance of the rye agriculture in Germany

Table 2.5. Energy utilization in each stage of the wheat bread, rye bread and hamburger bun making processes

Stage of processing	Energy utilization
Cleaning of the grains (0.6 kWh) [120]	2.2 MJ/ton grain
Flour milling plant with Africa, 60 t/24h, 263 kW, 79.4% wheat flour extraction 89.5% rye flour extraction	379 MJ/ton grain
Dough preparation with Meiying (China), model HWY75, dough kneading machine capacity 450 kg/h, power 2.20 kWs for the wheat flour 0.73 kW for the rye flour	Wheat bread: 17.6 MJ/ton dough Rye bread: 5.9 MJ/ton dough Bun: 17.6 MJ/ton dough
Dough dividing with Haidier (China), model HDR-2000, power 1.5 kW, dividing rate 7s/piece, each piece weighs 50-850 g	Wheat bread: 21.0 MJ/ton dough Rye bread: 21.0 MJ/ton dough Bun: 97.2 MJ/ton dough
Fermentation in Berg (China), model XF-16FC, bread proofer equipped with 16 trays in 620 mm x 970 mm x 2100 mm dimensions, power 0.85 kW	Wheat bread 9.2 MJ/ton dough Rye bread: 9.2 MJ/ton dough Bun: 49.0 MJ/ton dough
Baking in Zhengzhou Ditai (China), model 239-YXDF60 oven, capacity 60 kg/h, power 10.8 kW	648 MJ/ton bread
Cooling in Hebei Aocno (China), model ACN-C 1000 bread cooler, operating at cooling capacity of 500 kg/20 min, power 15 kW	36 MJ/ton bread
Slicing with Atlas slicer (Taiwan), slicing capacity 1800 loaves/h, slicing thickness 12 mm, power 2.4 kW	Wheat bread: 9.6 MJ/ton bread Rye bread: 9.6 MJ/ton bread Bun: 3.0 MJ/ton bread
Packaging with Dachuan, model DF-450W packaging capacity 1 bag/s, power 3.6 kW)	Wheat bread: 7.2 MJ/ton bread Rye bread: 7.2 MJ/ton bread Bun: 4.2 MJ/ton bread

Mass and energy inputs and mass outputs of each processing stage during the production of one ton of wheat and rye bread and hamburger bun are given in Tables 2.6 – 2.8. Bread is considered to be marketed in packages made of biodegradable [121] polylactic acid (4 g each).

Table 2.6. Mass and energy inputs and mass outputs of each processing stage during production of one ton wheat bread

	INPUT		**OUTPUT**	
Flour Production	Grain (kg)	834	Flour (kg)	668
	Water (kg)	7.0	Bran (kg)	173
	Electricity for cleaning (kWh)	0.6		
	Electricity for milling (kWh)	263		
Dough preparation	Flour (kg)	668	Dough (kg)	1130
	Water (kg)	434		
	Yeast (kg)	14		
	Salt (kg)	14		
	Sugar (kg)	-		
	Margarine (kg)	-		
	Electricity for kneading (kWh)	2.20		
	Electricity for dividing	1.50		
Fermentation	Unfermented dough (kg)	1130	Fermented dough (kg)	1130
	Electricity (kWh)	0.85		
Baking	Dough (kg)	1130	Bread (kg)	1000
	Electricity (kWh)	10.8	Ethanol (kg)	0.95
Cooling	Electricity (kWh)	15	CO_2 (kg)	0.91
Slicing	Electricity	2.4	Water (kg)	128.14
Packaging	Polylactic acid (kg)	8	Bread in packages	1000+16
	Electricity (kW)	3.6		

Table 2.7. Mass and energy inputs and mass outputs of each processing stage during production of one ton rye bread

	INPUT		**OUTPUT**	
Flour Production	Grain (kg)	772	Flour (kg)	697 kg
	Water (kg)	7.0	Bran (kg)	82 kg
	Electricity for cleaning (kWh)	0.6		
	Electricity for milling (kWh)	263		
Dough preparation	Flour (kg)	697	Dough (kg)	1130
	Water (kg)	418		
	Yeast (kg)	5		
	Salt (kg)	10		
	Sugar (kg)	-		
	Margarine (kg)	-		
	Electricity for kneading (kWh)	0.73		
	Electricity for dividing	1.50		
Fermentation	Unfermented dough (kg)	1130	Fermented dough (kg)	1130
	Electricity (kWh)	0.85		
Baking	Dough (kg)	1130	Bread (kg)	1000
	Electricity (kWh)	10.8	Ethanol (kg)	0.95
Cooling	Electricity (kWh)	15	CO_2 (kg)	0.91
Slicing	Electricity	2.4	Water (kg)	128.14
Packaging	Polylactic acid (kg)	8	Bread in packages	1000+8
	Electricity (kW)	3.6		

Table 2.8. Mass and energy inputs and mass outputs of each processing stage during production of one ton hamburger bun

	INPUT		**OUTPUT**	
Flour Production	Grain (kg)	935	Flour (kg)	749
	Water (kg)	8.0	Bran (kg)	194
	Electricity for cleaning (kWh)	0.6		
	Electricity for milling (kWh)	263		
Dough preparation	Flour (kg)	749	Dough (kg)	1400
	Water (kg)	487		
	Yeast (kg)	29		
	Salt (kg)	10		
	Sugar (kg)	88		
	Margarine (kg)	36		
	Electricity for kneading (kWh)	2.20		
	Electricity for dividing	1.50		
Fermentation	Unfermented dough (kg)	1400	Fermented dough (kg)	1400
	Electricity (kWh)	0.85		
Baking	Dough (kg)	1400	Bread (kg)	1000
	Electricity (kWh)	10.8	Ethanol (kg)	0.95
Cooling	Electricity (kWh)	15	CO_2 (kg)	0.91
Slicing	Electricity	2.4	Water (kg)	398.14
Packaging	Polylactic acid (kg)	5	Bread in packages	1000+5
	Electricity (kW)	3.6		

2.2.2. Modeling of Agriculture and Bun Making Processes

The first stage of the food production is the cultivation of the plants. The plants convert the energy from the Sun into chemical energy with photosynthesis, and then the chemical energy is used to fuel the biological activities of the plants, including the growth. Only the light, which is in the wavelength range of 400 to 700 nm (which constitutes about 45 % of the total solar energy), may be used in photosynthesis. About 25 % of the referred 45 % may be absorbed by the plants; the rest is lost by various reasons including reflection. Receiving non-optimal levels of radiation reduces the efficiency of photosynthesis further; therefore, only 3 to 6 % of total solar radiation may be used in photosynthesis [122, 123]. Ways to increase the photosynthetic efficiency of the plants is being actively researched to improve their yields, including those of the grain crops [124].

The pollutants such as sulphur dioxide and herbicides (weed killers) inhibit the photosynthesis [125,126]. The rate of photosynthesis is affected by the temperature, the optimum is reported as 25°C for the winter wheat [127].

Soils deficient in nitrate, magnesium or iron give rise to chlorophyll deficient plants and reduce the rate of photosynthesis [128]. The cropping intensity increases with the balanced use of water, fertilizers, pesticides [129]. The moisture content of the grain wheat is 13.5-15.0 % [115].

Plants may not uptake all of the water and the chemical fertilizers available in the soil [130, 131]. The nitrogen use efficiency decreases with denitrification and the subsequent loss of the gaseous nitrogen from the soil [132]. Fertilizer management practices may reduce energy utilization up to 72 %; consequently, herbicide utilization and pollution also decrease [127, 133-135]. The use of the appropriate fertilizers in the agriculture systems is also reported to increase the water uptake [130].

In Turkey annually, 101.88 kg/ha of nitrogenous and 72.2 kg/ha of phosphorus chemical fertilizers are used and the crop yield is 2.39 ton/ha [106, 107]. In Germany both the chemical fertilizer use e.g., 145 kg/ha of nitrogenous, 37 kg/ha phosphorus and 41 kg/ha potassium [108] and the crop yield are higher, e.g., 7.98 ton/ha [118]. In Turkey 200 kg/ha of seeds [136], 40 kg/ha nitrogen fertilizer and 50 kg/ha phosphorus fertilizer [109] are used in the agriculture and 2.6 ton/ha [109] of rye grain is produced. In Germany the same

amount of seeds are used, 98 kg/ha nitrogen fertilizer and 24 kg/ha phosphorus fertilizer and 44 kg/ha potassium fertilizer [110] are utilized to produce 5.7 ton/ha of rye grain [118].

Agriculture is modeled as a continuous process where the non-renewable inputs are chemical fertilizers, water, seed and carbon dioxide, and the outputs are grain and straw [107, 106, 137].

For both wheat and rye agriculture, the same agro-chemicals, i.e., herbicide dicamba, insecticide methomyl and the fungicide thiram [131, 132, 112] and the same amount of seeds, 227.7 kg/ha, are assumed to be used [107] both in Turkey and Germany.

It was assumed that all the transportation was carried out with 10 ton capacity heavy-duty trucks traveling at a velocity of 90 km/h and consuming 0.287 L diesel oil/km [116]. Additionally, 165.6 liter diesel/ha [106] is consumed in wheat agriculture and 124.3 liter diesel/ha is consumed in rye agriculture [111]. The density of diesel oil is about 0.771 kg/L [138] its energy equivalent is 45.7 MJ/L [106] and it has the chemical exergy of 44.4 MJ/kg [139].

All thermodynamic data was given in Tables 2.9-2.10. Some of the thermodynamic properties were not readily available in the literature, and estimated with the group contribution method based on the molecular structures (Table 2.3 and Table 2.11). In accordance with this method, the molecular structure of a compound is decomposed into a set of smaller molecular substructures [140] and then the sum of the thermodynamic properties of these substructures are added up to estimate that of the structure.

The rye grain to straw ratio was 2/1 [141]. Table 2.12 shows all the inputs and outputs of energy and exergy in wheat and rye agriculture.

2.2.3. Estimation of Thermodynamic Properties

The temperature of dough during fermentation and the temperature of baking were assumed to be 35ºC and 95ºC, respectively [61]. Most of the thermodynamic data were collected from the literature as given in Tables 2.9 and 2.10.

The ideal gas standard enthalpy of formation (ΔH^o) of a chemical compound is calculated according to Joback's group contribution method scheme as [95]:

$$\Delta H^o = 68.29\ kJ/mol + \sum_{i=1}^{n} N_i \Delta H_i \tag{2.18}$$

Gibbs free energy of formation is needed to calculate the chemical exergies [95]:

$$\Delta G^o = 53.88\ kJ/mol + \sum_{i=1}^{n} N_i \Delta G_i \tag{2.19}$$

The standard chemical exergy is calculated from the exergy of a reversible formation reaction by following the same procedure as Szargut et al [99]. The chemical exergy of a compound is calculated with the summation of Gibbs free energy of a compound and the chemical exergy additions of each element.

$$ex_{ch}^o = \Delta G^o + \sum_{i=1}^{n} N_i (ex_{ch,i}^o) \tag{2.20}$$

The thermodynamic properties of the agro-chemicals methomyl and thiram were calculated with the group estimation methods, as well as starch. Wheat and rye seeds consist of 60-70% starch. It was assumed that the seeds were completely composed of starch and the starch monomer $(C_6H_{10}O_5)_n$ was taken as the repeating unit for the seeds [143]. The calculations are given in Table 2.11 in detail.

2.2.4. Thermodynamic Analysis

Mass, energy and exergy balance is performed for each operation.

The system boundary for the "farm to fork" bread production is un-steady state sytem due to the photosyntesis reaction. the rate of photosynthesis, yield of solar power usage, intake of fertilizers into plant structure, type of the seeds used in agriculture are some of important parameters in this unsteady-state flow system.

The governing equations for unsteady – state flow system are:

Mass balance:

$$m_{system} = \sum m_{in} - \sum m_{out} \tag{2.21}$$

Energy balance:

$$\Delta E_{system} = \sum (mH)_{in} - \sum (mH)_{out} + \sum_{k} Q_k - W \tag{2.22}$$

Exergy balance:

$$\Delta Ex_{system} = \sum (mex)_{in} - \sum (mex)_{out} + \sum_{k} Q_k \left(1 - \frac{T_0}{T_k}\right) - W - ex_{loss} \tag{2.23}$$

where *k* is the number of heat sources and *ex* is the flow availability of a stream (neglecting the kinetic and potential energy contribution):

$$ex = h - T_0 s - \sum x_i \mu_i^o \tag{2.24}$$

The exergy destroyed due to the mixing process is calculated for ideal mixture as in Equation 2.25:

$$ex_{loss,\ mixing} = R_u T_o \sum m_i ln(y_i) \tag{2.25}$$

The cumulative degree of perfection (CDP) is the ratio of the chemical exergy of the product to the sum of the exergies of all the raw materials and the fuel consumed during production [39]:

$$CDP = \frac{\sum m(ex)_{products}}{\sum m(ex)_{raw\ materials} + \sum m(ex)_{fuels}} \tag{2.26}$$

The cumulative exergy consumption (CExC) and cumulative carbon dioxide emissions are also calculated in this study to find out the total exergy and carbon dioxide emissions during bread production.

Table 2.9. Specific enthalpy and exergy values fork bread production

	Δh_f^o		ex_{ch}^o	
Diesel oil	45.7 MJ/kg	[106]	44.4 MJ/kg	[39]
Nitrogen fertilizer	66.1 MJ/kg	[53]	3.68 MJ/kg	[88]
Phosphate fertilizer	12.4 MJ/kg	[53]	10.5 MJ/kg	[37]
Potassium fertilizer	11.2 MJ/kg	[53]	0.26 MJ/kg	[88]
Herbicide (dicamba)	2.3 MJ/kg	[80]	18.4 MJ/kg	[89]
Insecticide (methomyl)	1.4 MJ/kg	[58]	23.2 MJ/kg	[90]
Fungicide (thiram)	0.9 MJ/kg	[80]	27.9 MJ/kg	[90]
Seed	15.7 MJ/kg	[81]	19.8 MJ/kg	[90]
Water	0.10 MJ/kg	[58]	0.05 MJ/kg	[88]
Electricity from fossil fuel			1 MJ/MJ	[91]
Electricity used in agriculture	228 MJ/ton grain	[82]		
Wheat grain	14.7 MJ/kg	[26]	17.6 MJ/kg	[92]
Rye grain	14.7 MJ/kg	[26]	17.6 MJ/kg	[92]
Straw	12.5 MJ/kg	[26]	2.1 MJ/kg	[93]
Flour	15.2 MJ/kg	[83]	18.4 MJ/kg	[58]
Bran	6.0 MJ/kg	[83]	3.1 MJ/kg	[58]
Salt	7.0 MJ/kg	[84]	0.24 MJ/kg	[88]
Sugar	7.1 MJ/kg	[58]	16.7 MJ/kg	[94]
Yeast	5.4 MJ/kg	[58]	21.4 MJ/kg	[58]
Margarine	2.1 MJ/kg	[85]	39.9 MJ/kg	[37]
Carbon dioxide	8.9 MJ/kg	[85,86]	0.5 MJ/kg	[59]
Ethanol	0.5 MJ/kg	[58,87]	30.4 MJ/kg	[95]
Wheat bread	9.6 MJ/kg	[83]	10.0 MJ/kg	[58]
Rye bread	10.1 MJ/kg	[83]	10.7 MJ/kg	[58]
Hamburger bun	11.5 MJ/kg	[83]	14.5 MJ/kg	[58]
Polylactic acid	3.4 MJ/kg	[58]	21.5 MJ/kg	[58]

Table 2.10. Specific CEnC, Specific CExC and Specific CCO_2E for bread production

	Specific CEnC	**Specific CExC**	**Specific CCO_2E**
Diesel oil	57.5 MJ/kg [142]	53.2 MJ/kg [59]	0.94 kg/kg [48]
Nitrogen fertilizer	78.2 MJ/kg [97]	32.7 MJ/kg [59]	7.11 kg/kg [4]
Phosphate fertilizer	17.5 MJ/kg [97]	7.5 MJ/kg [99]	2.7 kg/kg [4]
Potassium fertilizer	13.8 MJ/kg [97]	4.6 MJ/kg [100]	25.0 kg/kg [4]
Herbicide (dicamba)	198.8 MJ/kg [96]	368.0 MJ/kg [101]	6.3 kg/kg [62]
Insecticide (methomyl)	198.8 MJ/kg [96]	344.0 MJ/kg [101]	5.1 kg/kg [62]
Fungicide (thiram)	198.8 MJ/kg [96]	256.0 MJ/kg [101]	3.9 kg/kg [62]
Seed	2.8 MJ/kg [98]	18.7 MJ/kg [102]	0.23 kg/kg [42]
Water	0.06 MJ/kg [58]	0.25 MJ/kg [59]	0.085 kg/kg [33]
Electricity from fossil fuel	1.0 MJ/MJ [58]	4.17 MJ/MJ [59]	0.14 kg/MJ [105]
Electricity used in agriculture			
Wheat grain	3.65 MJ/kg	4.7 MJ/kg	0.25 kg/kg
Rye grain	2.65 MJ/kg	3.9 MJ/kg	0.20 kg/kg
Straw			
Flour	17.9 MJ/kg [42]	17.5 MJ/kg [42]	
Bran			
Salt	0.357 MJ/kg [59]	0.297 MJ/kg [59, 103]	
Sugar	16.0 MJ/kg [42]	26.0 MJ/kg [42]	
Yeast	41 MJ/kg [59]	171 MJ/kg [33,104]	5.74 kg/kg [59,104]
Margarine	39 MJ/kg [42]	39.6 MJ/kg [42]	
Carbon dioxide			
Ethanol			
Wheat bread	18.9 MJ/kg	29.1 MJ/kg	1.5 kg/kg
Rye bread	12.8 MJ/kg	22.6 MJ/kg	1.8 kg/kg
Hamburger bun	23.4 MJ/kg	38.5 MJ/kg	1.1 kg/kg
Polylactic acid	54.0 MJ/kg [42]	78.0 MJ/kg [42]	1.8 kg/kg [42]

Table 2.11. Estimation of the thermodynamic properties which are not readily available in the literature [95].

Atomic group	**Occurrence**	***ΔH (kJ/mol)***	***ΔG (kJ/mol)***
Methomyl			
$-CH_3$	3	-76.45	-43.96
-S-	1	41.87	33.12
$-\underset{\vert}{C}=$	1	83.99	92.36
=N-	1	23.61	-
-O-	1	-132.22	-105.00
$-\underset{\vert}{C}=O$	1	-133.22	-120.50
-NH-	1	53.47	89.39
		$\sum H^o$= -223.56 kJ/mol	$\sum G^o$= -88.63 kJ/mol
Thiram			
$-CH_3$	4	-76.45	-43.96
$-\underset{\vert}{N}-$	2	123.34	163.16
$-\underset{\vert}{C}=$	2	83.99	92.36
-S-	2	41.87	33.12
=S	2	-17.33	-22.99
		$\sum H^o$= -226.23 kJ/mol	$\sum H^o$= 409.34 kJ/mol

Table 2.12. Total energy and exergy input and output during the agriculture of the wheat grain and rye grain in Turkey and Germany

	Energy inflow (MJ/ha)		**Exergy inflow (MJ/ha)**	
Wheat grain inputs				
	Turkey	Germany	Turkey	Germany
Diesel oil	5842	5842	5675	5675
Nitrogen fertilizer	2694	3834	150.0	213
Phosphate fertilizer	269	89	227.6	117
Potassium fertilizer	-	46	-	1
Herbicide	2.60	2.60	20.6	20.6
Insecticide	0.78	0.78	12.8	12.8
Fungicide	1.01	1.01	34.5	34.5
Seed	3575	3575	4508	4508
Irrigation	120	635	60	318
Electricity	543	1573	543	1573
TOTAL	$\sum(mH)_{in}$ 13047	$\sum(mH)_{in}$ 15598	$\sum(mex)_{in}$ 11232	$\sum(mex)_{in}$ 12473
Wheat grain outputs				
Grain	35037	41950	117306	140448
Straw	2795	474	49875	8379
TOTAL	$\sum(mH)_{out}$ 37832	$\sum(mH)_{out}$ 42424	$\sum(mex)_{out}$ 167181	$\sum(mex)_{out}$ 148827
		CDP_{grain}: 3.73		CDP_{grain}: 11.26
Rye grain inputs				
Diesel oil	4378	4255	4378	4255
Nitrogen fertilizer	1058	58.9	2593	144.3
Phosphate fertilizer	186	157.6	89	75.7
Potassium fertilizer	-	-	51	1.14
Herbicide	2.60	20.6	2.60	20.6
Insecticide	0.78	12.8	0.78	12.8
Fungicide	1.01	34.5	1.01	34.5
Seed	3140	3960	3140	3960
Irrigation	198	99	473	237
Transportation	6	3.65	6	3.65
Electricity	591	591	1286	1286
TOTAL	$\sum(mh)_{in}$ 9561	$\sum(mh)_{in}$ 12020	$\sum(mex)_{in}$ 9193	$\sum(mex)_{in}$ 10031
Rye grain outputs				
Grain	38073	45584	87612	104896
Straw	16188	2745	37250	6258
TOTAL	$\sum(mh)_{out}$ 54261	$\sum(mh)_{out}$ 12862	$\sum(mex)_{out}$ 48329	$\sum(mex)_{out}$ 111154
		CDP_{grain}: 4.96		CDP_{grain}: 10.46

2.3. SOURDOUGH

2.3.1. Experimental Data

Kinetic models developed by Yöndem et al [144] are employed to obtain continuous mathematical relations between microbial concentrations, lactic acid and CO_2 production and volume increase in dough by following the same procedure as Değerli et al (2015) [145]. Sourdough was made of 61 % flour, 0.1 % sugar, 2.5 % microbial culture, 0.6 % salt and 35.8 % water. The kneading time was 7 minutes as reported by Yöndem et al (1992) [144]. In the first set of the experimental data temperature was 25ºC, where the percentage of the bacteria in the inoculum increased with 20 % increments between 0 to 100 %. The second set of the data was pertinent to leavening with 80 % yeast and 20 % bacteria inoculum, while the temperature was increasing with 5ºC increments between 20 to 40ºC (Table 2.13). Constants of the kinetic models were recalculated from the data and then thermodynamic analyses were carried out based on this information. Kinetic models were also given in Table 2.14.

Table 2.13. Experimental design during 240 min of leavening process with different initial yeast and bacteria combinations at different temperatures

CASE	Inoculum
1	0% *L. plantarum* and 100% *S. cerevisiae* at 25ºC
2	20% *L. plantarum* and 80% *S. cerevisiae* at 25ºC
3	40% *L. plantarum* and 60% *S. cerevisiae* at 25ºC
4	60% *L. plantarum* and 40% *S. cerevisiae* at 25ºC
5	80% *L. plantarum* and 20% *S. cerevisiae* at 25ºC
6	100% *L. plantarum* and 0% *S. cerevisiae* at 25ºC
7	20% *L. plantarum* and 80% *S. cerevisiae* at 20ºC
8	20% *L. plantarum* and 80% *S. cerevisiae* at 30ºC
9	20% *L. plantarum* and 80% *S. cerevisiae* at 35ºC
10	20% *L. plantarum* and 80% *S. cerevisiae* at 40ºC

Table 2.14. Kinetic models (adapted from Yöndem et al) [144]

Exponential growth	$\frac{dX}{dt}=\mu X$	(2.27)
Stationary phase	$\frac{dX}{dt}=0$	(2.28)
Logistic growth	$\frac{dX}{dt}=\mu X\left(1-\frac{X}{X_{max}}\right)$	(2.29)
Death phase	$\frac{dX}{dt}=-kx$	(2.30)
Death phase	$\frac{dX}{dt}=-k(X-X_d)$	(2.31)
Lactic acid production in the growth phase	$\frac{dL}{dt}=\alpha X+\beta\frac{dX}{dt}$	(2.32)
Lactic acid production in the death phase	$\frac{dL}{dt}=-\varepsilon\frac{dX}{dt}$	(2.33)
CO_2 production	$\frac{dG}{dt}=\alpha_1 Y+\alpha_2 X+\beta_1\frac{dY}{dt}+\beta_2\frac{dX}{dt}$	(2.34)
Dough volume increase	$\frac{dV}{dt}=\emptyset\left(1-\frac{V}{V_{max}}\right)\frac{dG}{dt}$	(2.35)

2.3.2. Modeling

Lactic acid fermentation of *L. plantarum* and alcoholic fermentation of *Saccharomyces cerevisiae* are described with Equations (2.36) and (2.37), respectively [146, 93]:

$$C_6H_{12}O_6+0.19H_2O+0.09NH_3\rightarrow 1.13CO_2+0.75C_3H_6O_3+0.75C_2H_5OH+0.75H_2+ 0.38CH_3COOH+0.37CH_{1.77}O_{0.49}N_{0.24} \quad (2.36)$$

$$C_6H_{12}O_6+0.12NH_3\rightarrow 1.54CO_2+1.30C_2H_60+0.43C_3H_8O_3+0.59CH_{1.75}O_{0.45}N_{0.2} \quad (2.37)$$

The products of the lactic acid fermentation are lactic acid, CO_2 and ethanol due to facultative homofermentative characteristics of *L. plantarum*, whereas the products of alcoholic fermentation are ethanol and CO_2. While fermenting one molecule of glucose, hetero fermentative lactic acid bacteria allocate 50 % of it for the roduction of lactic acid and the rest is utilized for the production of ethanol, acetate or CO_2. The ratio of acetate to

ethanol production depends on the oxidation-reduction potential of the system [147]. The empirical chemical formula of *L. plantarum* and *S. cerevisiae* are suggested as $CH_{1.77}O_{0.49}N_{0.24}$ [148] and $CH_{1.75}O_{0.45}N_{0.2}$ [149].

Stanke et al (2014) [150] developed a mechanistic model to simulate the expansion of the volume of the wheat dough during proofing by using the engineering Bernoulli equation-e.g., a special form of the first law of thermodynamics. Mass balance (Equation 2.38), the first law of thermodynamics (Equation 2.39) and the expansion work (Equation 2.40) are stated in this study as:

$$\left(\sum N\right)_2 - \left(\sum N\right)_1 = \left(\sum G\right) - \left(\sum C\right) \tag{2.38}$$

$$\left(\sum NH\right)_2 - \left(\sum NH\right)_1 = Q - W \tag{2.39}$$

$$W_{expansion} = -p\Delta V \tag{2.40}$$

Enthalpy of formation of the substances other temperatures is calculated from:

$$H_T^o = H^o + C_p T \tag{2.41}$$

Specific heat capacities of substances are given in Table 2.15. Exergy is not a conserved quantity, but mass and energy are. Hence, internal and external irreversibilities cause exergy destruction. Exergy balance (e.g, the second law of thermodynamics) is expressed as:

$$\left(\sum Nex\right)_2 - \left(\sum Nex\right)_1 + \sum Q\left(1 - \frac{T_O}{T}\right) - W = ex_{destroyed} \tag{2.42}$$

Table 2.15. Thermodynamical data of the compounds

	***Cp* (kJ/mol K)**	**$\Delta H_{f298K}°$ (kJ/mol)**	***ex*° (kJ/mol)**
Glucose	0.220 [151]	-1271.1 [86]	2955 [145]
Ammonia	0.357 [86]	- 46.2 [155]	340 [86]
Carbon dioxide	0.037 [86]	- 393.5 [97]	20 [86]
Ethanol	0.110 [86]	- 276.0 [86]	1400 [157]
Glycerol	0.222 [152]	- 669.6 [86]	212 [158]
Lactic acid	0.372 [86]	- 694.08 [86]	1747 [98]
Water	0.075 [153]	- 285.8 [155]	0.9 [157]
Acetic acid	0.140 [154]	- 484.5 [86]	907.2 [157]
Hydrogen	0.029 [86]	0 [86]	236.09 [157]
Yeast	0.339 [95]	- 133.13 [156]	529.6 [95]
Bacterium	0.354 [95]	- 96.01 [156]	571.4 [95]

2.3.3. Estimation Of Thermodynamic Properties Of Biomass

Group contribution method is employed to estimate the spesific heat capacity and chemical exergy of yeast and bacteria. The specific heat capacity of yeast and bacteria is estimated with Hurst and Herrison's modification of Kopp's rule [95] in Equation 2.11.

The standard chemical exergy is calculated (Table 2.3) by following the same procedure as Szargut et al., (2005) [99]:

$$ex_{ch} = nG^o + \sum_{i=1}^{n} N_i\left(ex^o_{ch,i}\right) \tag{2.20}$$

The entropy of formation is needed to find the Gibbs free energy of yeast and bacteria. According to Battley (1999) [93]:

$$G^o = H^o - T\Delta S^o \tag{2.43}$$

$$\Delta S^o = -0.813 \sum S^o_{atoms} \tag{2.16}$$

3. RESULTS AND DISCUSSION

3.1. SEROGROUP C ANTIGEN PRODUCTION BY *NEISSERIA MENINGITIDIS*

3.1.1. Kinetic Modeling

The experimental data and kinetic models were compared for three cases by using the Equation (2.1) for microbial growth, Equation (2.2) for antigen production and Equation (2.3) for substrate utilization models. The graphs for uncontrolled case, controlled pH case and controlled dissolved oxygen case are depicted in Figure 3.1, 3.2 and 3.3, respectively. The kinetic constants were given in Table 3.1.

Table 3.1. Parameters of the kinetic models

	without control	**pH controlled**	**dissolved oxygen control**
M (1/h)	0.6	0.65	0.56
x_{max} (g/L)	1.83	2.05	2.85
x_0 (g/L)	0.063	0.06	0.048
α_{exp}	$9.9x10^{-3}$	$4.0\ x10^{-3}$	$5.0\ x10^{-3}$
β_{exp}	$2.0x10^{-2}$	$3.8\ x10^{-3}$	$3.3\ x10^{-2}$
α_{st}	$7.5\ x10^{-3}$	-	$3.0\ x10^{-3}$
β_{st}	$1.0\ x10^{-5}$	-	$2.0\ x10^{-3}$
$Y_{x\ exp}$	0.8	2.7	4.0
$Y_{p\ exp}$	0.12	2.3	0.18
$Y_{x\ st}$	0.6	-	1.0
$Y_{p\ st}$	0.12	-	0.07
k_m (1/h)	$5.0\ x10^{-5}$	0.41	0.06

An almost perfect agreement between the kinetic model equations and the experimental data is observed. This is of crucial importance to achieve, since the deviation of the kinetic model from the experimental data would consequently reduce the reliability of the thermodynamic analysis.

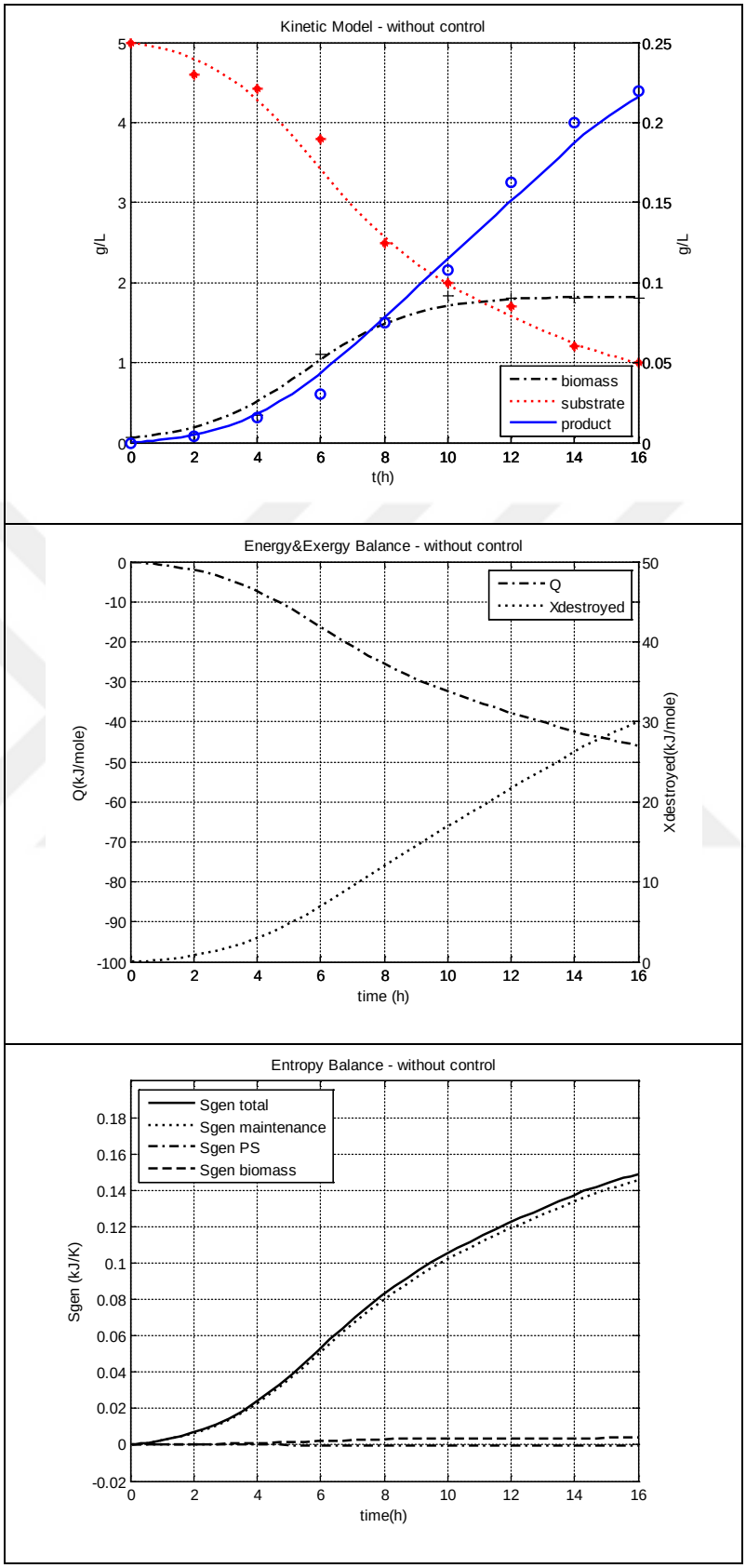

Figure 3.1. Kinetic and thermodynamic analysis for without pH and dissolved oxygen

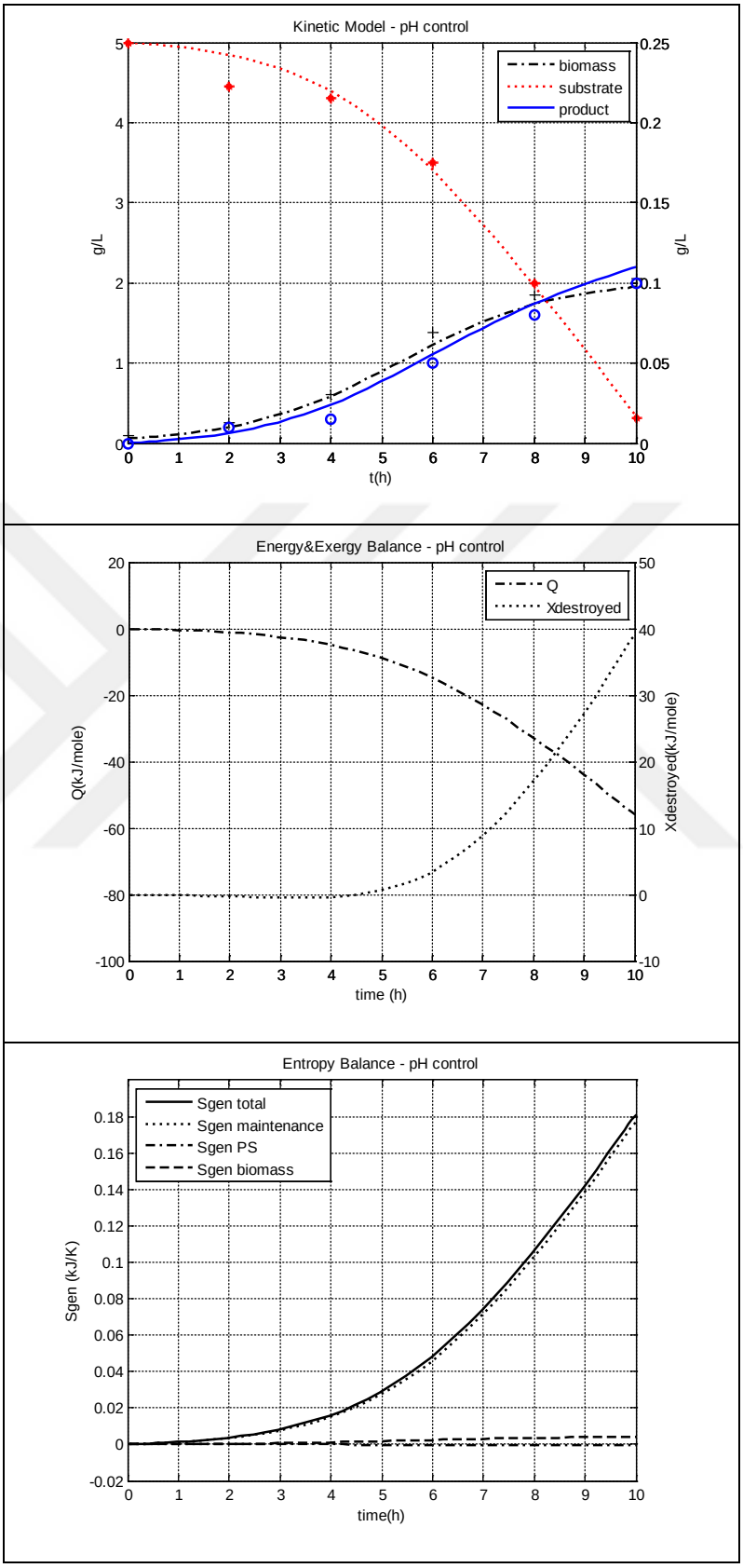

Figure 3.2. Kinetic and thermodynamical analysis for pH control

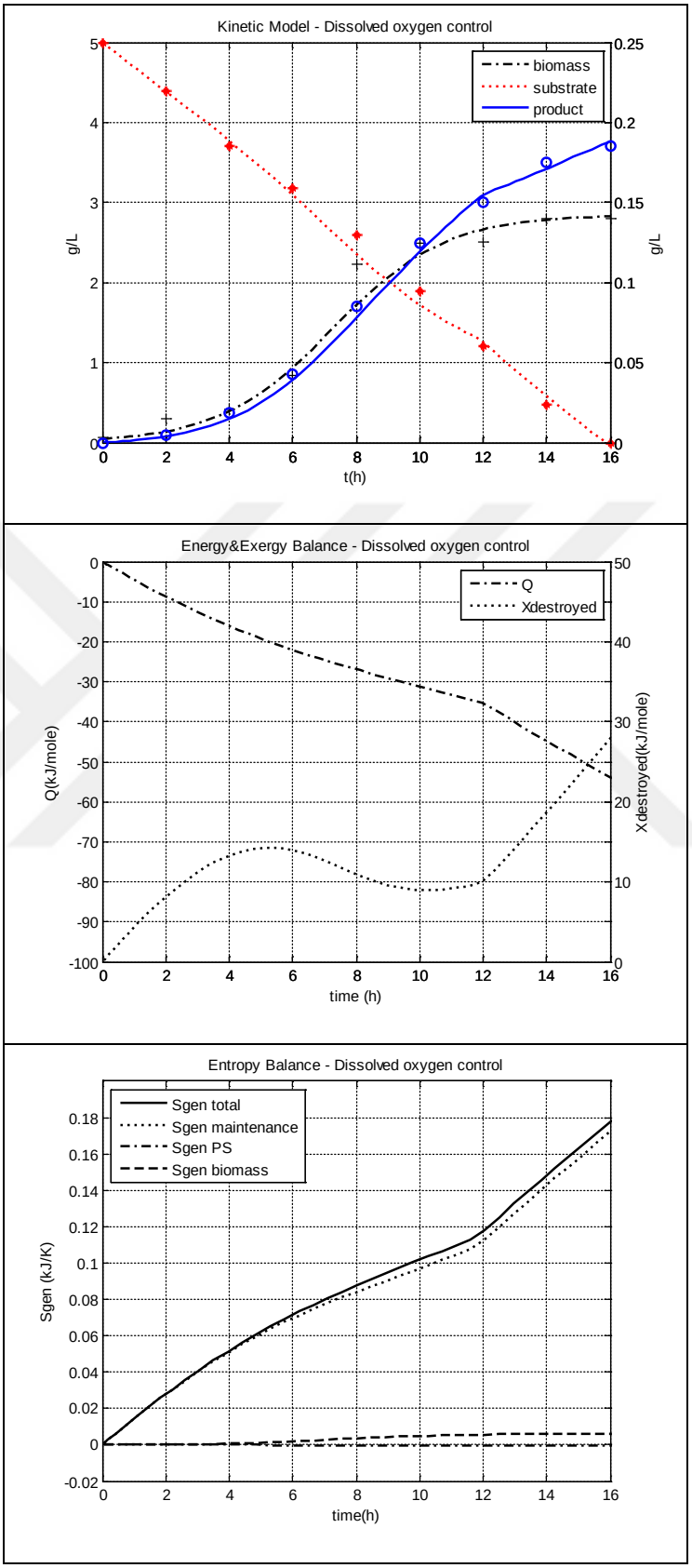

Figure 3.3. Kinetic and thermodynamical analysis for dissolved oxygen control

The analysis has not covered the death phase. In the cases where uncontrolled or dissolved oxygen is controlled, experimental data pertinent to the first 16 hours of the cultivation are analyzed while the process time is 10 hours in pH controlled cultivation. In uncontrolled process, the amount of glucose consumed is 4.01 g/L, while the maximum biomass concentration x_{max} attained is 0.83 g/L and the achieved antigen production is 0.21 g/L. When the pH is controlled, the data is analyzed for the first ten hours of cultivation, where the amount of glucose consumed is 4.65 g/L, x_{max} attained is 1.95 g/L, while the amount of antigen produced is 0.11 g/L. When the dissolved oxygen is controlled at 10 %, the glucose was completely consumed, x_{max} achieved is 2.83 g/L, and the antigen production is 0.19 g/L. The standard errors between the experimental data and the model are low (Table 3.2).

Table 3.2. Standard errors of estimate of the kinetic models

	uncontrolled	**pH controlled**	**dissolved oxygen controlled**
$SE_{\text{microbial growth}}$ (g/L)	0.080	0.093	0.195
$SE_{\text{product formation}}$ (g/L)	9.3×10^{-3}	6.7×10^{-3}	4.4×10^{-3}
$SE_{\text{substrate consumption}}$ (g/L)	0.157	0.173	0.119

3.1.2. Mass Balance

Glucose is consumed for maintenance, antigen and biomass production. The nitrogen content of *N. meningitidis* in the empirical chemical formula of the bacteria, as suggested by Rittman and McCarthy [88], is employed to determine the amount of the glutamic acid incorporated into the structure of the biomass.

3.1.3. Thermodynamic Properties

The specific heat capacity of the serogroup C antigen is 115 kJ/mol K (Table 2.1) as calculated with the data given in Table 2.3 [95]. By using the specific heat capacity of serogroup C antigen, enthalpy of formation at 308 K was calculated with equation (2.12) as - 4.7 $x10^5$ kJ/mol (Table 2.1). The Gibbs free energy and enthalpy of formation at 298 K are used to find out the standard molar entropy of formation of n-acetylneuraminic acid

(Table 2.2) with the group contribution method. The standard molar entropy of formation, $\Delta S°_{f298}$ of serogroup antigen C is calculated with equation (2.13) as - 419.0 kJ/ mol K and the absolute entropy, $S°$ is found as 242 kJ/mol K by equation (2.14) (Table 2.1). The total X_{chne} is calculated from Equation (2.15) and listed in in Table 2.3, the standard chemical exergy of serogroup antigen C is found to be $1.6x10^6$ kJ/mol (Table 2.1). After using the chemical formula of the biomass as suggested by Battley (1999) [93] the standard molar entropy of formation is found to be - 0.74 kJ/mol K and the standard molar entropy of formation of biomass is found to be 0.138 kJ/mol K by using Table 2.3. The enthalpy of formation of *N. meningitidis* is assumed to be the same as that of *Saccharomyces cerevisiae*, -512.6 kJ/mol at 298 K (Table 2.1), for the unit carbon biomass formula of 95 g/mol as calculated by Battley (1999) [93]. The specific heat capacity of the bacterial chemical unit carbon formula is calculated as 0.135 kJ/mol K with Equation (2.11) (Table 2.1). Therefore, the enthalpy of formation at 308 K is figured out as -511.3 kJ/mol using Equation (2.12). Eventually, the standard chemical exergy of bacteria is calculated as 2037.1 kJ/mol and tabulated in Table 2.1 by using Equation (2.15).

3.1.4. Thermodynamic Modeling

The reaction occurred at 308 K, with heat loss from the system to the environment. It is stated in Table 3.3 that the heat loss in the uncontrolled batch process is 26.0 kJ/g biomass, whereas the heat loss in pH and dissolved oxygen controlled processes are 28.1 kJ/g biomass and 19.3 kJ/g biomass, respectively.

Heat is generated by the reactions constituting the steps of the energy metabolism [34,35]. The difference between the sum of the Gibbs free energies of the products and the reactants of these reactions is released to the environment as heat. Equation (2.7) relates the amount of heat released with the exergy destroyed. This relation was presented graphically in Figures 3.1, 3.2 and 3.3.

Table 3.3. Summary of the thermodynamic assessment

	uncontrolled	**pH controlled**	**dissolved oxygen controlled**
x_{max} (g/L)	1.83	2.05	2.85
x_0 (g/L)	0.063	0.060	0.048
Heat loss (kJ/L)	46.0	55.9	54.0
Entropy generation (kJ/K L)	0.149	0.181	0.195
Exergy destruction (kJ/L)	30.0	39.1	28.0
Heat loss/($x_{max} - x_0$) (kJ/g)	26.0	28.1	19.3
Entropy generation/($x_{max} - x_0$) (kJ/g)	0.084	0.091	0.070
Exergy destruction/($x_{max} - x_0$) (kJ/g)	17.0	19.6	10.0
$Q_{antigen}/Q_{total}$ (%)	-0.43	-0.30	-0.36
Exergetic efficiency of antigen production (%)	7.52	5.54	3.28
Exergetic efficiency of microbial growth (%)	72.64	66.99	92.68
T_0 (K)	298	298	298

The amount of exergy destroyed is determined as 17.0 kJ/g biomass, 19.6 kJ/g biomass, and 10.0 kJ/g biomass for uncontrolled, pH controlled and dissolved oxygen controlled processes, respectively (Table 3.3). The entropy generation is 0.084 kJ/g K biomass, 0.091 kJ/g K biomass, and 0.070 kJ/g K biomass under these conditions (Table 3.3). The entropy generation associated with maintenance is almost the same as the total entropy generation. The entropy generation due to the growth of biomass is the second highest; whereas that of the antigen production is approximately zero, due to the relatively small mass of the antigen produced. The loss of the metabolically generated heat is the major cause of the entropy generation, and the exergy destruction. They propagate proportionally with the heat loss. Due to the exothermic reactions, the heat loss comes out with negative sign; hence absolute value of heat loss concludes that higher amounts of heat loss bring about more exergy destruction meaning that the heat loss causes the loss of the available energy and entropy generation. Therefore, the pH controlled process which caused the production of the smallest amount of antigen, in spite of the highest glucose consumption and biomass production in the least processing time of 10 hours is the least efficient process with the

maximum values of heat loss, exergy destruction and entropy generation per unit mass as it can be seen in Table 3.3. The second efficient process regarding of the heat loss, is the dissolved oxygen controlled cultivation. The most efficient antigen production is obtained in the uncontrolled batch process. The stress conditions triggers antigen production in the process with the lowest glucose consumption, biomass production, heat loss, exergy destruction and entropy generation. The exergetic efficiency of antigen production is 7.52%, 5.54% and 3.28% in the uncontrolled, pH controlled and dissolved oxygen controlled processes, respectively, indicating that the least efficient antigen production process is the cultivation with dissolved oxygen control, while the most efficient is the uncontrolled cultivation (Table 3.3).

The relation between heat generation and exergy destruction is mathematically formulated in Equation (2.7). This relation is visualized in Figures 3.1-3.2, which imply that in the batch culture, heat generation is the major cause of the destruction of the exergy. In Figure 3.3, between the inflection point of the microbial growth, e.g., the point when the term ($1-x/x_{max}$) of the logistic equation starts to be influential, and the stationary phase, e.g., when the net microbial growth stops, a decline in the amount of the exergy destroyed by the microorganism is observed. Although it is unaccounted in the model, in batch cultures, the inflection point may be the indicator of the shift from using the main carbon source to the secondary carbon sources, therefore when the exergy destruction is correlated with the glucose consumption such a behavior may be observed.

It is shown in Table 3.4 that the smallest heat release per unit biomass production, smallest exergy destruction per unit biomass production and the smallest entropy generation per unit biomass is achieved when the dissolved oxygen concentration is controlled. These results may indicate the most efficient utilization of the energy metabolism, among all the alternatives, when there is always a certain amount of dissolved oxygen is present in the medium. The largest heat loss per unit biomass production, the largest exergy loss per unit biomass production, and the largest entropy generation per unit biomass production are accounted for the pH controlled experiment. This result indicates that although higher biomass concentration is attained when pH of the medium is controlled when compared with that of the uncontrolled cultivation, the growth is actually achieved under thermodynamically unfavorable conditions, as revealed by the higher heat release, exergy loss, and entropy generation. The smallest maximum biomass concentration is reported in

the uncontrolled medium, indicating that when the medium is not favorable for growth, the cells are not forced to grow further in the expense of exergy.

It is also shown in Table 3.4 that the rate of heat release per unit mass for antigen production to total heat release per unit mass in uncontrolled process, pH controlled process and dissolved oxygen controlled process are calculated as 0.43%, 0.30% and 0.36%, respectively (Table 3.4). These values have negative signs, indicating the heat release. From these results, it can be concluded that the rate of heat release per unit mass for antigen production to total heat release per unit mass in uncontrolled process is found to be higher than that of the pH controlled and the dissolved oxygen controlled processes.

Exergetic efficiency of antigen production is calculated and varies between 3.28% and 7.52%, where the highest efficiency is calculated for the uncontrolled cultivation. Exergetic efficiency of microbial growth is calculated and found to vary between 66.99% and 92.68% , where the highest efficiency is calculated for the dissolved oxygen controlled cultivation. Implying that the exergetic efficiency of microbial production and antigen production are not parallel, confirming the discussion that the antigen is produced best under the stress conditions [85].

One of the major findings of this study is relating the entropy generation with the microbial processes that glucose is used for. Since entropy generation is related with the irreversibilities, we may expect it to increase with the damage collected with the biomass, as the cells get older. In Figures 3.1-3.3 almost all the entropy generated appears to be caused by the glucose utilization for maintenance, e.g., the healing of the damaged cells.

3.2. *"FARM TO FORK"* BREAD PRODUCTION

3.2.1. Agriculture

Table 2.12 shows that with the input of 13047 MJ/ha of energy and 11232 MJ/ha of exergy 2388.5 kg/ha of wheat grain in produced in Turkey, whereas 15598 MJ/ha of energy and 12473 MJ/ha of exergy are utilized to produce 7980 kg/ha wheat grain in Germany. In Turkey 9561 MJ/ha of energy and 9193 MJ/ha of exergy are utilized to produce 2590 kg/ha rye grain. In Germany, 12020 MJ/ha of energy and 10031 MJ/ha of exergy are

utilized to produce 5960 kg/ha rye grain. When these values are substitutes into Equation (2.26) from Table 2.12, CDP of the wheat agriculture is calculated as 3.73 Turkey and 11.26 in Germany. The CDP of the rye agriculture is 4.96 in Turkey and 10.46 in Germany.

3.2.2. The Breadmaking Process

The initial stages of the bread or bun making are consisting of the flour production from the grains, kneading and dividing the dough (Table 2.5). Milling is the process of breaking open the grain and releasing the starchy center. Milling facilities receive the grains from the trucks and then clean and dry them. The tougher outer layers of the grains may be removed and used for other purposes, e.g., bran is used for breakfast cereals or animal feed [66]. The cleaning of grains is assumed to utilize 0.6 kWh/ton of energy [67] (Table 2.5). The level of moisture in the grains was taken as 15%. The grains need to be moisturized before milling [68], the moisture was taken as 16% after moisturizing. The moisture content decreases to 12% after milling [49, 69]**.** The plant employed in this study had the capacity of milling 60 tons of grains in 24 hours with the utilization of 263 kW of electric power. 79.4% of the wheat grain mass wheat and 89.5% rye converted into flour and 379 MJ of energy is utilized for milling of 1 ton grain (Table 2.5). A typical flour production plant uses 50 % electric power input for milling and grinding, 30 % of it for pneumatic conveying and 11 % of it for mechanical conveying [70].

Mass balances for flour production and following steps are presented in Tables 3.4, 3.5 and 3.6. Water added to the grains to make their water content to 16% before milling is equivalent to 0.84% of the grain mass. The details of the mass and energy balances pertinent to the flour production stages of the wheat and rye bread and the hamburger bun making processes are given in Tables 3.4, 3.5 and 3.6.

Table 3.4. Energy and exergy balances during production of one ton of wheat bread

	INPUTS	**Total energy inflow (MJ)**	**Total exergy inflow (MJ)**	**OUTPUTS**	**Total energy outflow (MJ)**	**Total exergy outflow (MJ)**
Flour production	Grain	12259.8	14678.4	Flour	10153.6	12291.2
	Water	0.6	0.4	Bran	1038.0	536.3
	Electricity for cleaning	1.7	1.7	Heat rejected	1389.7	-
	Electricity for milling	319	319	Exergy destroyed		2172.2
Dough preparation and diving	Flour	10153.6	12291.2	Unfermented dough	10414.2	12037.8
	Water	43.4	21.7			
	Yeast	75.6	299.6			
	Salt	98.0	3.4			
	Electricity for kneading	19.9	19.9	Exergy destroyed due to mixing		578.1
	Electricity for dividing	23.7	23.7	Total exergy destroyed		621.7
Fermentation	Unfermented dough	10414.2	12037.8	Fermented dough	10424.6	12037.8
	Electricity for fermenter	10.4	10.4	Exergy destroyed		10.4
Baking	Fermented dough	10424.6	12037.8	Bread	9600	10000
	Electricity for oven	732	732	Water	12.8	9.0
Cooling	Electricity for cooler	36.0	36.0	Carbon dioxide	8.2	0.5
Slicing	Electricity for slicer	9.6	9.6	Ethanol	0.7	28.9
				Heat rejected	1580.5	
				Exergy destroyed		2777.0
Packaging	Bread	9600	10000	Bread in packages and delivered	10335.4	10172.0
	Polylactic acid	27.2	172.0			
	Electricity for packaging	7.2	7.2			
Transportation	Packaged bread	701	681			
				Exergy destroyed		688.2

Table 3.5. Energy and exergy balances during production of one ton of rye bread

	INPUTS	**Total energy inflow (MJ)**	**Total exergy inflow (MJ)**	**OUTPUTS**	**Total energy outflow (MJ)**	**Total exergy outflow (MJ)**
Flour production	Grain	11348.4	14308.8	Flour	10685.6	12015.2
	Water	0.7	0.4	Bran	738	381.3
	Electricity for cleaning	1.7	1.7	Heat rejected	466.2	
	Electricity for milling	293	293	Exergy destroyed		1612.9
Dough preparation and dividing	Flour	10685.6	12015.2	Unfermented dough	10854.8	11224.5
	Water	41.8	20.9			
	Yeast	27	107			
	Salt	70	2.4			
	Electricity for kneading	6.7	6.7	Exergy destroyed due to the mixing		921.0
	Electricity for dividing	23.7	23.7	Total exergy destroyed		951.4
Fermentation	Unfermented dough	10854.8	11224.5	Fermented dough	10865.2	11224.5
	Electricity for fermenter	10.4	10.4	Exergy destroyed		10.4
Baking	Fermented dough	10865.2	11224.5	Bread	10100.0	10700.0
	Electricity for oven	732	732	Water	12.8	9.0
Cooling	Electricity for cooler	36	36	Carbon dioxide	8.2	0.5
Slicing	Electricity for slicer	9.6	9.6	Ethanol	0.7	28.9
Packaging	Bread	10100.0	10700.0	Heat rejected	1521.1	
	Polylactic acid	27.2	172.0	Exergy destroyed		1463.7
	Electricity for packaging	7.2	7.2	Bread in packages and delivered	10835.4	10872.0
Transportation	Packaged bread	701	681	Exergy destroyed		688.2

Table 3.6. Energy and exergy balances during production of one ton of hamburger buns

	INPUTS	**Energy inflow (MJ)**	**Exergy inflow (MJ)**	**OUTPUTS**	**Energy outflow (MJ)**	**Exergy outflow (MJ)**
Flour production	Grain	13744.5	16456.0	Flour	11384.8	13781.6
	Water	0.8	0.4	Bran	1164.0	601.4
	Electricity for cleaning	1.9	1.9	Heat rejected	1552.6	
	Electricity for milling	354	354	Exergy destroyed		2429.5
Dough preparation and dividing	Flour	11384.8	13781.6	Unfermented dough	12510.3	16001.8
	Water	48.7	24.4			
	Yeast	156.6	620.6			
	Salt	70	2.4			
	Sugar	616	1258.4			
	Margarine	73.5	1396.5			
	Electricity for kneading	24.6	24.6			
	Electricity for dividing	136.1	136.1			
				Exergy destroyed due to the mixing		953.4
				Total exergy destroyed		1114.1
Fermentation	Unfermented dough	12510.3	16001.8	Fermented dough	12578.9	16001.8
	Electricity for fermenter	68.6	68.6			
				Exergy destroyed		68.6
Baking	Fermented dough	12578.9	16001.8	Hamburger buns	11500.0	14500.0
	Electricity for oven	907	907	Water	39.8	27.9
Cooling	Electricity for cooler	36	36	Carbon dioxide	8.2	0.5
Slicing	Electricity for slicer	3.0	3.0	Ethanol	0.7	28.9
				Heat rejected	1976.2	
				Exergy destroyed		2390.5
Packaging	Hamburger buns	11500.0	14500.0	Hamburger buns delivered in packages	12375.2	14607.5
	Polylactic acid	17.0	107.5			
	Electricity for packaging	4.2	4.2			
Transportation	Hamburger buns	701	681			
				Exergy destroyed		685.2

The kneading machine had a capacity of 450 kg/h and utilizing 2.2 kW of electric power. In order to produce one ton dough for wheat flour 17.6 MJ work needed to be done. In rye dough, the mixing energy for the production of rye bread is 1/3 times of that of the wheat dough kneading due to the difference in pentosan content [159] (Table 2.5). The common steps of the dough preparation and dividing are explained in detail by Cauvain and Young [61].

The dough divider has the capacity of cutting and rounding 50 - 850 g of pieces of dough in 7 seconds by utilizing 0.75 kW of energy (Table 2.5). A 65 g hamburger bun was assumed to be produced with 58.0 g of wheat flour. The dough weight of the dough for making one roll of hamburger bun was 108 g. During the mixing of ingredients in bread formulation, exergy destroyed occurs according to Equation 2.25. The exergy destroyed due to the mixing is 578.1 MJ/ton wheat bread, 921.0 MJ/ton rye bread and 953.4 MJ/ton hamburger buns. Also, total exergy destroyed in dough preparation and dividing is 621.7 MJ/ton wheat bread, 951.4 MJ/ton rye bread and 1114.1 MJ/ton hamburger buns.

After mixing of all ingredients, carbon dioxide and ethanol are produced due to the consumption of glucose by the yeast. During one hour of fermentation, yeast consumes 1.86 g of glucose and produces 0.95 g of ethanol and 0.91 g of carbon dioxide in 1 kg of dough (Tables 3.4-3.6) [69]. The energy utilization during fermentation is 9.2 MJ/ton of wheat and rye dough, while this value is 49.0 MJ/ton of for hamburger bun dough (Table 3.5). In the wheat and rye bread production, the baking oven has the capacity of 100 kg/h and power of 10.8 kW and the energy utilization is 648 MJ/ton bread (Table 2.5). The duration of baking is assumed as 45 minutes; the wheat and rye bread loss 13% of their weights in the oven during the baking process [70], the weight loss is assumed to be 40% in hamburger buns [6]. After the baking process, the loaves are cooled on the racks that allow the air to circulate around them and prevent the crusts from becoming soggy. The cooling machine used in this study has the capacity of 1000 kg/h and utilizes 167 kW of power. The energy consumption is 36 MJ for cooling of 1 ton of bread (Table 2.5). The wheat and rye bread loaves are assumed as 500 g in weight and sliced into 15 slices/bread. Wheat bread is made of 59.1% wheat flour, 38.5% water, 1.2% yeast and 1.2% salt. Rye bread formulation consists of 61.7% rye flour, 37.0% water, 0.4% yeast and 0.9% salt. Hamburger bun is composed of 53.5% wheat flour, 34.8% water, 2.1% yeast, 0.7% salt, 6.3% sugar and 2.6% margarine [71,72]. The hamburgers are sliced in two in the middle of

the bun, slicing is done horizontally in a single stroke [73]. The slicing machine has the capacity of 1800 loaves/hour and utilized 2.4 kW of power. The energy consumption for the slicing the wheat or rye bread is 9.6 MJ/ ton and 3 MJ/ton hamburger bun (Table 2.5). Eight buns are packaged together for shipping to the restaurants. The packaging machine operated at the rate of 1 bag/s with the power requirement of 3.6 kW; and the packaging material was selected as 4 g per package and 4 g each. The energy consumption for the packaging of the wheat bread is 7.2 MJ/ton bread for 1 ton wheat bread and rye bread. The hamburger bun packs contains 8 rolls and the energy consumption is 4.2 MJ/ton hamburger buns.

In Table 3.4, the energy and exergy balances of baking, cooling, slicing and packaging are given for 1 ton wheat bread. The heat rejected is 1580.5 MJ/ton wheat bread and exergy destroyed is 2777.0 MJ/ton wheat bread. The same values are presented for 1 ton rye bread in Table 3.5 and for 1 ton hamburger bun in Table 3.6. The heat loss is 1521.1 MJ/ton rye bread and exergy destroyed is 1463.7 MJ/ton rye bread. The heat loss is 1976.2 MJ/ton hamburger buns and exergy destroyed is 2390.5 MJ/ton.

In overall, hamburger bun production has the maximum energy consumption due to the higher weight loss in baking. Rye bread production has the minimum energy consumption due to lower energy consumption in agriculture of rye grain with respect to agriculture of wheat grain, less energy consumption in dough preparation and higher flour production efficiency.

Transportation is the last step of the bread production. Heavy-duty trucks (capacity=10 tons, velocity=90 km/h) utilize 0.287 L/km of fuel [52]. The data of the transportation of grains to the flour factory was calculated in the agriculture as 51 MJ/ton bread and the distance between the farm and flour factory was assumed to be 50 km [37]. Transportation is also needed to deliver the flour to baking factory and to deliver breads to market. The total distance for those was assumed to be 550 km [37]. Therefore, total energy consumption for the transportation is 701 MJ/ton bread and exergy consumption 681 MJ/ton bread.

3.2.3. The values of CEnC, CExC and CCO_2E

The values of CEnC, CExC and CCO_2E for the wheat and rye grain production both in Turkey and Germany, and the contribution of each ingredient to these sums are given in Table 3.7. The CEnC of wheat grain production is 5.4 MJ/kg in Turkey and 1.9 MJ/kg in Germany while CExC of wheat grain production is 6.7 MJ/kg in Turkey and 2.7 MJ/kg in Germany. The CCO_2E of wheat grain cultivation is 0.3 kg/kg in Turkey and 0.2 kg/kg in Germany (Table 3.7). Diesel consumption contributes 57.27 % and 58.88 % of the total CEnC in Turkey and Germany, respectively. The chemical fertilizers produce the highest CEnC 27.87 % of the total in Turkey, and 31.49 % of the total in Germany. The highest contribution to the CExC is made by diesel in both countries: in Turkey 42.84 % and 31.01% in Germany. The most important contributor to carbon dioxide emission is made by the chemical fertilizers: 48.92% in Turkey, and 36.55% in Germany. A high contribution, 36.22%, to CCO_2E was made by irrigation in Germany.

The CEnC of the rye grain produced in Turkey is 3.5 MJ/kg and 1.8 MJ/kg in Germany while CExC of rye grain production 5.4 MJ/kg in Turkey and 2.4 MJ/kg in Germany (Table 3.7). The CCO_2E is 0.2 kg/kg rye grain in both countries. The diesel consumption comprises 61.58 % and 51.03% of the total CEnC in Turkey and Germany, respectively. The chemical fertilizers make the highest contribution to CEnC by 16.85% and 30.02% in Turkey and Germany, respectively. The highest contribution was made to the CExC by diesel utilization and seed production in both countries. The contribution of diesel to CExC is 36.88% and 35.48% in Turkey and Germany, respectively while contribution of the seeds to the CExC is 26.97% and 25.95% in Turkey and Germany, respectively. The most important contributor to carbon dioxide emission is irrigation in Turkey (30.83%) and the chemical fertilizers (39.44%) in Germany. When we compare the grains, rye agriculture require lower energy utilization and has lower values of CEnC, CExC and CCO_2E.

The values of CEnC, CExC and CCO_2E are presented for the wheat and rye grain agriculture in Turkey and Germany in Table 3.7, and for the bread making process in Table 3.8. The values of CEnC, CExC and CCO_2E were higher during hamburger bun production when compared to those of the wheat and rye bread production processes due to the higher weight loss occurring during the baking process. In both wheat and rye the bread making processes the flour production stage made the highest contribution to the calculated values

of CEnC, CExC and CCO_2E, whereas in the hamburger bun production process the flour production had the second highest contribution to the total after that of the dough production (Table 3.8).

Nylund and Erkkilä [160] after making measurements with 18 to 60 ton capacity trucks running under dynamic load cycles including simulations of transportation at freeway, highway and delivery conditions with the load ranging between 0 to 100 % of the total loading capacity of the trucks, reported that although the fuel consumption increases with the load, fuel consumption per ton of the load per km traveled decreases as the pay load increases. Their results varied substantially with the type of the truck and the engine. Large range of fuel consumption and carbon dioxide emission factor variations were also reported by the other researchers [161,162] under varying conditions of transportation. Therefore the carbon dioxide emission calculations of this study pertinent to transportation are valid under the conditions they are calculated and subject to change as the type, speed of transportation.

It is stated in Tables 3.4, 3.5 and 3.6 that 6269.5 MJ/ton wheat bread, 4726.6 MJ/ton rye bread and 6687.9 MJ/ton hamburger bun of exergy are destroyed during production of one ton of wheat bread, rye bread and hamburger buns. Tsatsarones [163] while discussing the definitions and nomenclature in exergy analysis states that the thermodynamic inefficiencies of a system, associated with the irreversibilities (entropy generation) cause exergy destruction within the system boundaries. The exergy destruction results in the transfer of exergy (through material and energy streams) to the surroundings.

Table 3.9 shows that the amount of the land required to produce the same amount of wheat in Turkey is 3.34 times of that required in Germany, this ratio is 2.30 with rye pointing the lower efficiency of the conversion of the solar energy into the grain mass in Turkey. The ratio of the values of the CDPs achieved in Germany to those achieved in Turkey is 3 with the wheat grain and 2 with the rye grain indicating the higher level of renewability of the German agriculture.

Table 3.7. The values of the CEnC, CExC and CCO_2E as calculated for wheat and rye grain agriculture in Turkey and Germany

	TURKEY			**GERMANY**		
Wheat grain						
	CEnC (MJ/kg)	CExC (MJ/kg)	CCO_2E (kg/kg)	CEnC MJ/kg)	CExC (MJ/kg)	CCO_2E (MJ/kg)
Wheat grain	5.4 MJ/kg	6.7 MJ/kg	0.3 kg/kg	1.9 MJ/kg	2.7 MJ/kg	0.2 kg/kg
Contribution of each input to the total (%)						
Diesel	57.27	42.84	17.00	58.88	31.01	8.13
Chemical fertilizers	27.87	9.43	48.92	31.49	9.12	36.55
Chemicals (pesticides)	5.18	4.86	1.75	4.29	3.52	0.84
Seed	4.97	26.83	7.35	4.12	19.42	3.51
Irrigation	0.56	1.88	14.31	2.46	7.24	36.22
Electricity	4.23	14.16	10.67	10.16	29.69	14.77
Rye grain						
	CEnC (MJ/kg)	CExC (MJ/kg)	CCO_2E (kg/kg)	CEnC (MJ/kg)	CExC (MJ/kg)	CCO_2E (kg/kg)
	3.5	5.4	0.2	1.8	2.4	0.2
Contribution of each input to the total (%)						
Diesel	61.58	36.88	16.48	51.03	35.48	8.72
Chemical fertilizers	16.85	10.80	28.15	30.02	9.41	39.44
Chemicals (pesticides)	7.41	5.57	2.28	6.14	5.36	1.21
Seed	6.24	26.97	8.39	5.17	25.95	4.45
Irrigation	1.34	3.57	30.83	2.63	8.21	38.84
Electricity	6.58	16.21	13.87	5.01	15.59	7.34

Table 3.8. The values of the CEnC, CExC and CCO_2E as calculated for the white bread and rye bread and hamburger bun production processes, and the percentage of contribution of each stage of the processes to the total

	Wheat bread			**Rye bread**			**Hamburger bun**		
	CEnC (MJ/kg)	**CExC (MJ/kg)**	**CCO_2E (kg/kg)**	**CEnC (MJ/kg)**	**CExC (MJ/kg)**	**CCO_2E (kg/kg)**	**CEnC (MJ/kg)**	**CExC (MJ/kg)**	**CCO_2E (kg/kg)**
	9.7	16.6	0.9	7.2	14.7	0.7	13.6	25.2	1.1
Contribution of each stage of the processes to the total (%)									
Agriculture	31.4	23.6	24.2	28.5	20.5	22.3	25.1	17.4	22.3
Flour making	40.0	31.6	29.6	32.7	28.9	28.3	27.8	23.3	27.0
Dough making	6.7	16.2	14.4	9.1	18.3	10.0	30.9	37.5	22.0
Fermentation	0.1	0.3	0.1	0.1	0.3	0.1	0.5	1.1	1.0
Baking	7.5	18.4	11.9	10.2	20.8	14.7	6.7	15.0	12.1
Cooling	0.4	0.9	0.6	0.5	1.0	0.7	0.3	0.6	0.5
Slicing	0.1	0.2	0.1	0.1	0.3	0.1	0.0	0.1	0.0
Packaging	4.5	3.8	1.7	6.1	4.3	2.2	2.0	1.6	1.0
Transportation	9.4	5.1	17.3	12.7	5.7	21.5	6.7	3.3	14.2

Table 3.9. Land, energy and exergy utilization per ton of wheat and rye bread and hamburger bun production in Turkey and Germany

	Wheat bread production in Turkey	**Wheat bread production in Germany**	**Rye bread production in Turkey**	**Rye bread production in Germany**	**Hamburger bun production in Turkey**	**Hamburger bun production in Germany**
Land utilization (ha/ton)	0.326	0.098	0.301	0.137	0.367	0.110
Energy utilization (MJ/ton)	18,200	15,300	15,400	14,100	21,400	18,100
Exergy utilization (MJ/ton)	20,500	17,900	18,500	17,100	25,800	22,900

3.3. SOURDOUGH

Mass of a bacterium is 8.23×10^{-13} g [164] and mass of yeast cell is 7.9×10^{-11} g [165]. The amounts of carbon dioxide, lactic acid, yeast and bacteria are calculated with data provided by Yondem, et al. (1992) [144] and summarized in Table 3.10. The amounts of other chemicals are found out by using equations (1) and (2). Kinetic models as used by Yöndem et al [144] are summarized in Table 2.14.

During leavening at 25°C when yeast to bacteria ratio was changing with 20 % increments between 0 to 100 %, the largest CO_2 production in 100 g dough, (2.40 g) and the largest expansion work (0.0216 kJ) was obtained with 80 % *S. cerevisiae* and 20 % *L. plantarum* inoculum. Therefore, the same yeast to bacteria colony ratio was assessed further for the temperatures of 20°C, 30°C, 35°C and 40°C. The energy and exergy changes in each case of the leavening process take place in Table 3.11. The optimum temperature was 35ºC under these conditions, where the CO_2 production for 100 g dough was the maximum (4.27 g CO_2) and the highest expansion work of 0.0334 kJ (Table 3.11). Variation of the microbial population, CO_2 and lactic acid production, heat generation and exergy loss with time during leavening with 80 % *S. cerevisiae* and 20 % *L. plantarum* at 25 and 35ºC is presented in Figure 3.4 and Figure 3.5, respectively. At other temperatures, the case at 35ºC led to the production of the maximum amount of CO_2. Although the amount of the lactic acid production was the same at both 20 and 35 ºC with 80 % *S. cerevisiae* and 20 % *L. plantarum* inoculum, amount of the CO_2 produced at 35ºC was almost two times of that of the levening carried out at 25ºC. Energy and exergy changes in each case of the leavening process are summarized in Table 3.11, and energy and exergy charts for leavening with different yeast-bacteria ratios for ten cases are presented in Figures 3.4-3.13 regarding Tables 3.10 and 3.11.

There are reports in the literature [76] indicating that the members of the initial inoculum survive in the dough, but the final population attained is always different. The reason for this observation is the heterogeneous nature of the dough, e.g., every micro-environment behaves like a different ecosystem, therefore the dough must be regarded as a heterogeneous ecosystem. The heterogeneous ecosystems started drawing attention recently [166, 167] and what they are describing is analogous to the conditions prevailing in the dough. In the forests, heterogeneity leads to the need for different forest services, whereas in the dough the variability causes proliferation of different microorganisms.

Sutherland et al.[167] after stating that structural attributes including forest age and forest type, understory plants, woody debris, had significant effects on the creation of distinct ecosystems, each of which may require different services. The nonhomogeneous physical conditions, e.g., compactness of the chemicals and chemical compounds, create the diversity in the dough. In the dough ecosystem metabolites created by one microorganism is made available to the others [79], if the nutrients are different in the micro-environment, even the promotion or inhibition of any member of the inoculum may eventually lead to the establishment of a totally different ecosystem. As a result, different goal function values, e.g., exergy utilization, as shown in Figure 3.15, may be observed. The peaks in Figure 3.15 refer to the conditions where the microorganisms were enjoying the most positive interaction. At these points metabolites produced by one organism may be uptaken by the other one; extracellular enzymes produced by one of the microorganisms may be helping both to enhance the growth. In the dough, presence of the fermentable sugars is highly limited [168]. Extracellular enzymes secreted any of the microorganisms may hydrolyze the large molecules, such as starch, and make them available for both of the species co-existing in the medium. Such a behavior make more exergy available for the microbial species. The mechanism of how extracellular enzyme production may help the microbial species to obtain nutrients for their further growth was described by Bayindirli et al. [169]. In Figure 3.15. At 35^{o}C the maximum exergy utilization was attained probably because of such a mechanism.

Table 3.10. Energy and exergy changes in each case of the leavening process

	ENERGY BALANCE TERMS (kJ)				**EXERGY BALANCE TERMS (kJ)**				
CASE	Energy utilization (kJ)	Expansion work (kJ)	Heat release (kJ)	Unused exergy (kJ)	Exergy utilization (kJ)	Expansion work (kJ)	Heat release (kJ)	Exergy destruction (kJ)	Unused exergy (kJ)
1	36.64	0.0263	0.37	36.24	85.52	0.0263	0.00362	28.12	57.37
2	45.95	0.0216	0.21	45.72	108.23	0.0216	0.0035	32.50	76.38
3	31.73	0.0148	0.59	31.13	74.57	0.0148	0.098	24.36	50.19
4	27.95	0.0116	0.98	26.96	64.18	0.0116	0.0165	19.87	44.28
5	10.88	0.0130	0.10	10.77	26.80	0.0130	0.0017	7.21	19.58
6	8.94	0.0045	2.40	6.54	12.24	0.0045	0.0445	0.81	11.38
7	8.64	0.0030	1.09	7.55	14.00	0.0030	0	2.23	11.94
8	58.33	0.0158	0.10	58.21	148.05	0.0158	0.0033	45.90	102.13
9	**77.00**	**0.0337**	**4.10**	**72.87**	**196.0**	**0.0337**	**0.20**	**60.81**	**135.06**
10	4.13	0.0042	0.41	3.72	11.25	0.0042	0.0262	1.12	10.10

Table 3.11. Yeast and bacteria growth, glucose consumption, lactic acid and CO_2 production, energy and exergy utilization, heat generation, exergy destruction and expansion work performance in each case of the experiments

CASE	Δn_{yeast} (mol)	$\Delta n_{bacteria}$ (mol)	Glucose (mol)	Lactic Acid (mol)	CO_2 (mol)	Energy utilization (kJ)	Exergy utilization (kJ)	Q (kJ)	$Ex_{destroyed}$ (kJ)	Expansion Work (kJ)
1	0.0037	-	0.0285	-	0.00440	36.64	85.52	-0.37	28.12	0.0263
2	**0.0019**	**0.0001**	**0.0361**	**0.0039**	**0.0527**	**45.95**	**108.23**	**-0.21**	**32.50**	**0.0216**
3	0.0014	0.0002	0.0244	0.0018	0.0369	31.73	74.57	-0.59	24.36	0.0148
4	0.0024	0.0004	0.0206	0.0026	0.0314	27.95	64.18	-0.98	19.87	0.0116
5	0.0008	0.0004	0.0082	0.0023	0.0114	10.88	26.80	-0.10	7.21	0.0130
6	-	0.0001	0.0040	0.0031	0.0074	8.94	12.24	-2.40	0.81	0.0044
7	0.0002	0.0001	0.0047	0.0025	0.0079	8.64	14.00	-1.09	2.23	0.0030
8	**0.0073**	**0.0002**	**0.0491**	**0.0026**	**0.0732**	**58.33**	**148.05**	**-0.10**	**45.90**	**0.0156**
9	**0.0043**	**0.0005**	**0.0654**	**0.0039**	**0.0971**	**77.00**	**196.07**	**-4.10**	**60.81**	**0.0334**
10	0.0000	0.0001	0.0037	0.0026	0.0040	4.13	11.25	-0.41	1.12	0.0042

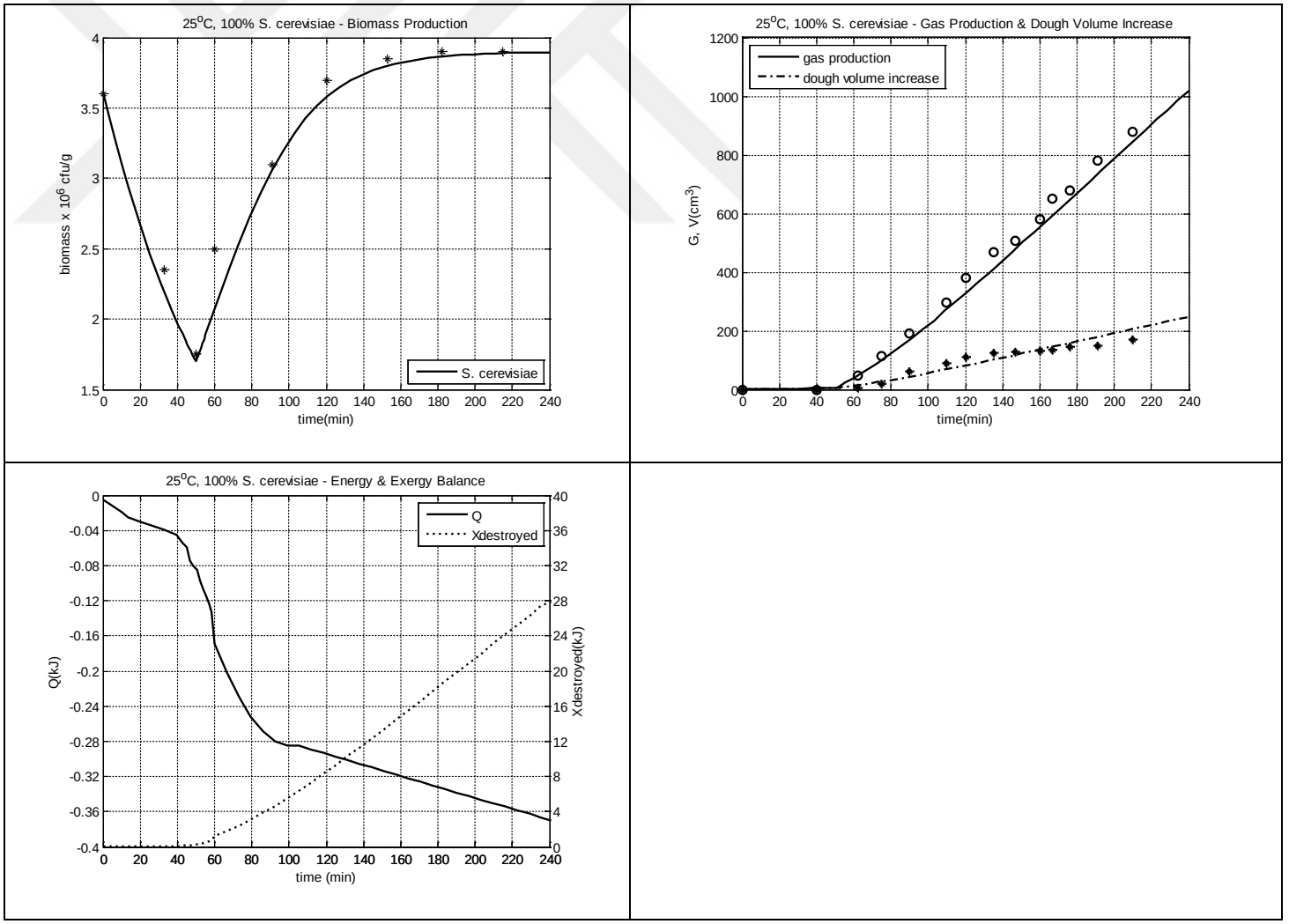

Figure 3.4. Kinetic and thermodynamic analysis for leavening with 100% *S. cerevisiae* and 0 % *L. plantarum* at 25 ºC.

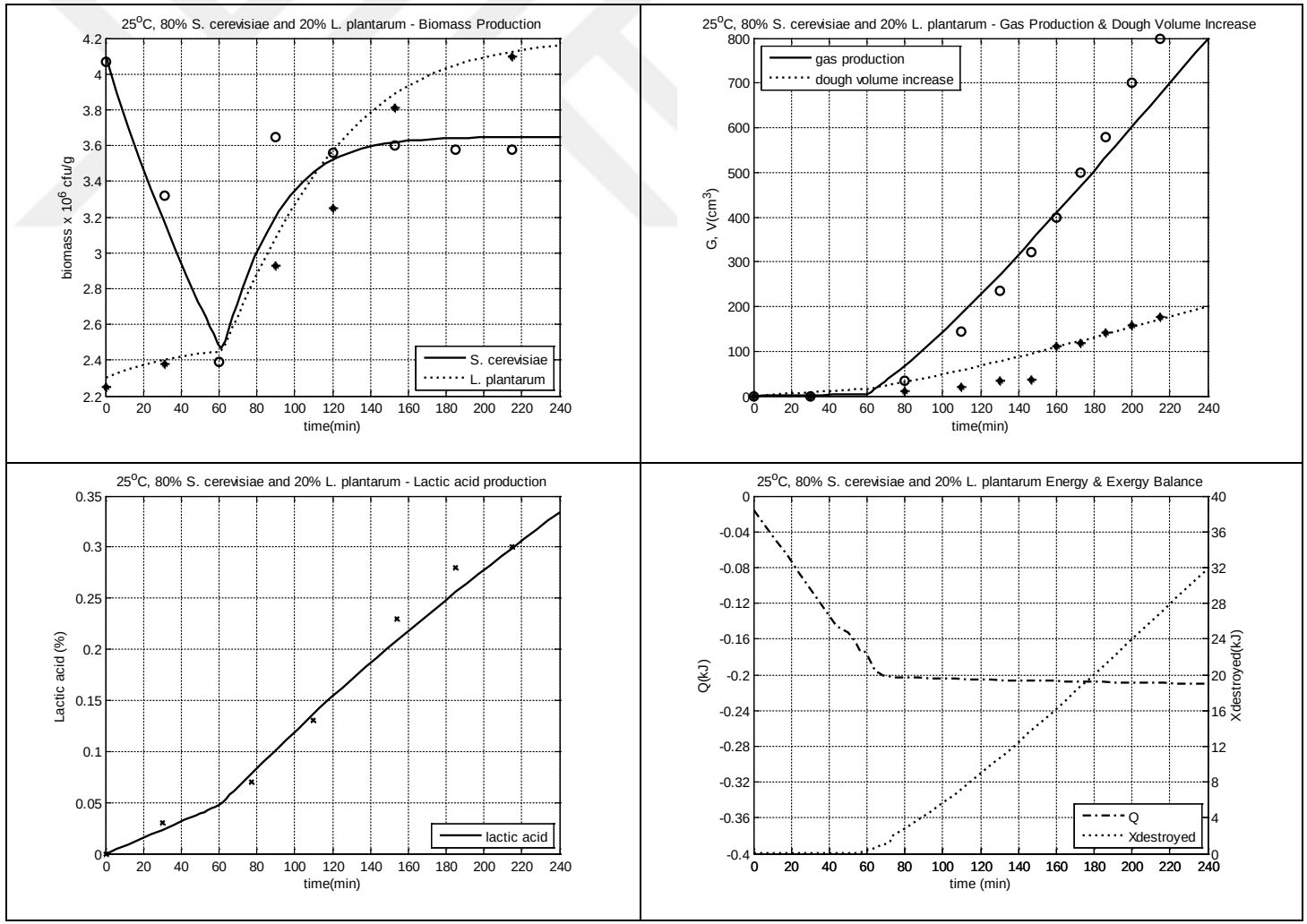

Figure 3.5. Kinetic and thermodynamic analysis for leavening with 80% *S. cerevisiae* and 20 % *L. plantarum* at 25 ºC

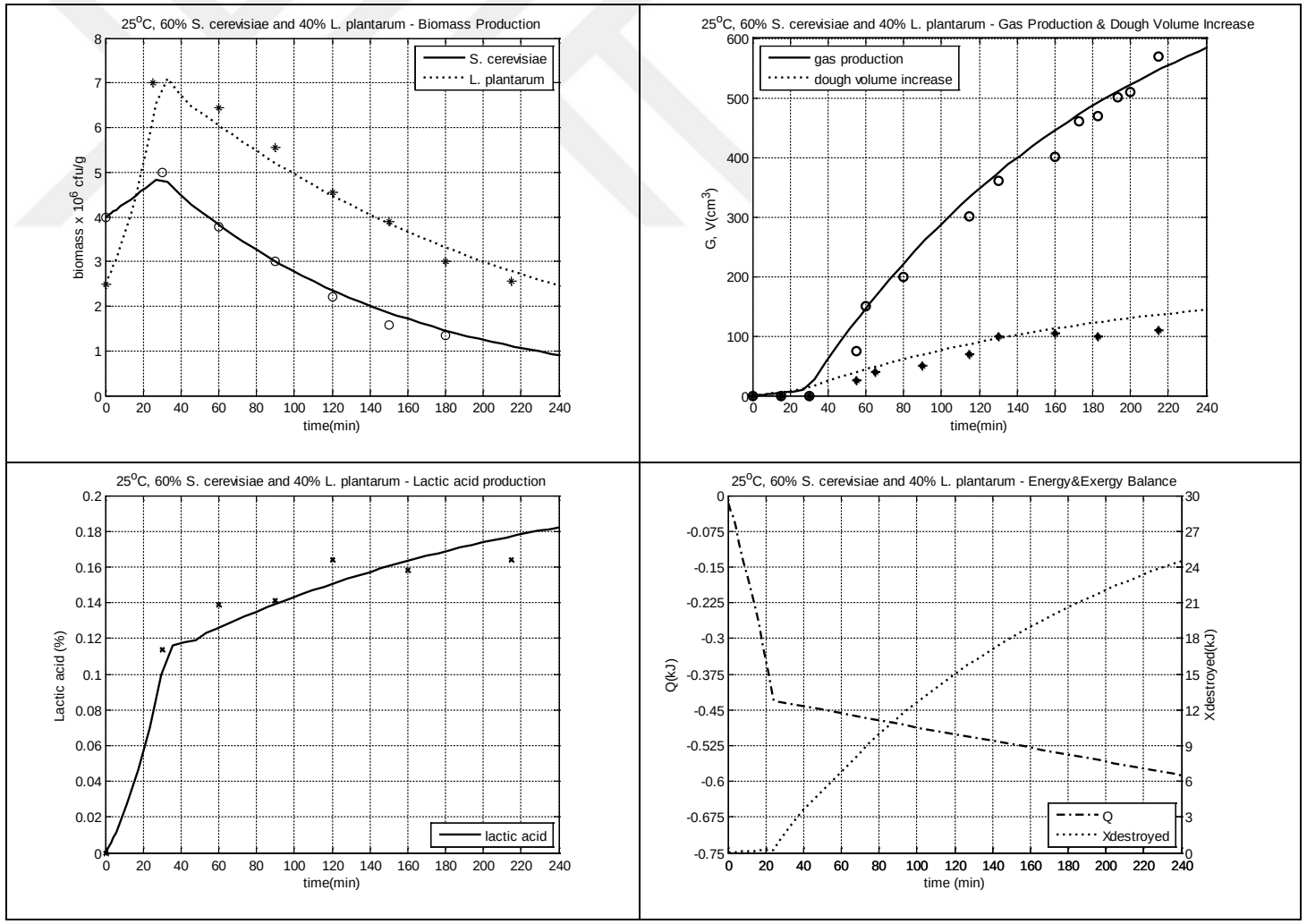

Figure 3.6. Kinetic and thermodynamic analysis for leavening with 60% *S. cerevisiae* and 40 % *L. plantarum* at 25 ºC

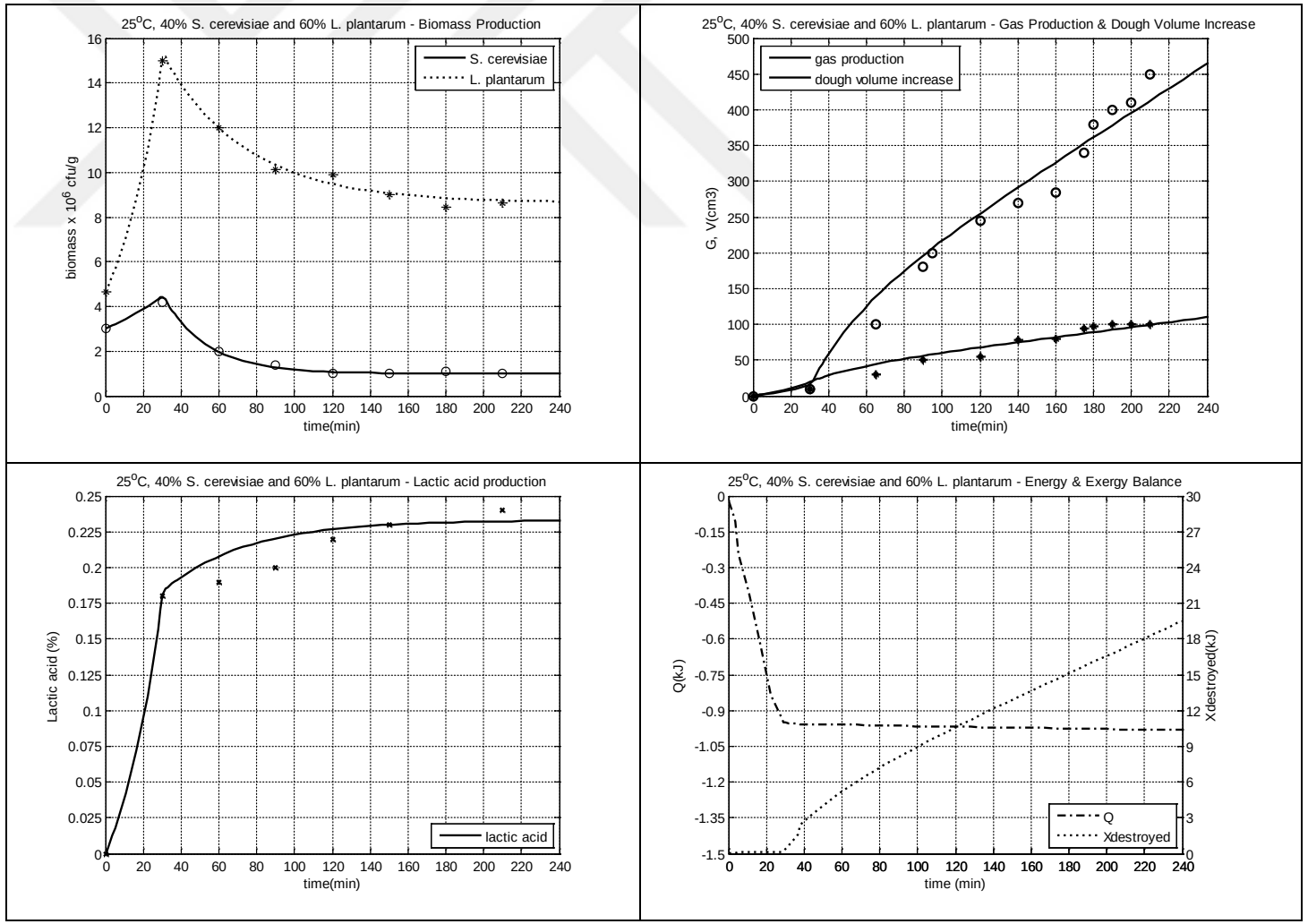

Figure 3.7. Kinetic and thermodynamic analysis for leavening with 40% *S. cerevisiae* and 60 % *L. plantarum* at 25 ºC

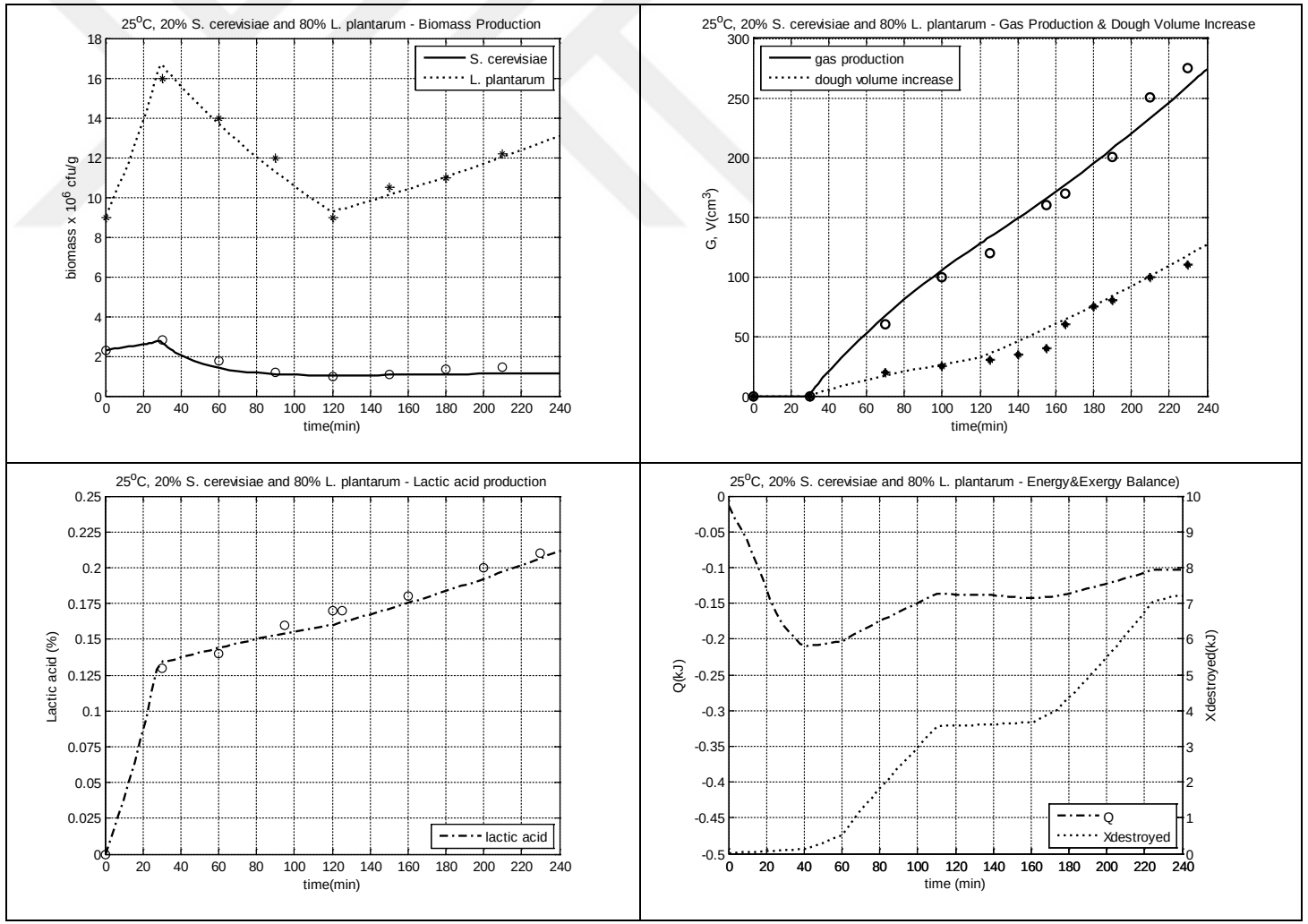

Figure 3.8. Kinetic and thermodynamic analysis for leavening with 20% *S. cerevisiae* and 80 % *L. plantarum* at 25 ºC

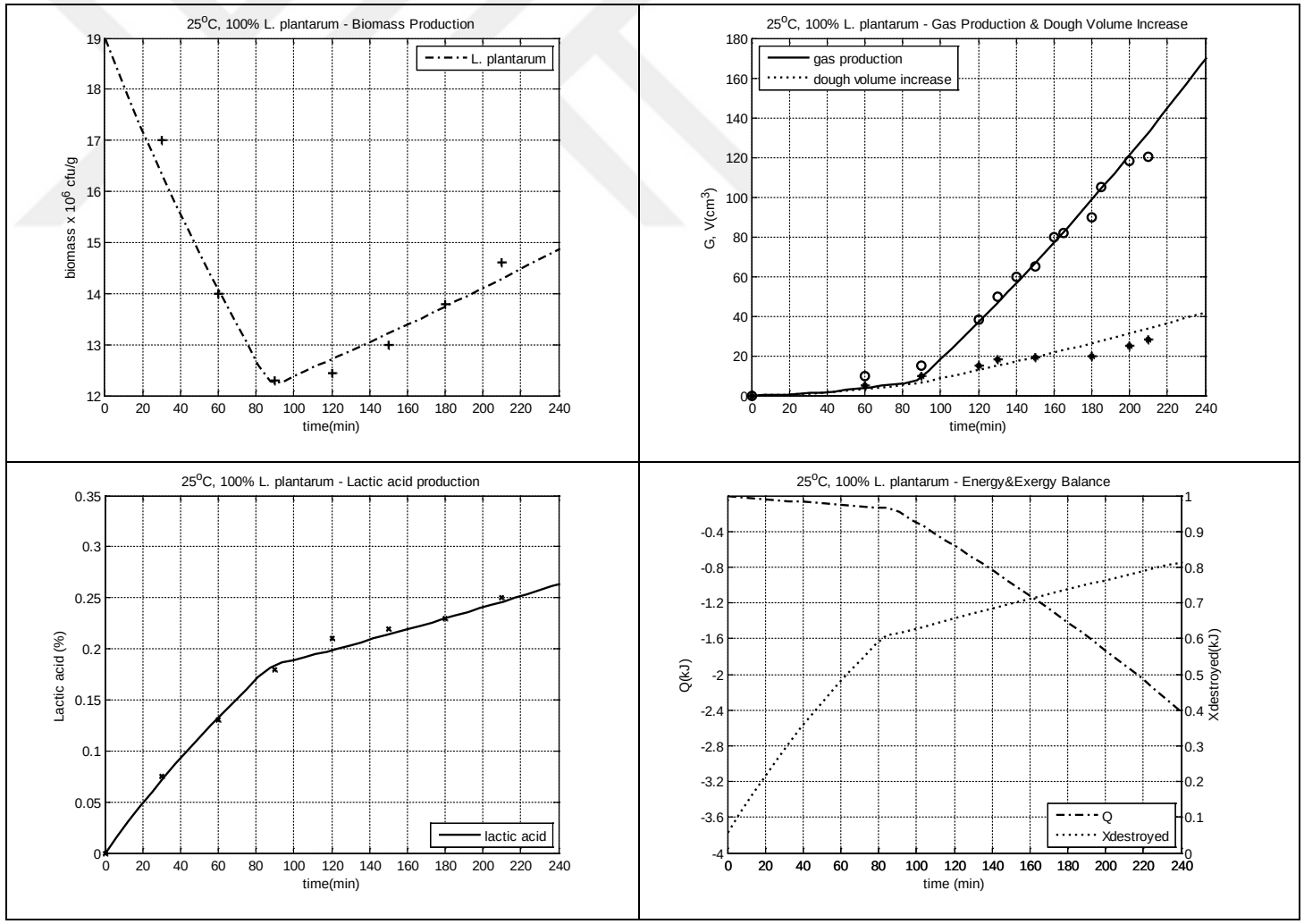

Figure 3.9. Kinetic and thermodynamic analysis for leavening with 0% *S. cerevisiae* and 100 % *L. plantarum* at 25 ºC

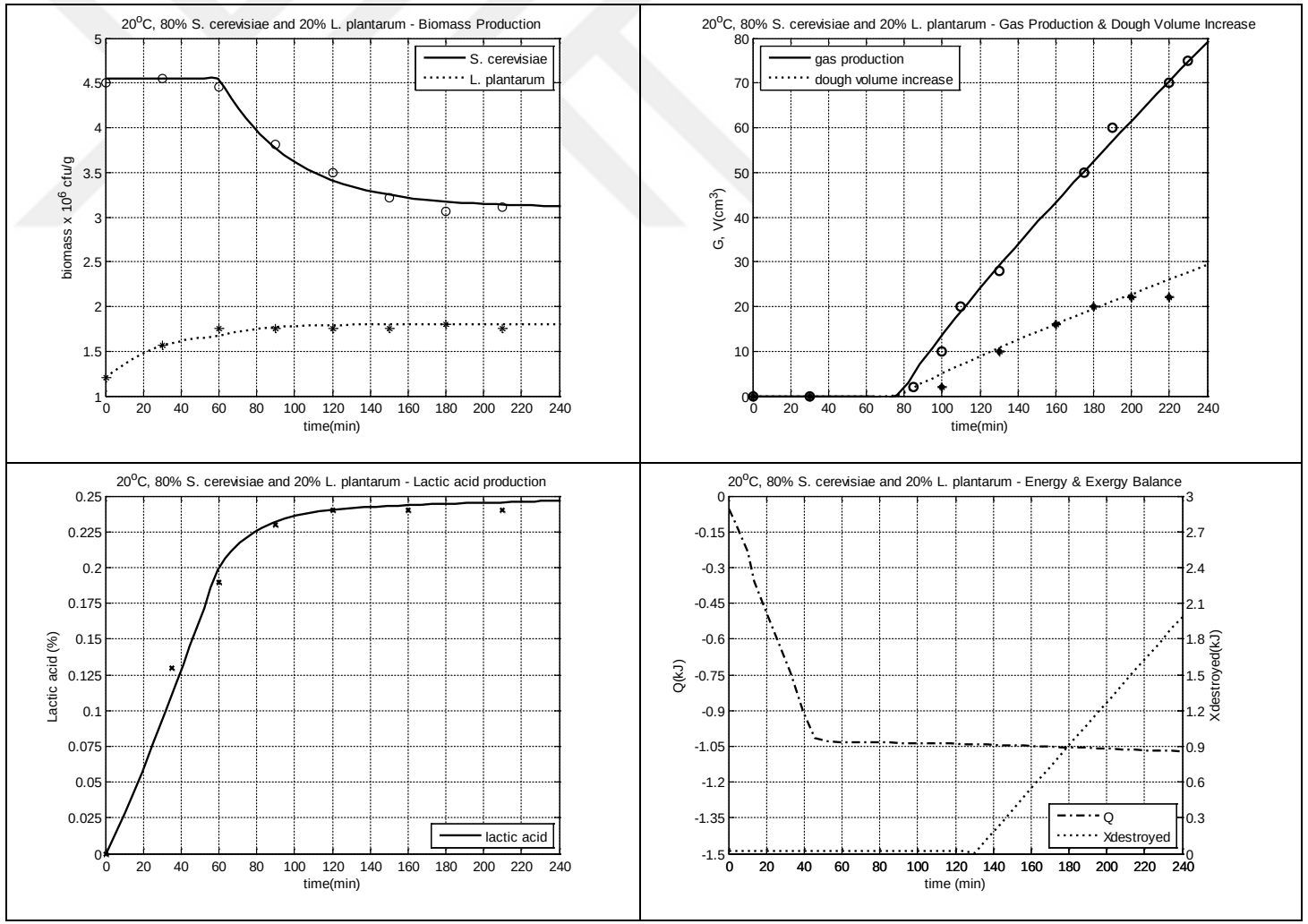

Figure 3.10. Kinetic and thermodynamic analysis for leavening with 80% *S. cerevisiae* and 20 % *L. plantarum* at 20 ºC

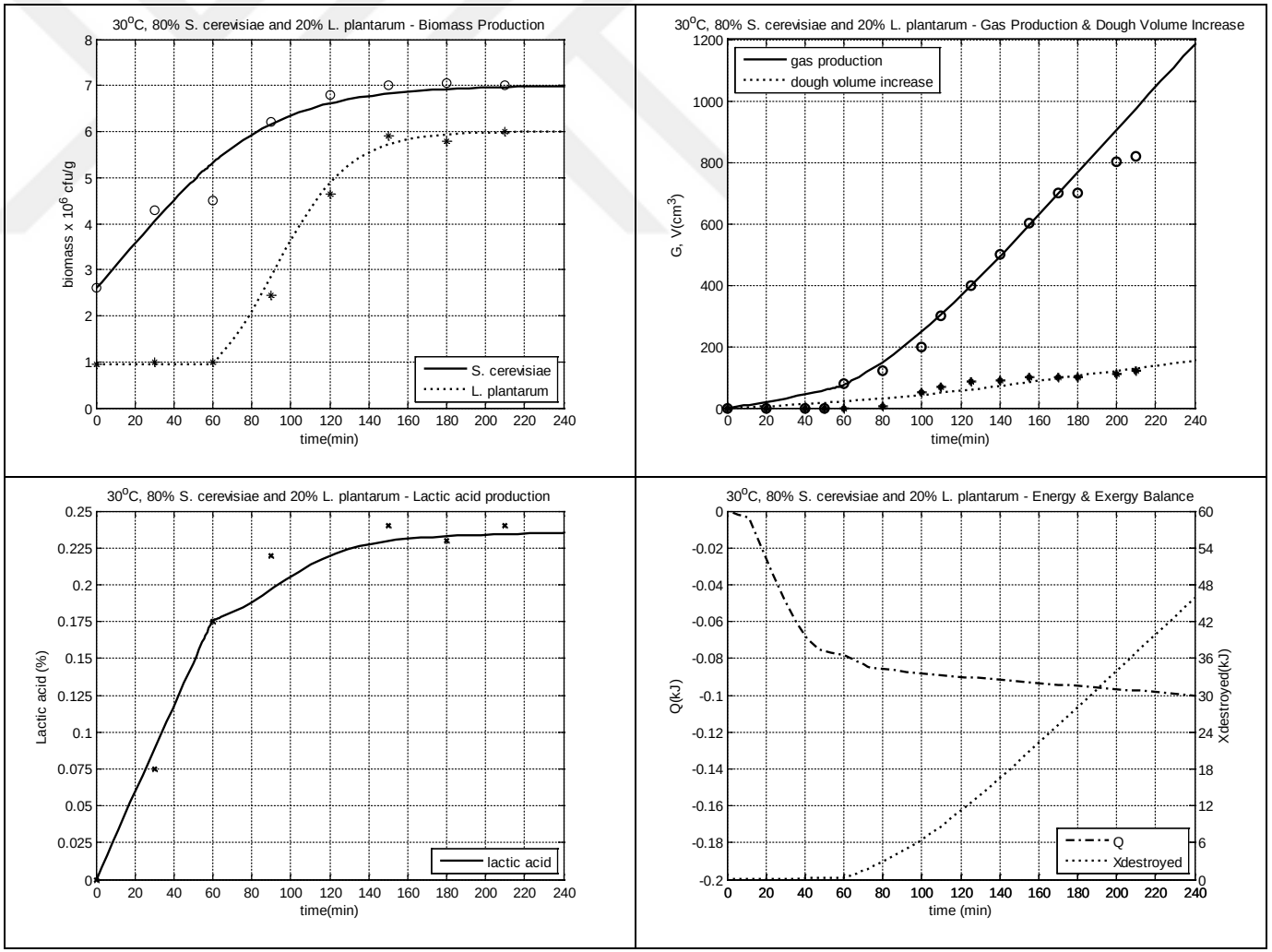

Figure 3.11. Kinetic and thermodynamic analysis for leavening with 80% *S. cerevisiae* and 20 % *L. plantarum* at 30 ºC

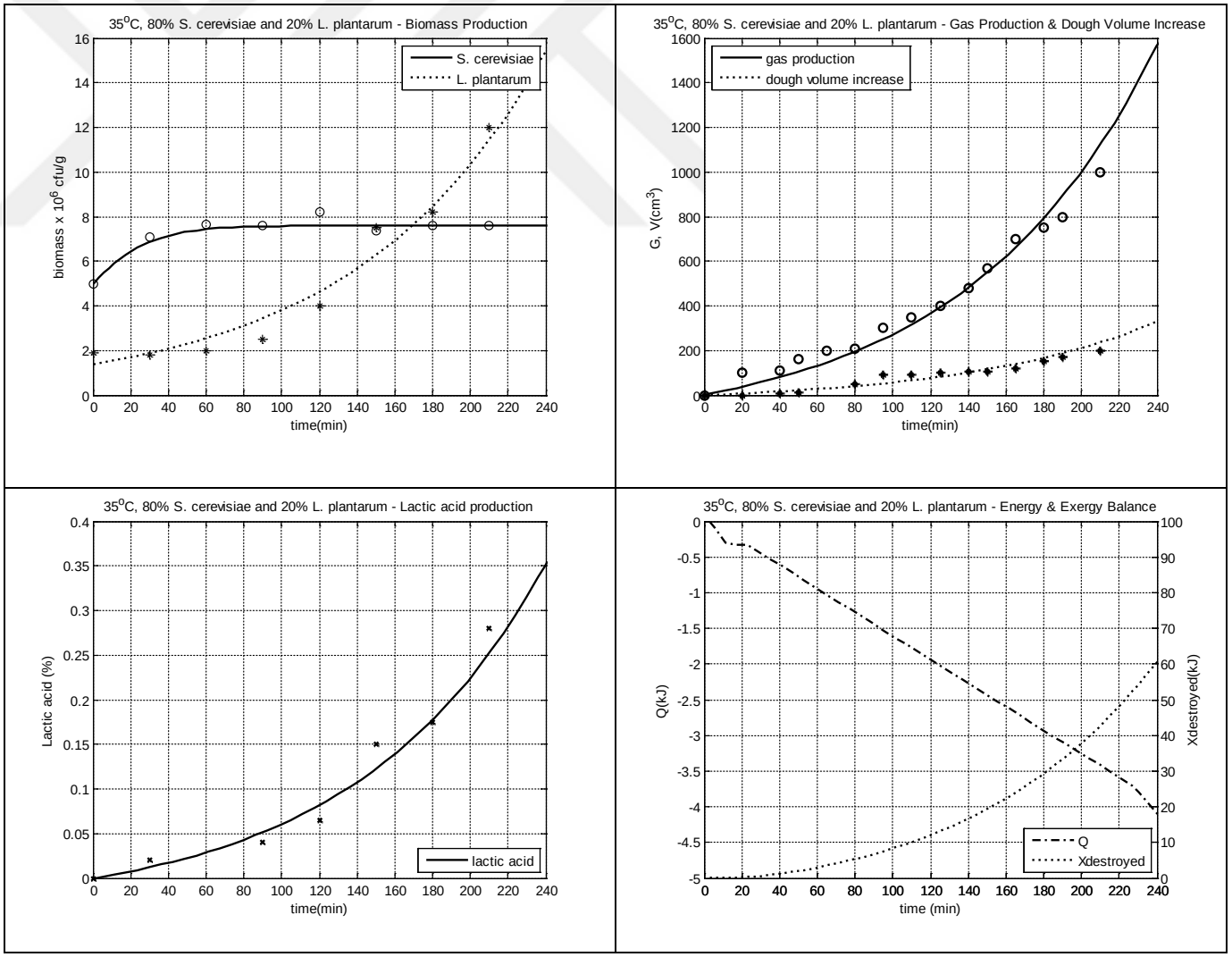

Figure 3.12. Kinetic and thermodynamic analysis for leavening with 80% *S. cerevisiae* and 20 % *L. plantarum* at 35 ºC

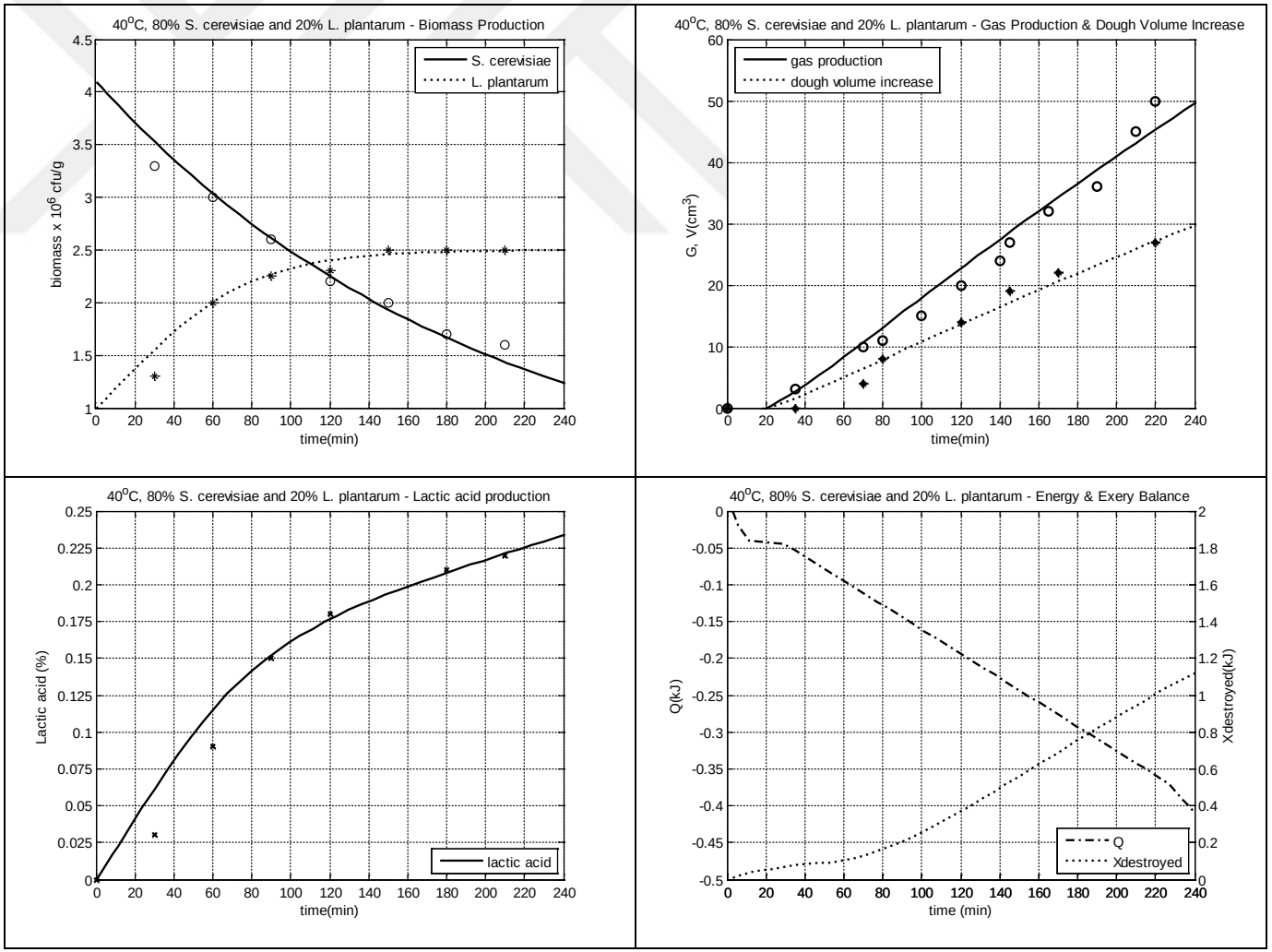

Figure 3.13. Kinetic and thermodynamic analysis for leavening with 80% *S. cerevisiae* and 20 % *L. plantarum* at 40 ºC

Maximum carbon dioxide production and dough volume were obtained in Model 9 and the energy-exergy flows are represented in Figure 3.14.

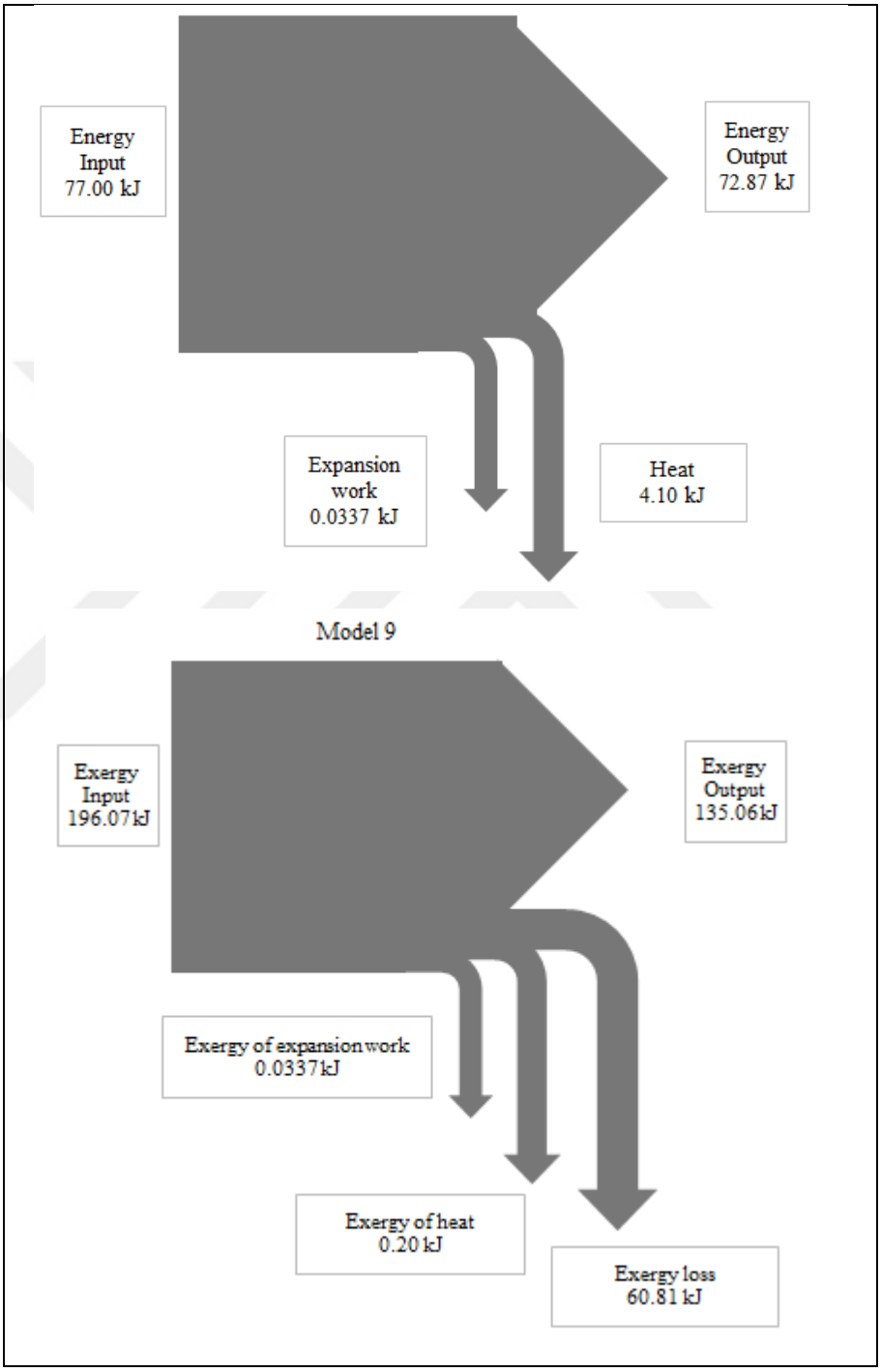

Figure 3.14. Energy and exergy charts for leavening with 80% yeast and 20% bacteria inoculum at 35ºC

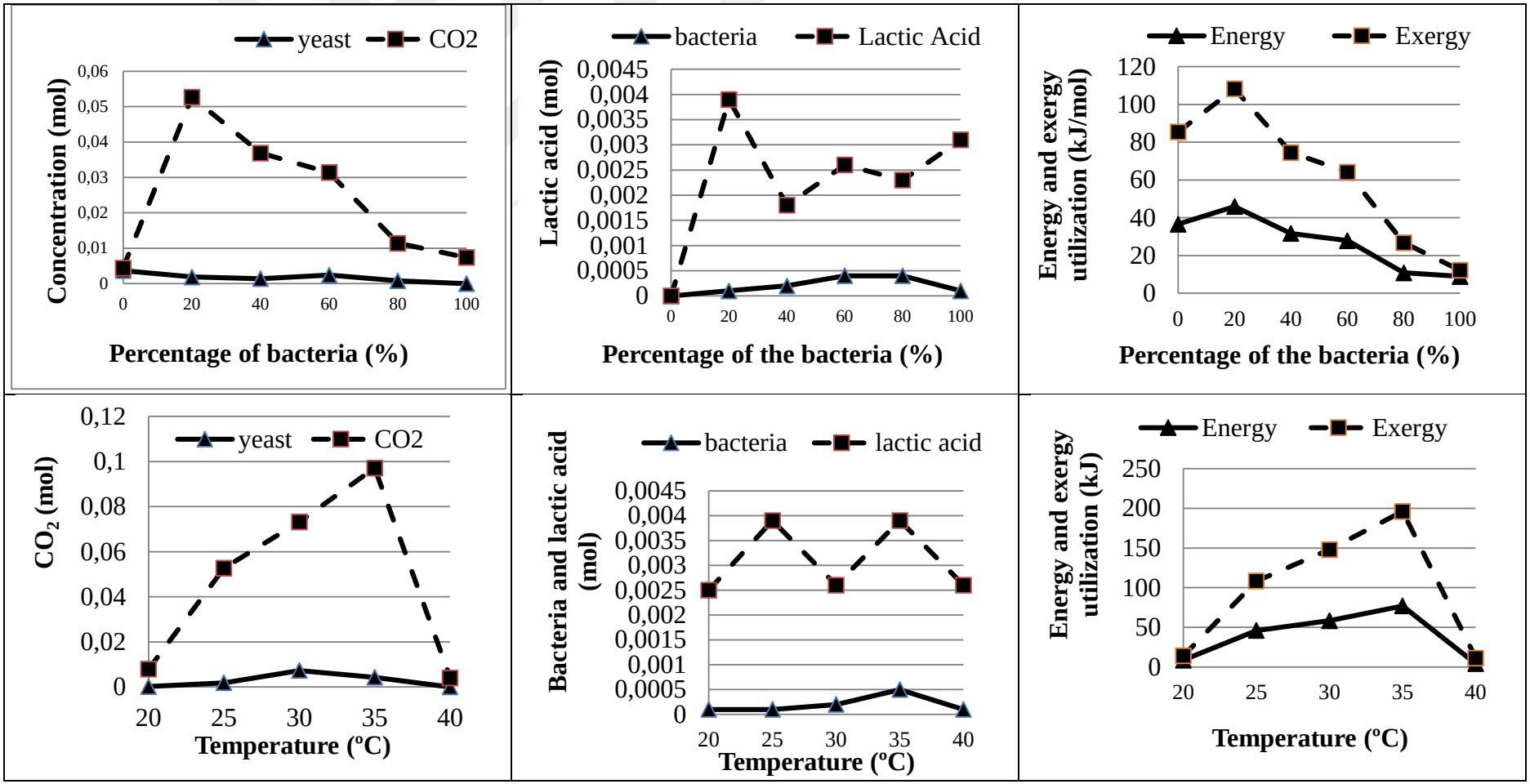

Figure 3.15. Variation of CO_2 and lactic acid production, energy and exergy utilization with the inoculum (% yeast and % bacteria) composition and the leavening temperature

4. CONLUSION

Kinetic and thermodynamic models provide great contribution to interpret experimental results to investigate the product yield, energy and exergy efficiency of biochemical processes. The study has three biochemical process investigated by kinetic models and thermodynamic laws.

The first study comprises the vaccine production of serogroup C antigen of *N. meningitidis* for three conditions: without control of pH and dissolved oxygen, pH control and dissolved oxygen control. Thermodynamic analysis shows that the maximum heat loss, entropy generation and exergy destruction per unit biomass produced was accounted in the pH controlled cultivation; implying that the microbial growth achieved under highly unfavorable conditions, by destructing high amounts of exergy, producing large amounts of heat, and generating entropy. The smallest heat and entropy production per unit biomass produced, and the smallest amount of exergy destruction per unit biomass cultivation are achieved when dissolved oxygen concentration is controlled to guarantee the presence of oxygen, the final electron acceptor of the energy metabolism. The exergetic efficiency of microbial production and antigen production are not parallel that the antigen is produced best under the stress conditions.

The second study comprises “farm to fork” bread production and shows all the steps in each process of breadmaking. Wheat bread, rye bread and hamburger bun production were analyzed for both Turkey and Germany. Table 3.9 shows that the amount of the land required to produce the same amount of wheat in Turkey is 3.34 times of that required in Germany, this ratio is 2.30 with rye pointing the lower efficiency of the conversion of the solar energy into the grain mass in Turkey. The ratio of the values of the CDPs achieved in Germany to those achieved in Turkey was 3 with the wheat grain and 2 with the rye grain indicating the higher level of renewability of the German agriculture. The ratio of the values of the CExCs and CEnCs (Table 3.7) achieved in Turkey to those achieved in Germany was 2.8 with the wheat grain and 2.25 with the rye grain indicating that in Turkey more than two times of the exergy and energy utilized in Germany was needed to produce the same amounts of grains. The ratio of the values of the CCO_2Es (Table 3.7) achieved in Turkey to those achieved in Germany was 1.5 with the wheat grain and 1.0 with the rye grain indicating that in Turkey 1.5 times of the carbon dioxide of that of

Germany was emitted to produce the same amount of wheat grains, while it was the same with rye in both countries. Specific energy utilization for rye bread production is almost the same in Turkey and Germany; but it is 12 % higher in Turkey for wheat bread and hamburger bun making processes (Table 3.9). Hamburger bun production requires the maximum energy utilization due to the higher weight loss in baking. The maximum amount of exergy, 6687.9 MJ, is destroyed during production of one ton hamburger buns (Tables 3.4, 3.5 and 3.6).

Third study comprises of the leavening process of sourdough with different ratios of *L. plantarum* and *S. cerevisiae*. Kinetic models are employed to simulate variation of the colony forming units of *L. plantarum* and *S. cerevisiae* in unit mass of dough during leavening. Apparent chemical reactions describing lactic acid fermentation by *L. plantarum* and alcoholic fermentation by *S. cerevisiae* in association with kinetic models of lactic acid and CO_2 production are employed together to calculate the exergy utilization rates. The inoculum of mixed cultures had a varying combination of the microorganisms between 0 to 100 %, with 20 % increments. Leavening was carried out with 5 ^oC of increments between 20 and 40 ^oC. The total exergy utilization in these experiments varied due to different patterns of interaction depending on the composition of the inoculum and the leavening temperature. The maximum exergy utilization occurred with the inoculum consisting of 80 % *S. cerevisiae* and 20 % *L. plantarum* at 35^oC. Under these conditions the maximum carbon dioxide production (42.7 g CO_2/kg dough), expansion work (0.334 kJ/kg dough) and dough volume increase (3,300 cm^3/kg dough) are obtained. These results indicate clearly that the exergy utilization and the microbial activity optima were actually the same, confirming the expectation that the microorganisms need to utilize exergy to maintain their activity and also appropriate microbial activity is needed to extract the required exergy from the dough.

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APPENDIX A: MATLAB CODES FOR KINETIC MODEL OF ANTIGEN PRODUCTION BY *NEISSERIA MENINGITIDIS*

CASE I: Without Control

Function m-file

```
function dx= sode_wout(t,x);
% This function models substrate consumption
mu = 0.6;
xmax = 1.83;
km=0.00005;

if t<=14;
    alpha = 0.0099;
    beta = 0.02;
    Yx=0.8;
    Yp=0.12;
    dx1 = mu*x(1)*(1-(x(1)/xmax));
    dx2 = alpha*x(1) + beta*dx1;
    dx3=-(((1/Yx)*dx1)+((1/Yp)*dx2)+(km*x(3)));
end
if t>14;
   alpha=0.0075;
   beta=0.00001;
   Yx=0.6;
   Yp=0.12;
    dx1 = mu*x(1)*(1-(x(1)/xmax));
    dx2 = alpha*x(1) + beta*dx1;
   dx3=-(((1/Yx)*dx1)+((1/Yp)*dx2)+(km*x(1)));
end

dx=[dx1; dx2;dx3];
```

Kinetic Model m-file

```
clear all
close all
format compact
global mu xmax

% enter the constants
mu=0.6;
xmax=1.83;

% enter the data
tData1=[0:2:16];
a=[0.06 0.11 0.35 1.10 1.55 1.83 1.80 1.8 1.8];
x1= [0.06; 0.11; 0.35; 1.10; 1.55; 1.83; 1.80; 1.8; 1.8];
ps = [0 0.004 0.016 0.03 0.075 0.108 0.163 0.20 0.22];
s = [5 4.6 4.42 3.8 2.5 2.0 1.7 1.2 1.0];

[t,x] = ode45('sode_wout', [0 16], [0.063 0 5]);

plot (t, x(:,1), 'k-.', 'LineWidth', 2.0)
hold on
[ax, h1, h2]=plotyy(t, x(:,3), t, x(:,2));

set(ax(1),'ylim',[0 5],'ytick',[0:5],'ycolor','black');
set(ax(2),'ylim',[0 0.25],'ytick',[0:0.05:0.25],'ycolor','black');
set(h1,'LineStyle',':','color','red','LineWidth',2);
set(h2,'LineStyle','-','color','blue','LineWidth',2);
legend ('biomass', 'substrate','product', 'Location', 'SouthEast');
plot(tData1, a, 'k+')
[ax, h3, h4]=plotyy(tData1, s, tData1, ps);
set(ax(1),'ylim',[0 5],'ytick',[0:5],'ycolor','black');
set(ax(2),'ylim',[0 0.25],'ytick',[0:0.05:0.25],'ycolor','black');
set(h3, 'LineStyle', '*', 'LineWidth', 2.0, 'Color', 'red');
```

```
set(h4, 'LineStyle', 'o', 'LineWidth', 2.0, 'Color', 'blue');
set(get(ax(1),'Ylabel'),'String','g/L');
set(get(ax(2),'Ylabel'),'String','g/L');
grid on
xlabel('t(h)')
title ('Kinetic Model - without control')
```

Entropy Script m-file

```
clear all
close all

MW_glu=180;
MW_ps=88000;
MW_GA=147.13;
MW_biomass=95;
RU=285;
T=308;
T0=298;

%H, S, b of glucose, oxygen, GA, water, co2, ps, biomass
H_data=[-1272.2; 0.294; -1001.6; -285; -393.6; -467711;-511.3];
S_data=[0.209; 0.205;  0.188; 0.0091; 0.215; 242; 0.138];
b_data=[2955; 3.97; 2393.2; 0.9; 19.48 ; 1591953;2037.1];

[t,x] = ode45('sode_wout', [0 16], [0.063 0 5]);

% ENERGY & ENTROPY BALANCE for without control

% maintenance
for i=1:48;
   n_glu_m(i,:)=((x(i,3)-x(i+1,3))/MW_glu)-(((x(i+1,1)-x(i,1))*0.55)/MW_glu)-
(((x(i+1,2)-x(i,2))*RU)/MW_ps);
```

```
    Nh_glu_m=n_glu_m*H_data(1,:);
    Nh_oxygen=n_glu_m*6*H_data(2,:);
    Nh_CO2=n_glu_m*6*H_data(5,:);
    Nh_water_m=n_glu_m*6*H_data(4,:);
    NS_glu_m=n_glu_m*S_data(1,:);
    NS_oxygen=n_glu_m*6*S_data(2,:);
    NS_CO2=n_glu_m*6*S_data(5,:);
    NS_water_m=n_glu_m*6*S_data(4,:);
end

Qin_m=Nh_glu_m+Nh_oxygen;
Qout_m=Nh_CO2+Nh_water_m;
Q_m=cumsum(Qout_m-Qin_m);


NSin_m=NS_glu_m+NS_oxygen;
NSout_m=NS_CO2+NS_water_m;
deltaS_m=cumsum(NSout_m-NSin_m);
Sgen_m=deltaS_m-(Q_m/T);


%polysaccharide production part
for i=1:48;
    n_ps(i,:)=((x(i+1,2)-x(i,2))/MW_ps);
    Nh_glu_ps=n_ps*RU*H_data(1,:);
    Nh_GA_ps=n_ps*RU*H_data(3,:);
    Nh_water_ps=n_ps*RU*H_data(4,:);
    Nh_ps=n_ps*H_data(6,:);
    NS_glu_ps=n_ps*RU*S_data(1,:);
    NS_GA_ps=n_ps*RU*S_data(3,:);
    NS_water_ps=n_ps*RU*S_data(4,:);
    NS_ps=n_ps*S_data(6,:);
end
```

```
Qin_ps=Nh_glu_ps+Nh_GA_ps;
Qout_ps=Nh_ps+Nh_water_ps;
Q_ps=cumsum(Qout_ps-Qin_ps);

NSin_ps=NS_glu_ps+NS_GA_ps;
NSout_ps=NS_ps+NS_water_ps;
deltaS_ps=cumsum(NSout_ps-NSin_ps);
Sgen_ps=deltaS_ps-(Q_ps/T);

% substrate entering bacteria structure
for i=1:48;
m_biomass(i,:)=x(i+1,1)-x(i,1);
   n_biomass=m_biomass/MW_biomass;
   n_glu_biomass=(m_biomass*0.55)/MW_glu;
   n_GA_biomass=(m_biomass*0.15)/MW_GA;

   Nh_glu_biomass=n_glu_biomass*H_data(1,:);
   Nh_GA_biomass=n_GA_biomass*H_data(3,:);
   Nh_biomass=n_biomass*H_data(7,:);
   NS_glu_biomass=n_glu_biomass*S_data(1,:);
   NS_GA_biomass=n_GA_biomass*S_data(3,:);
   NS_biomass=n_biomass*S_data(7,:);
end

Qin_b=Nh_glu_biomass+Nh_GA_biomass;
Qout_b=Nh_biomass;
Q_b=cumsum(Qout_b-Qin_b);

NSin_b=NS_glu_biomass+NS_GA_biomass;
NSout_b=NS_biomass;
deltaS_b=cumsum(NSout_b-NSin_b);
Sgen_b=deltaS_b-(Q_b/T);
```

```
% TOTAL ENTROPY GENERATION
Sgen_total=Sgen_m+Sgen_ps+Sgen_b;

for i=1:48;
   time(i)=t(i+1);
end

plot (time,Sgen_total, 'k-', 'Linewidth',2)
hold on
plot (time,Sgen_m,'k:', 'Linewidth',2)
hold on
plot (time,Sgen_ps, 'k-.', 'Linewidth',2)
hold on
plot (time, Sgen_b, 'k--', 'Linewidth',2)

xlabel('time(h)')
ylabel('Sgen (kJ/K)')
legend('Sgen total','Sgen maintenance','Sgen PS','Sgen biomass','location','Northwest')
title ('Entropy Balance - without control')

grid on
xlim([0 16])
ylim([-0.02 0.20])
```

Energy – Exergy script m-file

```
clear all
close all

MW_glu=180;
MW_ps=88000;
MW_GA=147.13;
MW_biomass=95;
RU=285;
```

```
T=308;
T0=298;

%H, S, b of glucose, oxygen, GA, water, co2, ps, biomass
H_data=[-1272.2; 0.294; -1001.6; -285; -393.6; -467711;-511.3];
S_data=[0.209; 0.205;  0.188; 0.0091; 0.215; 242; 0.138];
b_data=[2955; 3.97; 2393.2; 0.9; 19.48 ; 1591953;2037.1];

[t,x] = ode45('sode_wout', [0 16], [0.063 0 5]);

% ENERGY AND EXERGY BALANCE for without control

% maintenance
for i=1:48;
   n_glu_m(i,:)=((x(i,3)-x(i+1,3))/MW_glu)-(((x(i+1,1)-x(i,1))*0.55)/MW_glu)-
(((x(i+1,2)-x(i,2))*RU)/MW_ps);
   Nh_glu_m=n_glu_m*H_data(1,:);
   Nh_oxygen=n_glu_m*6*H_data(2,:);
   Nh_CO2=n_glu_m*6*H_data(5,:);
   Nh_water_m=n_glu_m*6*H_data(4,:);
   Nb_glu_m=n_glu_m*b_data(1,:);
   Nb_oxygen=n_glu_m*6*b_data(2,:);
   Nb_CO2=n_glu_m*6*b_data(5,:);
   Nb_water_m=n_glu_m*6*b_data(4,:);
end

%polysaccharide production part
for i=1:48;
   n_ps(i,:)=((x(i+1,2)-x(i,2))/MW_ps);
   Nh_glu_ps=n_ps*RU*H_data(1,:);
   Nh_GA_ps=n_ps*RU*H_data(3,:);
   Nh_water_ps=n_ps*RU*H_data(4,:);
   Nh_ps=n_ps*H_data(6,:);
```

```
    Nb_glu_ps=n_ps*RU*b_data(1,:);
    Nb_GA_ps=n_ps*RU*b_data(3,:);
    Nb_water_ps=n_ps*RU*b_data(4,:);
    Nb_ps=n_ps*b_data(6,:);
end

% substrate entering bacteria structure
for i=1:48;
    m_biomass(i,:)=x(i+1,1)-x(i,1);
    n_biomass=m_biomass/MW_biomass;
    n_glu_biomass=(m_biomass*0.55)/MW_glu;
    n_GA_biomass=(m_biomass*0.15)/MW_GA;

    Nh_glu_biomass=n_glu_biomass*H_data(1,:);
    Nh_GA_biomass=n_GA_biomass*H_data(3,:);
    Nh_biomass=n_biomass*H_data(7,:);

    Nb_glu_biomass=n_glu_biomass*b_data(1,:);
    Nb_GA_biomass=n_GA_biomass*b_data(3,:);
    Nb_biomass=n_biomass*b_data(7,:);
end

Qin=Nh_glu_biomass+Nh_GA_biomass+Nh_glu_ps+Nh_GA_ps+Nh_glu_m+Nh_oxygen
;
Qout=Nh_biomass+Nh_ps+Nh_water_ps+Nh_CO2+Nh_water_m;
Q_total=cumsum(Qout-Qin);


Nbin=Nb_glu_biomass+Nb_GA_biomass+Nb_glu_m+Nb_oxygen+Nb_glu_ps+Nb_GA_p
s;
Nbout=Nb_biomass+Nb_CO2+Nb_water_m+Nb_ps+Nb_water_ps;
deltab=Nbin-Nbout;
Xdestroyed=cumsum(deltab)-Q_total*(1-(T0/T));
```

```
% antigen exergy efficiency calculation
Qin_ps=Nh_glu_ps+Nh_GA_ps;
Qout_ps=Nh_ps+Nh_water_ps;
Q_ps=cumsum(Qout_ps-Qin_ps);

Nbin_ps=Nb_glu_ps+Nb_GA_ps;
Nbout_ps=Nb_ps+Nb_water_ps;
deltab_ps=Nbin_ps-Nbout_ps;
Xdestroyed_ps=cumsum(deltab_ps)-Q_ps*(1-(T0/T));

disp('The exergetic efficieny of antigen production is %')
eff=sum(n_ps*b_data(6,:))/sum(Xdestroyed)*100
disp('Q_ps/Q_total is %')
q_ratio=sum(Q_ps)/sum(Q_total)*100

for i=1:48;
   time(i)=t(i+1);
end

[ax, h1, h2]=plotyy(time, Q_total, time, Xdestroyed)
 set(ax,'xlim',[0 16],'xtick',[0:2:16]);

set(get(ax(1),'Ylabel'),'String','Q(kJ/mole)')
set(get(ax(2),'Ylabel'),'String','Xdestroyed(kJ/mole)')

xlabel ('time (h)')
title ('Energy&Exergy Balance - without control')

set(ax(1),'ylim',[-100 0],'ytick',[-100:10:0],'ycolor','black');
set(ax(2),'ylim',[0 50],'ytick',[0:10:50],'ycolor','black');


set(h1,'LineStyle','-.','color','black','LineWidth',2);
```

```
set(h2,'LineStyle',':','color','black','LineWidth',2);
legend ('Q', 'Xdestroyed','Location', 'NorthEast');
legend ('Q', 'Xdestroyed','Location', 'NorthEast');

grid on
```

CASE II: pH Control

Function m-file

```
function dx= sode_pH(t,x);
% This function models substrate consumption
global alpha beta

mu = 0.65;
xmax = 2.05;
km=0.41;

alpha = 0.004;
beta = 0.038;
Yx=2.7;
Yp=2.3;
dx1 = mu*x(1)*(1-(x(1)/xmax));
dx2 = alpha*x(1) + beta*dx1;
dx3=-(((1/Yx)*dx1)+((1/Yp)*dx2)+(km*x(1)));

dx=[dx1; dx2;dx3];
```

Kinetic Model m-file

```
clear all
close all
format compact
global mu xmax

% enter the constants
```

```
mu=0.65;
xmax=2.05;

[t,x] = ode45('sode_pH', [0 10], [0.06 0 5]);

% enter the data
tData1=[0:2:10];
a=[0.1 0.260 0.600 1.380 1.850 2.05];
ps = [0 0.010 0.015 0.050 0.080 0.100];
s = [5 4.45 4.3 3.5 2.0 0.32];

plot (t, x(:,1), 'k-.', 'LineWidth', 2.0)
hold on
[ax, h1, h2]=plotyy(t, x(:,3), t, x(:,2));

set(ax(1),'ylim',[0 5],'ytick',[0:5],'ycolor','black');
set(ax(2),'ylim',[0 0.25],'ytick',[0:0.05:0.25],'ycolor','black');
set(h1,'LineStyle',':','color','red','LineWidth',2);
set(h2,'LineStyle','-','color','blue','LineWidth',2);
legend ('biomass', 'substrate','product', 'Location', 'NorthEast');
plot(tData1, a, 'k+')
[ax, h3, h4]=plotyy(tData1, s, tData1, ps);
set(ax(1),'ylim',[0 5],'ytick',[0:5],'ycolor','black');
set(ax(2),'ylim',[0 0.25],'ytick',[0:0.05:0.25],'ycolor','black');
set(h3, 'LineStyle', '*', 'LineWidth', 2.0, 'Color', 'red');
set(h4, 'LineStyle', 'o', 'LineWidth', 2.0, 'Color', 'blue');
set(get(ax(1),'Ylabel'),'String','g/L');
set(get(ax(2),'Ylabel'),'String','g/L');
grid on
xlabel('t(h)')
title ('Kinetic Model - pH control')
```

Entropy Script m-file

```
clear all
close all

MW_glu=180;
MW_ps=88000;
MW_GA=147.13;
MW_biomass=95;
RU=285;
T=308;
T0=298;

%H, S, b of glucose, oxygen, GA, water, co2, ps, biomass
H_data=[-1272.2; 0.294; -1001.6; -285; -393.6; -467711;-511.3];
S_data=[0.209; 0.205;  0.188; 0.0091; 0.215; 242; 0.138];
b_data=[2955; 3.97; 2393.2; 0.9; 19.48 ; 1591953;2037.1];

[t,x] = ode45('sode_pH', [0 10], [0.06 0 5]);

% ENERGY & ENTROPY BALANCE for pH control
 % maintenance
for i=1:48;
   n_glu_m(i,:)=((x(i,3)-x(i+1,3))/MW_glu)-(((x(i+1,1)-x(i,1))*0.55)/MW_glu)-
(((x(i+1,2)-x(i,2))*RU)/MW_ps);
   Nh_glu_m=n_glu_m*H_data(1,:);
   Nh_oxygen=n_glu_m*6*H_data(2,:);
   Nh_CO2=n_glu_m*6*H_data(5,:);
   Nh_water_m=n_glu_m*6*H_data(4,:);
   NS_glu_m=n_glu_m*S_data(1,:);
   NS_oxygen=n_glu_m*6*S_data(2,:);
   NS_CO2=n_glu_m*6*S_data(5,:);
   NS_water_m=n_glu_m*6*S_data(4,:);
end
```

```
Qin_m=Nh_glu_m+Nh_oxygen;
Qout_m=Nh_CO2+Nh_water_m;
Q_m=cumsum(Qout_m-Qin_m);

NSin_m=NS_glu_m+NS_oxygen;
NSout_m=NS_CO2+NS_water_m;
deltaS_m=cumsum(NSout_m-NSin_m);
Sgen_m=deltaS_m-(Q_m/T);

%polysaccharide production part
for i=1:48;
   n_ps(i,:)=((x(i+1,2)-x(i,2))/MW_ps);
   Nh_glu_ps=n_ps*RU*H_data(1,:);
   Nh_GA_ps=n_ps*RU*H_data(3,:);
   Nh_water_ps=n_ps*RU*H_data(4,:);
   Nh_ps=n_ps*H_data(6,:);
   NS_glu_ps=n_ps*RU*S_data(1,:);
   NS_GA_ps=n_ps*RU*S_data(3,:);
   NS_water_ps=n_ps*RU*S_data(4,:);
   NS_ps=n_ps*S_data(6,:);
end

Qin_ps=Nh_glu_ps+Nh_GA_ps;
Qout_ps=Nh_ps+Nh_water_ps;
Q_ps=cumsum(Qout_ps-Qin_ps);

NSin_ps=NS_glu_ps+NS_GA_ps;
NSout_ps=NS_ps+NS_water_ps;
deltaS_ps=cumsum(NSout_ps-NSin_ps);
Sgen_ps=deltaS_ps-(Q_ps/T);

% substrate entering bacteria structure
for i=1:48;
```

```
m_biomass(i,:)=x(i+1,1)-x(i,1);
   n_biomass=m_biomass/MW_biomass;
   n_glu_biomass=(m_biomass*0.55)/MW_glu;
   n_GA_biomass=(m_biomass*0.15)/MW_GA;

   Nh_glu_biomass=n_glu_biomass*H_data(1,:);
   Nh_GA_biomass=n_GA_biomass*H_data(3,:);
   Nh_biomass=n_biomass*H_data(7,:);
   NS_glu_biomass=n_glu_biomass*S_data(1,:);
   NS_GA_biomass=n_GA_biomass*S_data(3,:);
   NS_biomass=n_biomass*S_data(7,:);
end

Qin_b=Nh_glu_biomass+Nh_GA_biomass;
Qout_b=Nh_biomass;
Q_b=cumsum(Qout_b-Qin_b);

NSin_b=NS_glu_biomass+NS_GA_biomass;
NSout_b=NS_biomass;
deltaS_b=cumsum(NSout_b-NSin_b);
Sgen_b=deltaS_b-(Q_b/T);

% TOTAL ENTROPY GENERATION
Sgen_total=Sgen_m+Sgen_ps+Sgen_b;

for i=1:48;
   time(i)=t(i+1);
end

plot (time,Sgen_total, 'k-', 'Linewidth',2)
hold on
plot (time,Sgen_m,'k:', 'Linewidth',2)
hold on
```

```
plot (time,Sgen_ps, 'k-.', 'Linewidth',2)
hold on
plot (time, Sgen_b, 'k--', 'Linewidth',2)

xlabel('time(h)')
ylabel('Sgen (kJ/K)')
legend('Sgen total','Sgen maintenance','Sgen PS','Sgen biomass','location','Northwest')
title ('Entropy Balance - pH control')

grid on
xlim([0 10])
ylim([-0.02 0.20])
```

Energy – Exergy script m-file

```
clear all
close all
 MW_glu=180;
MW_ps=88000;
MW_GA=147.13;
MW_biomass=95;
RU=285;
T=308;
T0=298;

%H, S, b of glucose, oxygen, GA, water, co2, ps, biomass
H_data=[-1272.2; 0.294; -1001.6; -285; -393.6; -467711;-511.3];
S_data=[0.209; 0.205;  0.188; 0.0091; 0.215; 242; 0.138];
b_data=[2955; 3.97; 2393.2; 0.9; 19.48 ; 1591953;2037.1];



[t,x] = ode45('sode_pH', [0 10], [0.06 0 5]);
```

```
% ENERGY AND EXERGY BALANCE for without control

% maintenance
for i=1:48;
   n_glu_m(i,:)=((x(i,3)-x(i+1,3))/MW_glu)-(((x(i+1,1)-x(i,1))*0.55)/MW_glu)-
(((x(i+1,2)-x(i,2))*RU)/MW_ps);
   Nh_glu_m=n_glu_m*H_data(1,:);
   Nh_oxygen=n_glu_m*6*H_data(2,:);
   Nh_CO2=n_glu_m*6*H_data(5,:);
   Nh_water_m=n_glu_m*6*H_data(4,:);
   Nb_glu_m=n_glu_m*b_data(1,:);
   Nb_oxygen=n_glu_m*6*b_data(2,:);
   Nb_CO2=n_glu_m*6*b_data(5,:);
   Nb_water_m=n_glu_m*6*b_data(4,:);
end

 %polysaccharide production part
for i=1:48;
   n_ps(i,:)=((x(i+1,2)-x(i,2))/MW_ps);
   Nh_glu_ps=n_ps*RU*H_data(1,:);
   Nh_GA_ps=n_ps*RU*H_data(3,:);
   Nh_water_ps=n_ps*RU*H_data(4,:);
   Nh_ps=n_ps*H_data(6,:);
   Nb_glu_ps=n_ps*RU*b_data(1,:);
   Nb_GA_ps=n_ps*RU*b_data(3,:);
   Nb_water_ps=n_ps*RU*b_data(4,:);
   Nb_ps=n_ps*b_data(6,:);
end

% substrate entering bacteria structure
for i=1:48;
   m_biomass(i,:)=x(i+1,1)-x(i,1);
   n_biomass=m_biomass/MW_biomass;
```

```
    n_glu_biomass=(m_biomass*0.55)/MW_glu;
    n_GA_biomass=(m_biomass*0.15)/MW_GA;

    Nh_glu_biomass=n_glu_biomass*H_data(1,:);
    Nh_GA_biomass=n_GA_biomass*H_data(3,:);
    Nh_biomass=n_biomass*H_data(7,:);

    Nb_glu_biomass=n_glu_biomass*b_data(1,:);
    Nb_GA_biomass=n_GA_biomass*b_data(3,:);
    Nb_biomass=n_biomass*b_data(7,:);
end

Qin=Nh_glu_biomass+Nh_GA_biomass+Nh_glu_ps+Nh_GA_ps+Nh_glu_m+Nh_oxygen
;
Qout=Nh_biomass+Nh_ps+Nh_water_ps+Nh_CO2+Nh_water_m;
Q_total=cumsum(Qout-Qin);
Nbin=Nb_glu_biomass+Nb_GA_biomass+Nb_glu_m+Nb_oxygen+Nb_glu_ps+Nb_GA_p
s;
Nbout=Nb_biomass+Nb_CO2+Nb_water_m+Nb_ps+Nb_water_ps;
deltab=Nbin-Nbout;
Xdestroyed=cumsum(deltab)-Q_total*(1-(T0/T));

% antigen exergy efficiency calculation
Qin_ps=Nh_glu_ps+Nh_GA_ps;
Qout_ps=Nh_ps+Nh_water_ps;
Q_ps=cumsum(Qout_ps-Qin_ps);


Nbin_ps=Nb_glu_ps+Nb_GA_ps;
Nbout_ps=Nb_ps+Nb_water_ps;
deltab_ps=Nbin_ps-Nbout_ps;
Xdestroyed_ps=cumsum(deltab_ps)-Q_ps*(1-(T0/T));
```

```
disp('The exergetic efficieny of antigen production is %')
eff=sum(n_ps*b_data(6,:))/sum(Xdestroyed)*100

disp('Q_ps/Q_total is %')
q_ratio=sum(Q_ps)/sum(Q_total)*100


for i=1:48;
   time(i)=t(i+1);
end

[ax, h1, h2]=plotyy(time, Q_total, time, Xdestroyed)

set(ax,'xlim',[0 10],'xtick',[0:1:10]);

set(get(ax(1),'Ylabel'),'String','Q(kJ/mole)')
set(get(ax(2),'Ylabel'),'String','Xdestroyed(kJ/mole)')

xlabel ('time (h)')
title ('Energy&Exergy Balance - pH control')

set(ax(1),'ylim',[-100 20],'ytick',[-100:20:20],'ycolor','black');
set(ax(2),'ylim',[-10 50],'ytick',[-10:10:50],'ycolor','black');


set(h1,'LineStyle','-.','color','black','LineWidth',2);
set(h2,'LineStyle',':','color','black','LineWidth',2);
legend ('Q', 'Xdestroyed','Location', 'NorthEast');
legend ('Q', 'Xdestroyed','Location', 'NorthEast');

grid on
```

CASE III: DISSOLVED OXYGEN CONTROL

Function m-file

```
function dx= sode_O2(t,x);
% This function models substrate consumption
mu = 0.56;
xmax =2.85;
km=0.06;

if t<=12;
    alpha = 0.005;
    beta = 0.033;
    Yx=4;
    Yp=0.18;
    dx1 = mu*x(1)*(1-(x(1)/xmax));
    dx2 = alpha*x(1) + beta*dx1;
    dx3=-(((1/Yx)*dx1)+((1/Yp)*dx2)+(km*x(3)));
end
 if t>12;
   alpha=0.003;
   beta=0.00002;
   Yx=1;
   Yp=0.07;
   dx1 =mu*x(1)*(1-(x(1)/xmax));
   dx2 = alpha*x(1)+beta*dx1;
   dx3=-(((1/Yx)*dx1)+((1/Yp)*dx2)+(km*x(1)));
end

dx=[dx1; dx2;dx3];
```

Kinetic Model m-file

```
clear all
close all
format compact
global mu xmax
```

```
% enter the constants
mu=0.56;
xmax=2.85;

% enter the data
tData1=[0:2:16];
a=[0.07 0.300 0.410 0.840 2.225 2.499 2.510 2.800 2.800];
ps = [0 0.005 0.019 0.043 0.085 0.125 0.150 0.175 0.185];
s = [5 4.4 3.7 3.18 2.6 1.9 1.21 0.48 0];
%x1= [0.07; 0.320; 0.450; 0.930; 2.28; 2.42; 2.60; 2.800];



[t,x] = ode45('sode_O2', [0 16], [0.048 0 5]);

plot (t, x(:,1), 'k-.', 'LineWidth', 2.0)
hold on
[ax, h1, h2]=plotyy(t, x(:,3), t, x(:,2));

set(ax(1),'ylim',[0 5],'ytick',[0:5],'ycolor','black');
set(ax(2),'ylim',[0 0.25],'ytick',[0:0.05:0.25],'ycolor','black');
set(h1,'LineStyle',':','color','red','LineWidth',2);
set(h2,'LineStyle','-','color','blue','LineWidth',2);
legend ('biomass', 'substrate','product', 'Location', 'NorthEast');
plot(tData1, a, 'k+')
[ax, h3, h4]=plotyy(tData1, s, tData1, ps);
set(ax(1),'ylim',[0 5],'ytick',[0:5],'ycolor','black');
set(ax(2),'ylim',[0 0.25],'ytick',[0:0.05:0.25],'ycolor','black');
set(h3, 'LineStyle', '*', 'LineWidth', 2.0, 'Color', 'red');
set(h4, 'LineStyle', 'o', 'LineWidth', 2.0, 'Color', 'blue');
set(get(ax(1),'Ylabel'),'String','g/L');
set(get(ax(2),'Ylabel'),'String','g/L');
```

```
grid on
xlabel('t(h)')
title ('Kinetic Model - Dissolved oxygen control')
```

Entropy Script m-file

```
clear all
close all

MW_glu=180;
MW_ps=88000;
MW_GA=147.13;
MW_biomass=95;
RU=285;
T=308;
T0=298;

%H, S, b of glucose, oxygen, GA, water, co2, ps, biomass
H_data=[-1272.2; 0.294; -1001.6; -285; -393.6; -467711;-511.3];
S_data=[0.209; 0.205;  0.188; 0.0091; 0.215; 242; 0.138];
b_data=[2955; 3.97; 2393.2; 0.9; 19.48 ; 1591953;2037.1];


[t,x] = ode45('sode_O2', [0 18], [0.048 0 5]);

% ENERGY & ENTROPY BALANCE for oxygen control

% maintenance
for i=1:48;
   n_glu_m(i,:)=((x(i,3)-x(i+1,3))/MW_glu)-(((x(i+1,1)-x(i,1))*0.55)/MW_glu)-
(((x(i+1,2)-x(i,2))*RU)/MW_ps);
   Nh_glu_m=n_glu_m*H_data(1,:);
   Nh_oxygen=n_glu_m*6*H_data(2,:);
   Nh_CO2=n_glu_m*6*H_data(5,:);
```

```
    Nh_water_m=n_glu_m*6*H_data(4,:);
    NS_glu_m=n_glu_m*S_data(1,:);
    NS_oxygen=n_glu_m*6*S_data(2,:);
    NS_CO2=n_glu_m*6*S_data(5,:);
    NS_water_m=n_glu_m*6*S_data(4,:);
end

Qin_m=Nh_glu_m+Nh_oxygen;
Qout_m=Nh_CO2+Nh_water_m;
Q_m=cumsum(Qout_m-Qin_m);


NSin_m=NS_glu_m+NS_oxygen;
NSout_m=NS_CO2+NS_water_m;
deltaS_m=cumsum(NSout_m-NSin_m);
Sgen_m=deltaS_m-(Q_m/T);
 %polysaccharide production part
for i=1:48;
    n_ps(i,:)=((x(i+1,2)-x(i,2))/MW_ps);
    Nh_glu_ps=n_ps*RU*H_data(1,:);
    Nh_GA_ps=n_ps*RU*H_data(3,:);
    Nh_water_ps=n_ps*RU*H_data(4,:);
    Nh_ps=n_ps*H_data(6,:);
    NS_glu_ps=n_ps*RU*S_data(1,:);
    NS_GA_ps=n_ps*RU*S_data(3,:);
    NS_water_ps=n_ps*RU*S_data(4,:);
    NS_ps=n_ps*S_data(6,:);
end

Qin_ps=Nh_glu_ps+Nh_GA_ps;
Qout_ps=Nh_ps+Nh_water_ps;
Q_ps=cumsum(Qout_ps-Qin_ps);
```

```
NSin_ps=NS_glu_ps+NS_GA_ps;
NSout_ps=NS_ps+NS_water_ps;
deltaS_ps=cumsum(NSout_ps-NSin_ps);
Sgen_ps=deltaS_ps-(Q_ps/T);

% substrate entering bacteria structure
for i=1:48;
m_biomass(i,:)=x(i+1,1)-x(i,1);
   n_biomass=m_biomass/MW_biomass;
   n_glu_biomass=(m_biomass*0.55)/MW_glu;
   n_GA_biomass=(m_biomass*0.15)/MW_GA;

   Nh_glu_biomass=n_glu_biomass*H_data(1,:);
   Nh_GA_biomass=n_GA_biomass*H_data(3,:);
   Nh_biomass=n_biomass*H_data(7,:);
   NS_glu_biomass=n_glu_biomass*S_data(1,:);
   NS_GA_biomass=n_GA_biomass*S_data(3,:);
   NS_biomass=n_biomass*S_data(7,:);
end

Qin_b=Nh_glu_biomass+Nh_GA_biomass;
Qout_b=Nh_biomass;
Q_b=cumsum(Qout_b-Qin_b);

NSin_b=NS_glu_biomass+NS_GA_biomass;
NSout_b=NS_biomass;
deltaS_b=cumsum(NSout_b-NSin_b);
Sgen_b=deltaS_b-(Q_b/T);

% TOTAL ENTROPY GENERATION
Sgen_total=Sgen_m+Sgen_ps+Sgen_b;

for i=1:48;
```

```
    time(i)=t(i+1);
end

plot (time,Sgen_total, 'k-', 'Linewidth',2)
hold on
plot (time,Sgen_m,'k:', 'Linewidth',2)
hold on
plot (time,Sgen_ps, 'k-.', 'Linewidth',2)
hold on
plot (time, Sgen_b, 'k--', 'Linewidth',2)

xlabel('time(h)')
ylabel('Sgen (kJ/K)')
legend('Sgen total','Sgen maintenance','Sgen PS','Sgen biomass','location','Northwest')
title ('Entropy Balance - Dissolved oxygen control')

grid on

xlim([0 16]);
ylim([-0.02 0.20]);
```

Energy – Exergy Script m-file

```
clear all
close all

MW_glu=180;
MW_ps=88000;
MW_GA=147.13;
MW_biomass=95;
RU=285;
T=308;
T0=298;
```

```
%H, S, b of glucose, oxygen, GA, water, co2, ps, biomass
H_data=[-1272.2; 0.294; -1001.6; -285; -393.6; -467711;-511.3];
S_data=[0.209; 0.205;  0.188; 0.0091; 0.215; 242; 0.138];
b_data=[2955; 3.97; 2393.2; 0.9; 19.48 ; 1591953;2032.1];


[t,x] = ode45('sode_O2', [0 17], [0.048 0 5]);

% ENERGY AND EXERGY BALANCE for without control

% maintenance
for i=1:48;
   n_glu_m(i,:)=((x(i,3)-x(i+1,3))/MW_glu)-(((x(i+1,1)-x(i,1))*0.55)/MW_glu)-
(((x(i+1,2)-x(i,2))*RU)/MW_ps);
   Nh_glu_m=n_glu_m*H_data(1,:);
   Nh_oxygen=n_glu_m*6*H_data(2,:);
   Nh_CO2=n_glu_m*6*H_data(5,:);
   Nh_water_m=n_glu_m*6*H_data(4,:);
   Nb_glu_m=n_glu_m*b_data(1,:);
   Nb_oxygen=n_glu_m*6*b_data(2,:);
   Nb_CO2=n_glu_m*6*b_data(5,:);
   Nb_water_m=n_glu_m*6*b_data(4,:);
end


%polysaccharide production part
for i=1:48;
   n_ps(i,:)=((x(i+1,2)-x(i,2))/MW_ps);
   Nh_glu_ps=n_ps*RU*H_data(1,:);
   Nh_GA_ps=n_ps*RU*H_data(3,:);
   Nh_water_ps=n_ps*RU*H_data(4,:);
   Nh_ps=n_ps*H_data(6,:);
```

```
    Nb_glu_ps=n_ps*RU*b_data(1,:);
    Nb_GA_ps=n_ps*RU*b_data(3,:);
    Nb_water_ps=n_ps*RU*b_data(4,:);
    Nb_ps=n_ps*b_data(6,:);
end

% substrate entering bacteria structure
for i=1:48;
    m_biomass(i,:)=x(i+1,1)-x(i,1);
    n_biomass=m_biomass/MW_biomass;
    n_glu_biomass=(m_biomass*0.55)/MW_glu;
    n_GA_biomass=(m_biomass*0.15)/MW_GA;

    Nh_glu_biomass=n_glu_biomass*H_data(1,:);
    Nh_GA_biomass=n_GA_biomass*H_data(3,:);
    Nh_biomass=n_biomass*H_data(7,:);
     Nb_glu_biomass=n_glu_biomass*b_data(1,:);
    Nb_GA_biomass=n_GA_biomass*b_data(3,:);
    Nb_biomass=n_biomass*b_data(7,:);
end

Qin=Nh_glu_biomass+Nh_GA_biomass+Nh_glu_ps+Nh_GA_ps+Nh_glu_m+Nh_oxygen
;
Qout=Nh_biomass+Nh_ps+Nh_water_ps+Nh_CO2+Nh_water_m;
Q_total=cumsum(Qout-Qin);


Nbin=Nb_glu_biomass+Nb_GA_biomass+Nb_glu_m+Nb_oxygen+Nb_glu_ps+Nb_GA_p
s;
Nbout=Nb_biomass+Nb_CO2+Nb_water_m+Nb_ps+Nb_water_ps;
deltab=Nbin-Nbout;
Xdestroyed=cumsum(deltab)-Q_total*(1-(T0/T));
```

```
% antigen exergy efficiency calculation
Qin_ps=Nh_glu_ps+Nh_GA_ps;
Qout_ps=Nh_ps+Nh_water_ps;
Q_ps=cumsum(Qout_ps-Qin_ps);


Nbin_ps=Nb_glu_ps+Nb_GA_ps;
Nbout_ps=Nb_ps+Nb_water_ps;
deltab_ps=Nbin_ps-Nbout_ps;
Xdestroyed_ps=cumsum(deltab_ps)-Q_ps*(1-(T0/T));



disp('The exergetic efficieny of antigen production is %')
eff=sum(n_ps*b_data(6,:))/sum(Xdestroyed)*100

 disp('Q_ps/Q_total is %')
q_ratio=sum(Q_ps)/sum(Q_total)*100


for i=1:48;
   time(i)=t(i+1);
end

[ax, h1, h2]=plotyy(time, Q_total, time, Xdestroyed)

set(ax,'xlim',[0 16],'xtick',[0:2:16]);

set(get(ax(1),'Ylabel'),'String','Q(kJ/mole)')
set(get(ax(2),'Ylabel'),'String','Xdestroyed(kJ/mole)')

xlabel ('time (h)')
title ('Energy&Exergy Balance - Dissolved oxygen control')
```

```
set(ax(1),'ylim',[-100 0],'ytick',[-100:10:0],'ycolor','black');
set(ax(2),'ylim',[0 50],'ytick',[0:10:50],'ycolor','black');


set(h1,'LineStyle','-.','color','black','LineWidth',2);
set(h2,'LineStyle',':','color','black','LineWidth',2);
legend ('Q', 'Xdestroyed','Location', 'NorthEast');
legend ('Q', 'Xdestroyed','Location', 'NorthEast');

grid on
```

APPENDIX B: MATLAB CODES FOR KINETIC MODELS OF SOURDOUGH LEAVENING

MODEL 1: 0% *LACTOBACILLUS PLANTARUM* AND 100% *SACCHAROMYCES CEREVISIAE* AT 25ºC

Function m-file

```
function dx=model1(t,x);
% This function models substrate consumption

if t<=50;
    k_y_p1=0.015;
    alpha1_p1=3.6e-8;
    beta1_p1=0;
    phi_p1=0.99;
    Vmax=170;
    dx1=(-1)*k_y_p1*x(1);
    dx2=alpha1_p1*x(1)+beta1_p1*dx1;
    dx3=phi_p1*(1-x(3)/Vmax)*dx2;
end

if t>50;
   mu_y_p2=0.038;
   alpha1_p2=1.5*10^(-6);
   beta1_p2=1.5*10^(-5);
   phi_p2=0.24;
   xmax=3.9;
   Vmax=170;
   dx1= mu_y_p2*x(1)*(1-x(1)/xmax);
   dx2=alpha1_p2*x(1)+beta1_p2*dx1;
   dx3=phi_p2*(1-x(3)/Vmax)*dx2;
end
```

```
dx=[dx1;dx2;dx3];
```

Growth Script m-file

```
clear all
close all
format compact

% enter the data
time=[0 33 50 60 91 120 153 182 215];
gy=[3.6 2.35 1.75 2.5 3.1 3.7 3.85 3.9 3.9];


[t,x] = ode45('model1_ode', [0 240] , [3.6 0 0]);



 plot (t,x(:,1),'k-','LineWidth', 2.0)
 hold on

plot(time, gy,'k*')
grid on
xlabel('time(min)')
ylabel ('biomass x 10^6 cfu/g')
title ('25^oC, 100% S. cerevisiae - Biomass Production')
set(gca,'xlim',[0 240],'xtick',[0:20:240]);
legend ('S. cerevisiae', 'Location', 'SouthEast');
```

CO_2 Production Script m-file

```
clear all
close all
format compact
```

```
% enter the data
time=[0 40 62 75 90 110 120 135 147 160 167 176 191 210];
gas_yeast=[0 0 47 115 190 297 380 470 507 580 650 680 780 880];
dough_yeast=[0 0 5 20 60 90 112 125 127 130 135 145 148 170];


[t,x] = ode45('model1_ode', [0 240] , [3.6 0 0]);

gas_vol=10^6*x(:,2);

vol_inc=10^6*x(:,3);

 plot (t,gas_vol,'k-','LineWidth', 2)
 hold on
 plot (t,vol_inc, 'k-.', 'LineWidth', 2)
 hold on

plot (time, gas_yeast,'ko', 'LineWidth',2)
 hold on
plot (time, dough_yeast,'k*','LineWidth',2)

grid on
xlabel('time(min)')
ylabel ('G, V(cm^3)')
title ('25^oC, 100% S. cerevisiae - Gas Production & Dough Volume Increase')
set(gca,'xlim',[0 240],'xtick',[0:20:240]);


legend ('gas production','dough volume increase', 'Location', 'NorthWest');
```

Thermodynamic Model Script m-file

```
clear all
close all
```

```
ideal_GV=24e3;
pressure=1.01*101.325;
T0=293;
T=298;
wt_yeast=(7.9e-11)*(5)*(1e8);
wt_bacteria=(4.18e-13)*10*(1e8);
MW_yeast=23.75;
MW_bacteria=24.95;
MW_LA=90.08;
MW_H2=2;
MW_glucose=180.16;
MW_NaCl=58.44;
MW_water=18;

%enthalpy and chemical exergies of
% 1)glucose,
% 2)ammonium,
% 3)CO2,
% 4)ethanol,
% 5)glycerol,
% 6)yeast (Battley,1999),
% 7)LA (http://webbook.nist.gov/cgi/cbook.cgi?ID=C79334&Mask=2),
% 8)bacteria (Battley, E. coli K12),
% 9)water
H_data=[-1271.1, -47.2, -393.5, -276, -669.6, -133.13, -694.08, -96.01, -285.8, -484.5,0];
b_data=[2955 340 20 1400 212 529.6 1747 571.4 0.9 907.2 236.09];


[t,x] = ode45('model1_ode', [0 260], [3.6 0 0]);

% ENERGY AND EXERGY BALANCE FOR YEAST
for i=1:52;
```

```
n_yeast(i,:)=(x(i+1,1)-x(i,1))*wt_yeast/MW_yeast;
n_CO2(i,:)=(x(i+1,2)-x(i,2))/ideal_GV*(1e6);

n_glu(i,:)=(x(i+1,2)-x(i,2))/ideal_GV*(1e6)/1.54;
n_nh3(i,:)=(x(i+1,2)-x(i,2))/ideal_GV*(1e6)/1.54*0.12;
n_ethanol(i,:)=(x(i+1,2)-x(i,2))/ideal_GV*(1e6)/1.54*1.30;
n_gly(i,:)=(x(i+1,2)-x(i,2))/ideal_GV*(1e6)/1.54*0.43;
n_yeast(n_yeast<0)=0;
n_CO2(n_CO2<0)=0;
n_ethanol(n_ethanol<0)=0;

Nh_glu_yeast=(n_glu)*H_data(1,1);
Nh_nh3_yeast=(n_nh3)*H_data(1,2);
Nh_CO2_yeast=n_CO2*H_data(1,3);
Nh_ethanol=(n_ethanol)*H_data(1,4);
Nh_gly=(n_gly)*H_data(1,5);
Nh_yeast=(n_yeast)*H_data(1,6);

Nb_glu_yeast=(n_glu)*b_data(1,1);
Nb_nh3_yeast=(n_nh3)*b_data(1,2);
Nb_CO2_yeast=n_CO2*b_data(1,3);
Nb_ethanol=(n_ethanol)*b_data(1,4);
Nb_gly=(n_gly)*b_data(1,5);
Nb_yeast=(n_yeast)*b_data(1,6);


V(i,:)=(x(i+1,3)-x(i,3));
PV=pressure*V;

time(i)=t(i);

end
```

```
Nh_dough=(61.1/MW_glucose)*H_data(1,1)+(2.5/MW_yeast)*H_data(1,8)+(0.6/MW_NaCl)*(-411.0)+(35.8/MW_water)*H_data(1,9);
Nb_dough=(61.1/MW_glucose)*b_data(1,1)+(2.5/MW_yeast)*b_data(1,8)+(0.6/MW_NaCl)*(14.3)+(35.8/MW_water)*b_data(1,9);

%ENERGY BALANCE

Hin=Nh_glu_yeast+Nh_nh3_yeast;
Hout=Nh_CO2_yeast+Nh_ethanol+Nh_gly+Nh_yeast;
deltaH=Hout-Hin;
deltaH(deltaH>0)=-0.005;
Q_total=cumsum(deltaH)+cumsum(PV);


%EXERGY BALANCE
Nbin=Nb_glu_yeast+Nb_nh3_yeast;
Nbout=Nb_CO2_yeast+Nb_ethanol+Nb_gly+Nb_yeast;
deltab=(Nbin-Nbout);
deltab(deltab<0)=0.01;
Xdestroyed=cumsum(deltab)+Q_total*(1-(T0/T))-cumsum(PV);

disp('n_glu, n_CO2, n_yeast,Hin, Nbin')
moles=[sum(n_glu(1:49));sum(n_CO2(1:49));sum(n_yeast(1:49));sum(Hin(1:49));sum(Nbin(1:49))]

disp('Hout, Nbout')
out=[sum(Hout(1:49));sum(Nbout(1:49))]

secondlaw=[Q_total(49) Xdestroyed(49)]
expansion_work=sum(PV(1:49))

eff=sum(Nb_CO2_yeast)/Nb_dough*100
wt_CO2_ratio_for_100g=(sum(n_CO2))*44
```

```
[ax, h1, h2]=plotyy(time, Q_total, time, Xdestroyed)

set(ax,'xlim',[0 240],'xtick',[0:20:240]);

set(get(ax(1),'Ylabel'),'String','Q(kJ)')
set(get(ax(2),'Ylabel'),'String','Xdestroyed(kJ)')

xlabel ('time (min)')
title ('25^oC, 100% S. cerevisiae - Energy & Exergy Balance')

set(ax(1),'ylim',[-0.4 0],'ytick',[-0.4:0.04:0],'ycolor','black');
set(ax(2),'ylim',[0 40],'ytick',[0:4:40],'ycolor','black');


set(h1,'LineStyle','-','color','black','LineWidth',2);
set(h2,'LineStyle',':','color','black','LineWidth',2);
legend ('Q', 'Xdestroyed','Location', 'NorthEast');


grid on
```

MODEL 2: 20% *LACTOBACILLUS PLANTARUM* AND 80% *SACCHAROMYCES CEREVISIAE* AT 25ºC

Function m-file

```
function dx= model2(t,x);
% This function models substrate consumption

if t<=60;
   k_y_p1=8.3e-3;
   mu_b_p1=0.024;
   alpha_p1=0.33e-9;
   beta_p1=0.9e-11;
   alpha1_p1=1e-8;
```

```
    beta1_p1=0;
    alpha2_p1=1e-8;
    beta2_p1=1.3e-8;
    phi_p1=4.76;
    xmax_b_p1=2.5;
    Vmax=176;
    dx1=(-1)*k_y_p1*x(1);
    dx2=mu_b_p1*x(2)*(1-x(2)/xmax_b_p1);
    dx3=alpha_p1*x(2)+beta_p1*dx2;
    dx4=alpha1_p1*x(1)+alpha2_p1*x(2)+beta1_p1*dx1+beta2_p1*dx2;
    dx5=phi_p1*(1-x(5)/Vmax)*dx4;
   end

if t>60;
   mu_y_p2=0.044;
   mu_b_p2=0.024;
   alpha_p2=0.33e-9;
    beta_p2=0.4e-7;
   alpha1_p2=1.1e-7;
   alpha2_p2=1.1e-6;
   beta1_p2=1e-7;
   beta2_p2=1e-7;
   phi_p2=0.23;
   xmax_y_p2=3.65;
   xmax_b_p2=4.2;
   Vmax=176;
   dx1=mu_y_p2*x(1)*(1-x(1)/xmax_y_p2);
   dx2=mu_b_p2*x(2)*(1-x(2)/xmax_b_p2);
   dx3=alpha_p2*x(2)+beta_p2*dx2;
   dx4=alpha1_p2*x(1)+alpha2_p2*x(2)+beta1_p2*dx1+beta2_p2*dx2;
   dx5=phi_p2*(1-x(5)/Vmax)*dx4;
end
```

```
dx=[dx1;dx2;dx3;dx4;dx5];
```

Growth Script m-file

```
clear all
close all
format compact

% enter the data
tb=[0 31 90 120 153 215];
gb=[2.25 2.38 2.93 3.25 3.81 4.1];

ty=[0 31 60 90 120 153 185 215];
gy=[4.07 3.32 2.39 3.65 3.56 3.60 3.58 3.58];


[t,x] = ode45('model2_ode', 250, [4.1 2.3 0 0 0]);

plot (t, x(:,1), 'k-', 'LineWidth', 2.0)
hold on

plot (t,x(:,2),'k:', 'LineWidth',2.0)
plot (ty,gy,'ko', 'LineWidth', 2.0)
plot (tb,gb,'k*', 'LineWidth', 2.0)

grid on
xlabel('time(min)')
ylabel ('biomass x 10^6 cfu/g')
title ('25^oC, 80% S. cerevisiae and 20% L. plantarum - Biomass Production')

set(gca,'xlim',[0 240],'xtick',[0:20:240]);


legend ('S. cerevisiae','L. plantarum', 'Location', 'SouthEast');
```

CO_2 Production Script m-file

```
clear all
close all
format compact

% enter the data
time=[0 30 80 110 130 147 160 173 186 200 215];
gas_yeast=[0 0 33 144 235 322 400 500 580 700 800];
dough_yeast=[0 0 10 20 35 37 110 118 141 159 176];


[t,x] = ode45('model2_ode', 240, [4.1 2.25 0 0 0]);

 plot (t,10^6*x(:,4),'k-','LineWidth', 2)
 hold on
 plot (t,10^6*x(:,5), 'k:', 'LineWidth', 2)
 hold on

plot (time, gas_yeast,'ko', 'LineWidth',2)
 hold on
plot (time, dough_yeast,'k*','LineWidth',2)

grid on
xlabel('time(min)')
ylabel ('G, V(cm^3)')
title ('25^oC, 80% S. cerevisiae and 20% L. plantarum - Gas Production & Dough Volume Increase')
set(gca,'xlim',[0 240],'xtick',[0:20:240]);
legend ('gas production','dough volume increase', 'Location', 'NorthWest');
```

Lactic Acid Production Script m-file

```
clear all
close all
```

```
format compact

% enter the data
time=[0 30 77 110 154 185 215];
la=[0 0.03 0.07 0.13 0.23 0.28 0.30];



[t,x] = ode45('model2_ode', 240, [4.1 2.3 0 0 0]);

 plot (t,1000000*x(:,3),'k-','LineWidth', 2)
 hold on

plot (time, la,'kx', 'LineWidth',2)



grid on
xlabel('time(min)')
ylabel ('Lactic acid (%)')
title ('25^oC, 80% S. cerevisiae and 20% L. plantarum - Lactic acid production')
set(gca,'xlim',[0 240],'xtick',[0:20:240]);

legend ('lactic acid','Location', 'SouthEast');
```

Thermodynamic Model Script m-file

```
clear all
close all

ideal_GV=24e3;
pressure=1.01*101.325;
T0=293;
T=298;
wt_yeast=(7.9e-11)*(5)*(1e8);
```

```
wt_bacteria=(4.18e-13)*20*(1e8);
MW_yeast=23.75;
MW_bacteria=24.95;
MW_LA=90.08;
MW_H2=2;
MW_glucose=180.16;
MW_NaCl=58.44;
MW_water=18;


%enthalpy and chemical exergies of 1)glucose, 2)ammonium, 3)CO2, 4)ethanol,
%5)glycerol, 6)yeast (Battley,1999), 7)LA
(http://webbook.nist.gov/cgi/cbook.cgi?ID=C79334&Mask=2), 8)bacteria (Battley, E. coli
K12), 9)water
H_data=[-1271.1, -47.2, -393.5, -276, -669.6, -133.13, -694.08, -96.01, -285.8, -484.5,0];
b_data=[2955 340 20 1400 212 529.6 1747 571.4 0.9 907.2 236.09];

[t,x] = ode45('model2_ode', 260, [4.1 2.3 0 0 0]);



for i=1:48;

   % ENERGY AND EXERGY BALANCE FOR BACTERIA
   n_glu_yeast(i,:)=(((x(i+1,4)-x(i,4))/ideal_GV*(1e6)-((x(i+1,3)-
x(i,3))*(1e6)/MW_LA))/0.75*1.13)/1.54;
   n_nh3_yeast(i,:)=(((x(i+1,4)-x(i,4))/ideal_GV*(1e6)-((x(i+1,3)-
x(i,3))*(1e6)/MW_LA))/0.75*1.13)/1.54*0.12;
   n_CO2_yeast(i,:)=(((x(i+1,4)-x(i,4))/ideal_GV*(1e6)-((x(i+1,3)-
x(i,3))*(1e6)/MW_LA))/0.75*1.13);
   n_CO2_yeast(n_CO2_yeast<0)=0;
   n_ethanol_yeast(i,:)=(((x(i+1,4)-x(i,4))/ideal_GV*(1e6)-((x(i+1,3)-
x(i,3))*(1e6)/MW_LA))/0.75*1.13)/1.54*1.3;
```

```
    n_gly(i,:)=(((x(i+1,4)-x(i,4))/ideal_GV*(1e6)-((x(i+1,3)-
x(i,3))*(1e6)/MW_LA))/0.75*1.13)/1.54*0.43;
    n_yeast(i,:)=(x(i+1,1)-x(i,1))*wt_yeast/MW_yeast;
    n_yeast(n_yeast<0)=0;
    n_CO2_yeast(n_CO2_yeast<0)=0;
    Nh_glu_yeast=(n_glu_yeast)*H_data(1,1);
    Nh_nh3_yeast=(n_nh3_yeast)*H_data(1,2);
    Nh_CO2_yeast=n_CO2_yeast*H_data(1,3);
    Nh_ethanol_yeast=(n_ethanol_yeast)*H_data(1,4);
    Nh_gly=(n_gly)*H_data(1,5);
    Nh_yeast=(n_yeast)*H_data(1,6);
    Nb_glu_yeast=(n_glu_yeast)*b_data(1,1);
    Nb_nh3_yeast=(n_nh3_yeast)*b_data(1,2);
    Nb_CO2_yeast=n_CO2_yeast*b_data(1,3);
    Nb_ethanol_yeast=(n_ethanol_yeast)*b_data(1,4);
    Nb_gly=(n_gly)*b_data(1,5);
    Nb_yeast=(n_yeast)*b_data(1,6);



    n_glu_bacteria(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA/0.75;
    n_nh3_bacteria(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA/0.75*0.09;
    n_water(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA/0.75*0.19;
    n_CO2_bacteria(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA*1.13;
    n_CO2_bacteria(n_CO2_bacteria<0)=0;
    n_LA(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA;
    n_LA(n_LA<0)=0;
    n_ethanol_bacteria(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA;
    n_AA(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA/0.75*0.38;
    n_H2=(1e6)*(x(i+1,3)-x(i,3))/MW_LA;
    n_bacteria(i,:)=(x(i+1,2)-x(i,2))*wt_bacteria/MW_bacteria;
    n_bacteria(n_bacteria<0)=0;
    n_LA(n_LA<0)=0;
```

```
    Nh_glu_bacteria=(n_glu_bacteria)*H_data(1,1);
    Nh_nh3_bacteria=(n_nh3_bacteria)*H_data(1,2);
    Nh_water=n_water*H_data(1,9);
    Nh_CO2_bacteria=(n_CO2_bacteria)*H_data(1,3);
    Nh_ethanol_bacteria=(n_ethanol_bacteria)*H_data(1,4);
    Nh_LA=(n_LA)*H_data(1,7);
    Nh_AA=n_AA*H_data(1,10);
    Nh_H2=n_H2*H_data(1,11);
    Nh_bacteria=(n_bacteria)*H_data(1,8);
    Nh_water=(n_water)*H_data(1,9);
    Nb_glu_bacteria=(n_glu_bacteria)*b_data(1,1);
    Nb_nh3_bacteria=(n_nh3_bacteria)*b_data(1,2);
    Nb_water=(n_water)*b_data(1,9);
    Nb_CO2_bacteria=n_CO2_bacteria*b_data(1,3);
    Nb_ethanol_bacteria=n_ethanol_bacteria*b_data(1,4);
    Nb_LA=(n_LA)*b_data(1,7);
    Nb_AA=(n_AA)*b_data(1,10);
    Nb_H2=n_H2*b_data(1,11);
    Nb_bacteria=(n_bacteria)*b_data(1,8);


    V(i,:)=(x(i+1,5)-x(i,5));
    PV=pressure*V;
end


% m=100;
% cp=2.73*4.184;
% deltaT=5;
% Qin=m*cp*deltaT/1000;

Hin=Nh_glu_yeast+Nh_nh3_yeast+Nh_glu_bacteria+Nh_nh3_bacteria+Nh_water;
```

```
Hout=Nh_CO2_yeast+Nh_ethanol_yeast+Nh_gly+Nh_yeast+Nh_bacteria+Nh_ethanol_ba
cteria+Nh_CO2_bacteria+Nh_LA+Nh_H2+Nh_AA;
deltaH=Hout-Hin;
deltaH(deltaH>0)=-0.001;
Q_total=cumsum(deltaH)+cumsum(PV);

Xin_y= Nb_glu_yeast+Nb_nh3_yeast;
Xout_y=Nb_yeast+Nb_CO2_yeast+Nb_ethanol_yeast+Nb_gly;
Xy=(Xin_y-Xout_y);

Xin_b= Nb_glu_bacteria+Nb_nh3_bacteria+Nb_water;
Xout_b=Nb_bacteria+Nb_ethanol_bacteria+Nb_CO2_bacteria+Nb_LA+Nb_H2+Nb_AA;
Xb=(Xin_b-Xout_b);

deltab=Xy+Xb;
deltab(deltab<0)=0.01;

Xdestroyed=cumsum(deltab)+Q_total*(1-(T0/T))+cumsum(PV);



disp('n_glu_yeast+n_glu_bacteria,...n_CO2_yeast+n_CO2_bacteria, n_LA, n_yeast,
n_bacteria,Hin, Xin_y+Xin_b')
moles=[sum(n_glu_yeast(1:47))+sum(n_glu_bacteria(1:47));sum(n_CO2_yeast(1:47))+su
m(n_CO2_bacteria(1:47));sum(n_LA(1:47));...

sum(n_yeast(1:47));sum(n_bacteria(1:47));sum(Hin(1:47));sum(Xin_b(1:47)+Xin_y(1:47)
)]

secondlaw=[Q_total(47) Xdestroyed(47)]
disp('Hout, Nbout')
out=[sum(Hout(1:47));sum(Xout_b(1:47)+Xout_y(1:47))]
```

```
expansion_work=sum(PV(1:47))
Nh_dough=(61.1/MW_glucose)*H_data(1,1)+(2.5/MW_yeast)*H_data(1,8)+(0.6/MW_Na
Cl)*(-411.0)+(35.8/MW_water)*H_data(1,9);
Nb_dough=(61.1/MW_glucose)*b_data(1,1)+(2.5/MW_yeast)*b_data(1,8)+(0.6/MW_Na
Cl)*(14.3)+(35.8/MW_water)*b_data(1,9);
eff=sum(Nb_CO2_yeast+Nb_CO2_bacteria)/Nb_dough*100
wt_CO2_ratio_for_100g=(sum(n_CO2_yeast)+sum(n_CO2_bacteria))*44

for i=1:48;
   time(i)=t(i);
end

[ax, h1, h2]=plotyy(time, Q_total, time, Xdestroyed)

set(ax,'xlim',[0 240],'xtick',[0:20:240]);

set(get(ax(1),'Ylabel'),'String','Q(kJ)')
set(get(ax(2),'Ylabel'),'String','Xdestroyed(kJ)')

xlabel ('time (min)')
title ('25^oC, 80% S. cerevisiae and 20% L. plantarum Energy & Exergy Balance')

set(ax(1),'ylim',[-0.4 0],'ytick',[-0.4:0.04:0],'ycolor','black');
set(ax(2),'ylim',[0 40],'ytick',[0:4:40],'ycolor','black');


set(h1,'LineStyle','-.','color','black','LineWidth',2);
set(h2,'LineStyle',':','color','black','LineWidth',2);
legend ('Q', 'Xdestroyed','Location', 'SouthEast');

grid on
```

MODEL 3: 40% *LACTOBACILLUS PLANTARUM* AND 60% *SACCHAROMYCES CEREVISIAE* AT 25ºC

Function m-file

```
function dx= model3(t,x);
% This function models substrate consumption

if t<=30;
   mu_y_p1=0.007;
   mu_b_p1=0.036;
   alpha_p1=0.75e-9;
   beta_p1=1e-10;
   alpha1_p1=1.75e-8;
   alpha2_p1=1.75e-8;
   beta1_p1=1e-6;
   beta2_p1=1e-6;
   phi_p1=1.22;
   Vmax=110;
   dx1=mu_y_p1*x(1);
   dx2=mu_b_p1*x(2);
   dx3=alpha_p1*x(2)+beta_p1*dx2;
   dx4=alpha1_p1*x(1)+alpha2_p1*x(2)+beta1_p1*dx1+beta2_p1*dx2;
   dx5=phi_p1*(1-x(5)/Vmax)*dx4;

  end

if t>30;
  k_y_p2=8e-3;
  k_b_p2=5e-3;
  epsilon_p2=14e-9;
  alpha1_p2=4.0e-7;
  alpha2_p2=4.0e-7;
  beta1_p2=0;
```

```
  beta2_p2=0;
  phi_p2=0.23;
  Vmax=110;
  dx1=(-1)*k_y_p2*x(1);
  dx2=(-1)*k_b_p2*x(2);
  dx3=(-1)*epsilon_p2*dx2;
  dx4=alpha1_p2*x(1)+alpha2_p2*x(2)+beta1_p2*dx1+beta2_p2*dx2;
  dx5=phi_p2*(1-x(5)/Vmax)*dx4;

end

dx=[dx1;dx2;dx3;dx4;dx5];
```

Growth Script m-file

```
clear all
close all
format compact

% enter the data
tb=[0 25 60 90 120 150 180 215];
gb=[2.5 7.00 6.44 5.55 4.56 3.89 3.00 2.55];

ty=[0 30 60 90 120 150 180];
gy=[4.0 5.00 3.78 3.00 2.20 1.59 1.35];


[t,x] = ode45('model3_ode', 250, [4.0 2.5 0 0 0]);

plot (t, x(:,1), 'k-', 'LineWidth', 2.0)
hold on

plot (t,x(:,2),'k:', 'LineWidth',2.0)
```

```
plot (ty,gy,'ko')
plot (tb,gb,'k*')

grid on
xlabel('time(min)')
ylabel ('biomass x 10^6 cfu/g')
title ('25^oC, 60% S. cerevisiae and 40% L. plantarum - Biomass Production')

set(gca,'xlim',[0 240],'xtick',[0:20:240]);

legend ('S. cerevisiae','L. plantarum', 'Location', 'NorthEast');
```

CO_2 Production Script m-file

```
clear all
close all
format compact

% enter the data
time_gas=[0 15 30 55 60 80 115 130 160 173 183 193 200 215];
gas=[0 0 0 75 150 200 300 360 400 460 470 500 510 570];
time_dough=[0 15 30 55 65 90 115 130 160 183 215];
dough=[0 0 0 25 40 50 70 100 105 100 110];



[t,x] = ode45('model3_ode', 250, [4.1 2.5 0 0 0]);

 plot (t,10^6*x(:,4),'k-','LineWidth', 2)
 hold on
 plot (t,10^6*x(:,5), 'k:', 'LineWidth', 2)
 hold on

plot (time_gas, gas,'ko', 'LineWidth',2)
```

```
 hold on
plot (time_dough, dough,'k*','LineWidth',2)

grid on
xlabel('time(min)')
ylabel ('G, V(cm^3)')
title ('25^oC, 60% S. cerevisiae and 40% L. plantarum - Gas Production & Dough Volume Increase')
set(gca,'xlim',[0 240],'xtick',[0:20:240]);
legend ('gas production','dough volume increase', 'Location', 'NorthWest');
```

Lactic Acid Production Script m-file

```
clear all
close all
format compact

% enter the data
time_la=[0 30 60 90 120 160 215];
la=[0 0.114 0.139 0.141 0.164 0.158 0.164];



[t,x] = ode45('model3_ode', 240, [4.0 2.5 0 0 0]);

 plot (t,1000000*x(:,3),'k-','LineWidth', 2)
 hold on

plot (time_la, la,'kx', 'LineWidth',2)



grid on
xlabel('time(min)')
```

```
ylabel ('Lactic acid (%)')
title ('25^oC, 60% S. cerevisiae and 40% L. plantarum - Lactic acid production')
set(gca,'xlim',[0 240],'xtick',[0:20:240]);

legend ('lactic acid','Location', 'SouthEast');
```

Thermodynamic Model Script m-file

```
clear all
close all


ideal_GV=24e3;
pressure=1.01*101.325;
T0=293;
T=298;
wt_yeast=(7.9e-11)*(5)*(1e8);
wt_bacteria=(4.18e-13)*20*(1e8);
MW_yeast=23.75;
MW_bacteria=24.95;
MW_LA=90.08;
MW_H2=2;
MW_glucose=180.16;
MW_NaCl=58.44;
MW_water=18;


%enthalpy and chemical exergies of 1)glucose, 2)ammonium, 3)CO2, 4)ethanol,
%5)glycerol, 6)yeast (Battley,1999), 7)LA
(http://webbook.nist.gov/cgi/cbook.cgi?ID=C79334&Mask=2), 8)bacteria (Battley, E. coli
K12), 9)water
H_data=[-1271.1, -46.2, -393.5, -276, -669.6, -133.13, -694.08, -96.01, -285.8, -464.5,0];
b_data=[2955 340 20 1400 212 529.6 1746 571.4 0.9 907.2 236.09];
```

```
[t,x] = ode45('model3_ode', 260, [4.0 2.5 0 0 0]);

for i=1:52;

   % ENERGY AND EXERGY BALANCE FOR BACTERIA
   n_glu_yeast(i,:)=(((x(i+1,4)-x(i,4))/ideal_GV*(1e6)-((x(i+1,3)-
x(i,3))*(1e6)/MW_LA))/0.75*1.13)/1.54;
   n_nh3_yeast(i,:)=(((x(i+1,4)-x(i,4))/ideal_GV*(1e6)-((x(i+1,3)-
x(i,3))*(1e6)/MW_LA))/0.75*1.13)/1.54*0.12;
   n_CO2_yeast(i,:)=(((x(i+1,4)-x(i,4))/ideal_GV*(1e6)-((x(i+1,3)-
x(i,3))*(1e6)/MW_LA))/0.75*1.13);
   n_CO2_yeast(n_CO2_yeast<0)=0;
   n_ethanol_yeast(i,:)=(((x(i+1,4)-x(i,4))/ideal_GV*(1e6)-((x(i+1,3)-
x(i,3))*(1e6)/MW_LA))/0.75*1.13)/1.54*1.3;
   n_gly(i,:)=(((x(i+1,4)-x(i,4))/ideal_GV*(1e6)-((x(i+1,3)-
x(i,3))*(1e6)/MW_LA))/0.75*1.13)/1.54*0.43;
   n_yeast(i,:)=(x(i+1,1)-x(i,1))*wt_yeast/MW_yeast;
   n_yeast(n_yeast<0)=0;
   n_CO2_yeast(n_CO2_yeast<0)=0;
   Nh_glu_yeast=(n_glu_yeast)*H_data(1,1);
   Nh_nh3_yeast=(n_nh3_yeast)*H_data(1,2);
   Nh_CO2_yeast=n_CO2_yeast*H_data(1,3);
   Nh_ethanol_yeast=(n_ethanol_yeast)*H_data(1,4);
   Nh_gly=(n_gly)*H_data(1,5);
   Nh_yeast=(n_yeast)*H_data(1,6);
   Nb_glu_yeast=(n_glu_yeast)*b_data(1,1);
   Nb_nh3_yeast=(n_nh3_yeast)*b_data(1,2);
   Nb_CO2_yeast=n_CO2_yeast*b_data(1,3);
   Nb_ethanol_yeast=(n_ethanol_yeast)*b_data(1,4);
   Nb_gly=(n_gly)*b_data(1,5);
   Nb_yeast=(n_yeast)*b_data(1,6);
```

```
n_glu_bacteria(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA/0.75;
n_nh3_bacteria(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA/0.75*0.09;
n_water(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA/0.75*0.19;
n_CO2_bacteria(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA*1.13;
n_CO2_bacteria(n_CO2_bacteria<0)=0;
n_LA(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA;
n_LA(n_LA<0)=0;
n_ethanol_bacteria(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA;
n_AA(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA/0.75*0.38;
n_H2=(1e6)*(x(i+1,3)-x(i,3))/MW_LA;
n_bacteria(i,:)=(x(i+1,2)-x(i,2))*wt_bacteria/MW_bacteria;
n_bacteria(n_bacteria<0)=0;
n_LA(n_LA<0)=0;
Nh_glu_bacteria=(n_glu_bacteria)*H_data(1,1);
Nh_nh3_bacteria=(n_nh3_bacteria)*H_data(1,2);
Nh_water=n_water*H_data(1,9);
Nh_CO2_bacteria=(n_CO2_bacteria)*H_data(1,3);
Nh_ethanol_bacteria=(n_ethanol_bacteria)*H_data(1,4);
Nh_LA=(n_LA)*H_data(1,7);
Nh_AA=n_AA*H_data(1,10);
Nh_H2=n_H2*H_data(1,11);
Nh_bacteria=(n_bacteria)*H_data(1,8);
Nh_water=(n_water)*H_data(1,9);
Nb_glu_bacteria=(n_glu_bacteria)*b_data(1,1);
Nb_nh3_bacteria=(n_nh3_bacteria)*b_data(1,2);
Nb_water=(n_water)*b_data(1,9);
Nb_CO2_bacteria=n_CO2_bacteria*b_data(1,3);
Nb_ethanol_bacteria=n_ethanol_bacteria*b_data(1,4);
Nb_LA=(n_LA)*b_data(1,7);
Nb_AA=(n_AA)*b_data(1,10);
Nb_H2=n_H2*b_data(1,11);
Nb_bacteria=(n_bacteria)*b_data(1,8);
```

```
    V(i,:)=(x(i+1,5)-x(i,5));
    PV=pressure*V;
end


% m=100;
% cp=2.73*4.184;
% deltaT=5;
% Qin=m*cp*deltaT/1000;

Hin=Nh_glu_yeast+Nh_nh3_yeast+Nh_glu_bacteria+Nh_nh3_bacteria+Nh_water;
Hout=Nh_CO2_yeast+Nh_ethanol_yeast+Nh_gly+Nh_yeast+Nh_bacteria+Nh_ethanol_ba
cteria+Nh_CO2_bacteria+Nh_LA+Nh_H2+Nh_AA;
deltaH=Hout-Hin;
deltaH(deltaH>0)=-0.005;
Q_total=cumsum(deltaH)+cumsum(PV);

Xin_y= Nb_glu_yeast+Nb_nh3_yeast;
Xout_y=Nb_yeast+Nb_CO2_yeast+Nb_ethanol_yeast+Nb_gly;
Xy=(Xin_y-Xout_y);

Xin_b= Nb_glu_bacteria+Nb_nh3_bacteria+Nb_water;
Xout_b=Nb_bacteria+Nb_ethanol_bacteria+Nb_CO2_bacteria+Nb_LA+Nb_H2+Nb_AA;
Xb=(Xin_b-Xout_b);

deltab=Xy+Xb;
deltab(deltab<0)=0.02;

Xdestroyed=cumsum(deltab)+Q_total*(1-(T0/T))+cumsum(PV);

disp('n_glu_yeast+n_glu_bacteria,...n_CO2_yeast+n_CO2_bacteria, n_LA, n_yeast,
n_bacteria,Hin, Xin_y+Xin_b')
```

```
moles=[sum(n_glu_yeast(1:46))+sum(n_glu_bacteria(1:46));sum(n_CO2_yeast(1:46))+su
m(n_CO2_bacteria(1:46));sum(n_LA(1:46));...

sum(n_yeast(1:46));sum(n_bacteria(1:46));sum(Hin(1:46));sum(Xin_b(1:46)+Xin_y(1:46)
)]

disp('Hout, Nbout')
out=[sum(Hout(1:46));sum(Xout_b(1:46)+Xout_y(1:46))]

secondlaw=[Q_total(46) Xdestroyed(46)]

expansion_work=sum(PV(1:46))
Nh_dough=(61.1/MW_glucose)*H_data(1,1)+(2.5/MW_yeast)*H_data(1,8)+(0.6/MW_Na
Cl)*(-411.0)+(35.8/MW_water)*H_data(1,9);
Nb_dough=(61.1/MW_glucose)*b_data(1,1)+(2.5/MW_yeast)*b_data(1,8)+(0.6/MW_Na
Cl)*(14.3)+(35.8/MW_water)*b_data(1,9);
eff=sum(Nb_CO2_yeast+Nb_CO2_bacteria)/Nb_dough*100
wt_CO2_ratio_for_100g=(sum(n_CO2_yeast)+sum(n_CO2_bacteria))*44
for i=1:52;
   time(i)=t(i);
end

[ax, h1, h2]=plotyy(time, Q_total, time, Xdestroyed)

set(ax,'xlim',[0 240],'xtick',[0:20:240]);

set(get(ax(1),'Ylabel'),'String','Q(kJ)')
set(get(ax(2),'Ylabel'),'String','Xdestroyed(kJ)')

xlabel ('time (min)')
title ('25^oC, 60% S. cerevisiae and 40% L. plantarum - Energy&Exergy Balance')

set(ax(1),'ylim',[-0.75 0],'ytick',[-0.75:0.075:0],'ycolor','black');
```

```
set(ax(2),'ylim',[0 30],'ytick',[0:3:30],'ycolor','black');


set(h1,'LineStyle','-.','color','black','LineWidth',2);
set(h2,'LineStyle',':','color','black','LineWidth',2);
legend ('Q', 'Xdestroyed','Location', 'SouthEast');

grid on
```

MODEL 4: 60% *LACTOBACILLUS PLANTARUM* AND 40% *SACCHAROMYCES CEREVISIAE* AT 25ºC

Function m-file

```
function dx= model4(t,x);
% This function models substrate consumption

if t<=30;
   mu_y_p1=0.013;
   mu_b_p1=0.039;
   alpha_p1=0.67e-9;
   beta_p1=1e-10;
   alpha1_p1=1.15e-8;
   alpha2_p1=1e-8;
   beta1_p1=1e-6;
   beta2_p1=1e-6;
   phi_p1=1.25;
   Vmax=110;

   dx1=mu_y_p1*x(1);
   dx2=mu_b_p1*x(2);
   dx3=alpha_p1*x(2)+beta_p1*dx2;
   dx4=alpha1_p1*x(1)+alpha2_p1*x(2)+beta1_p1*dx1+beta2_p1*dx2;
   dx5=phi_p1*(1-x(5)/Vmax)*dx4;
```

```
  end

if t>30;
  k_y_p2=0.043;
  k_b_p2=0.023;
  epsilon_p2=0.75e-8;
  alpha1_p2=0.75e-6;
  alpha2_p2=1.1e-7;
  beta1_p2=0;
  beta2_p2=0;
  phi_p2=0.20;
  kd_y_p2=1.0;
  kd_b_p2=8.64;
  Vmax=110;

  dx1=(-1)*k_y_p2*(x(1)-kd_y_p2);
  dx2=(-1)*k_b_p2*(x(2)-kd_b_p2);
  dx3=(-1)*epsilon_p2*dx2;
  dx4=alpha1_p2*x(1)+alpha2_p2*x(2)+beta1_p2*dx1+beta2_p2*dx2;
  dx5=phi_p2*(1-x(5)/Vmax)*dx4;
end

dx=[dx1;dx2;dx3;dx4;dx5];
```

Growth Script m-file

```
clear all
close all
format compact

% enter the data
ty=[0 30 60 90 120 150 180 210];
gy=[3.0 4.2 2.0 1.4 1.0 1.0 1.1 1.0];
```

```
tb=[0 30 60 90 120 150 180 210];
gb=[4.64 15.0 12.0 10.11 9.89 9.00 8.45 8.64];


[t,x] = ode45('model4_ode', 250, [3 4.64 0 0 0]);

plot (t, x(:,1), 'k-', 'LineWidth', 2.0)
hold on

plot (t,x(:,2),'k:', 'LineWidth',2.0)
plot (ty,gy,'ko')
plot (tb,gb,'k*')

grid on
xlabel('time(min)')
ylabel ('biomass x 10^6 cfu/g')
title ('25^oC, 40% S. cerevisiae and 60% L. plantarum - Biomass Production')

set(gca,'xlim',[0 240],'xtick',[0:20:240]);

legend ('S. cerevisiae','L. plantarum', 'Location', 'NorthEast');
```

CO_2 Production Script m-file

```
clear all
close all
format compact

% enter the data
time_gas=[0 30 65 90 95 120 140 160 175 180 190 200 210];
gas=[0 10 100 180 200 245 270 285 340 380 400 410 450];
time_dough=[0 30 65 90 120 140 160 175 180 190 200 210];
dough=[0 10 30 50 55 78 80 95 97 100 100 100];
```

```
[t,x] = ode45('model4_ode', 250, [3.00 4.64 0 0 0]);

plot (t,10^6*x(:,4),'k-','LineWidth', 2)
hold on
plot (t,10^6*x(:,5), 'k-', 'LineWidth', 2)
hold on

plot (time_gas, gas,'ko', 'LineWidth',2)
hold on
plot (time_dough, dough,'k*','LineWidth',2)

grid on
xlabel('time(min)')
ylabel ('G, V(cm3)')
title ('25^oC, 40% S. cerevisiae and 60% L. plantarum - Gas Production & Dough Volume Increase')
set(gca,'xlim',[0 240],'xtick',[0:20:240]);
legend ('gas production','dough volume increase', 'Location', 'NorthWest');
```

Lactic Acid Production Script m-file

```
clear all
close all
format compact

% enter the data
time_la=[0 30 60 90 120 150 210];
la=[0 0.18 0.19 0.20 0.22 0.23 0.24];



[t,x] = ode45('model4_ode', 250, [3.0 4.64 0 0 0]);

plot (t,1000000*x(:,3),'k-','LineWidth', 2)
```

```
 hold on

plot (time_la, la,'kx', 'LineWidth',2)


grid on
xlabel('time(min)')
ylabel ('Lactic acid (%)')
title ('25^oC, 40% S. cerevisiae and 60% L. plantarum - Lactic acid production')
set(gca,'xlim',[0 240],'xtick',[0:20:240]);
set(gca,'ylim',[0 0.25],'ytick',[0:0.025:0.25]);

legend ('lactic acid','Location', 'SouthEast');
```

Thermodynamic Model Script m-file

```
clear all
close all


ideal_GV=24e3;
pressure=1.01*101.325;
T0=293;
T=298;
wt_yeast=(7.9e-11)*(5)*(1e8);
wt_bacteria=(4.18e-13)*20*(1e8);
MW_yeast=23.75;
MW_bacteria=24.95;
MW_LA=90.08;
MW_H2=2;
MW_glucose=180.16;
MW_NaCl=58.44;
MW_water=18;
```

```
%enthalpy and chemical exergies of 1)glucose, 2)ammonium, 3)CO2, 4)ethanol,
%5)glycerol, 6)yeast (Battley,1999), 7)LA
(http://webbook.nist.gov/cgi/cbook.cgi?ID=C79334&Mask=2), 8)bacteria (Battley, E. coli
K12), 9)water
H_data=[-1271.1, -52.2, -393.5, -276, -669.6, -133.13, -694.08, -96.01, -285.8, -484.5,0];
b_data=[2955 340 20 1400 212 529.6 1752 571.4 0.9 907.2 236.09];


[t,x] = ode45('model4_ode', 260, [3.0 4.64 0 0 0]);


for i=1:52;
   % ENERGY AND EXERGY BALANCE FOR BACTERIA
   n_glu_yeast(i,:)=(((x(i+1,4)-x(i,4))/ideal_GV*(1e6)-((x(i+1,3)-
x(i,3))*(1e6)/MW_LA))/0.75*1.13)/1.54;
   n_nh3_yeast(i,:)=(((x(i+1,4)-x(i,4))/ideal_GV*(1e6)-((x(i+1,3)-
x(i,3))*(1e6)/MW_LA))/0.75*1.13)/1.54*0.12;
   n_CO2_yeast(i,:)=(((x(i+1,4)-x(i,4))/ideal_GV*(1e6)-((x(i+1,3)-
x(i,3))*(1e6)/MW_LA))/0.75*1.13);
   n_CO2_yeast(n_CO2_yeast<0)=0;
   n_ethanol_yeast(i,:)=(((x(i+1,4)-x(i,4))/ideal_GV*(1e6)-((x(i+1,3)-
x(i,3))*(1e6)/MW_LA))/0.75*1.13)/1.54*1.3;
   n_gly(i,:)=(((x(i+1,4)-x(i,4))/ideal_GV*(1e6)-((x(i+1,3)-
x(i,3))*(1e6)/MW_LA))/0.75*1.13)/1.54*0.43;
   n_yeast(i,:)=(x(i+1,1)-x(i,1))*wt_yeast/MW_yeast;
   n_yeast(n_yeast<0)=0;
   n_CO2_yeast(n_CO2_yeast<0)=0;

   Nh_glu_yeast=(n_glu_yeast)*H_data(1,1);
   Nh_nh3_yeast=(n_nh3_yeast)*H_data(1,2);
   Nh_CO2_yeast=n_CO2_yeast*H_data(1,3);
   Nh_ethanol_yeast=(n_ethanol_yeast)*H_data(1,4);
```

```
Nh_gly=(n_gly)*H_data(1,5);
Nh_yeast=(n_yeast)*H_data(1,6);
Nb_glu_yeast=(n_glu_yeast)*b_data(1,1);
Nb_nh3_yeast=(n_nh3_yeast)*b_data(1,2);
Nb_CO2_yeast=n_CO2_yeast*b_data(1,3);
Nb_ethanol_yeast=(n_ethanol_yeast)*b_data(1,4);
Nb_gly=(n_gly)*b_data(1,5);
Nb_yeast=(n_yeast)*b_data(1,6);



n_glu_bacteria(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA/0.75;
n_nh3_bacteria(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA/0.75*0.09;
n_water(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA/0.75*0.19;
n_CO2_bacteria(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA*1.13;
n_CO2_bacteria(n_CO2_bacteria<0)=0;
n_LA(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA;
n_LA(n_LA<0)=0;
n_ethanol_bacteria(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA;
n_AA(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA/0.75*0.38;
n_H2=(1e6)*(x(i+1,3)-x(i,3))/MW_LA;
n_bacteria(i,:)=(x(i+1,2)-x(i,2))*wt_bacteria/MW_bacteria;
n_bacteria(n_bacteria<0)=0;
n_LA(n_LA<0)=0;

Nh_glu_bacteria=(n_glu_bacteria)*H_data(1,1);
Nh_nh3_bacteria=(n_nh3_bacteria)*H_data(1,2);
Nh_water=n_water*H_data(1,9);
Nh_CO2_bacteria=(n_CO2_bacteria)*H_data(1,3);
Nh_ethanol_bacteria=(n_ethanol_bacteria)*H_data(1,4);
Nh_LA=(n_LA)*H_data(1,7);
Nh_AA=n_AA*H_data(1,10);
Nh_H2=n_H2*H_data(1,11);
```

```
    Nh_bacteria=(n_bacteria)*H_data(1,8);
    Nh_water=(n_water)*H_data(1,9);
    Nb_glu_bacteria=(n_glu_bacteria)*b_data(1,1);
    Nb_nh3_bacteria=(n_nh3_bacteria)*b_data(1,2);
    Nb_water=(n_water)*b_data(1,9);
    Nb_CO2_bacteria=n_CO2_bacteria*b_data(1,3);
    Nb_ethanol_bacteria=n_ethanol_bacteria*b_data(1,4);
    Nb_LA=(n_LA)*b_data(1,7);
    Nb_AA=(n_AA)*b_data(1,10);
    Nb_H2=n_H2*b_data(1,11);
    Nb_bacteria=(n_bacteria)*b_data(1,8);



    V(i,:)=(x(i+1,5)-x(i,5));
    PV=pressure*V;
end


% m=100;
% cp=2.73*4.184;
% deltaT=5;
% Qin=m*cp*deltaT/1000;

Hin=Nh_glu_yeast+Nh_nh3_yeast+Nh_glu_bacteria+Nh_nh3_bacteria+Nh_water;
Hout=Nh_CO2_yeast+Nh_ethanol_yeast+Nh_gly+Nh_yeast+Nh_bacteria+Nh_ethanol_ba
cteria+Nh_CO2_bacteria+Nh_LA+Nh_H2+Nh_AA;
deltaH=Hout-Hin;
deltaH(deltaH>0)=-0.001;
Q_total=cumsum(deltaH)+cumsum(PV);

Xin_y= Nb_glu_yeast+Nb_nh3_yeast;
Xout_y=Nb_yeast+Nb_CO2_yeast+Nb_ethanol_yeast+Nb_gly;
Xy=(Xin_y-Xout_y);
```

```
Xin_b= Nb_glu_bacteria+Nb_nh3_bacteria+Nb_water;
Xout_b=Nb_bacteria+Nb_ethanol_bacteria+Nb_CO2_bacteria+Nb_LA+Nb_H2+Nb_AA;
Xb=(Xin_b-Xout_b);

deltab=Xy+Xb;
deltab(deltab<0)=0.02;

Xdestroyed=cumsum(deltab)+Q_total*(1-(T0/T))+cumsum(PV);

disp('n_glu_yeast+n_glu_bacteria,...n_CO2_yeast+n_CO2_bacteria, n_LA, n_yeast,
n_bacteria,Hin, Xin_y+Xin_b')
moles=[sum(n_glu_yeast(1:52))+sum(n_glu_bacteria(1:52));sum(n_CO2_yeast(1:52))+su
m(n_CO2_bacteria(1:52));sum(n_LA(1:52));...

sum(n_yeast(1:52));sum(n_bacteria(1:52));sum(Hin(1:52));sum(Xin_b(1:52)+Xin_y(1:52)
)]
disp('Hout, Nbout')
out=[sum(Hout(1:52));sum(Xout_b(1:52)+Xout_y(1:52))]

secondlaw=[Q_total(52) Xdestroyed(52)]

expansion_work=sum(PV(1:52))
Nh_dough=(61.1/MW_glucose)*H_data(1,1)+(2.5/MW_yeast)*H_data(1,8)+(0.6/MW_Na
Cl)*(-411.0)+(35.8/MW_water)*H_data(1,9);
Nb_dough=(61.1/MW_glucose)*b_data(1,1)+(2.5/MW_yeast)*b_data(1,8)+(0.6/MW_Na
Cl)*(14.3)+(35.8/MW_water)*b_data(1,9);
eff=sum(Nb_CO2_yeast+Nb_CO2_bacteria)/Nb_dough*100
wt_CO2_ratio_for_100g=(sum(n_CO2_yeast)+sum(n_CO2_bacteria))*44

for i=1:52;
   time(i)=t(i);
end
```

```
[ax, h1, h2]=plotyy(time, Q_total, time, Xdestroyed)

set(ax,'xlim',[0 240],'xtick',[0:20:240]);

set(get(ax(1),'Ylabel'),'String','Q(kJ)')
set(get(ax(2),'Ylabel'),'String','Xdestroyed(kJ)')

xlabel ('time (min)')
title ('25^oC, 40% S. cerevisiae and 60% L. plantarum - Energy & Exergy Balance')

set(ax(1),'ylim',[-1.5 0],'ytick',[-1.5:0.15:0],'ycolor','black');
set(ax(2),'ylim',[0 30],'ytick',[0:3:30],'ycolor','black');


set(h1,'LineStyle','-.','color','black','LineWidth',2);
set(h2,'LineStyle',':','color','black','LineWidth',2);
legend ('Q', 'Xdestroyed','Location', 'SouthEast');


grid on
```

MODEL 5: 80% *LACTOBACILLUS PLANTARUM* AND 20% *SACCHAROMYCES CEREVISIAE* AT 25ºC

Function m-file

```
function dx= model5(t,x);
% This function models substrate consumption

if t<30
   mu_y_p1=6e-3;
   mu_b_p1=0.021;
   alpha_p1=0.38e-9;
   beta_p1=1e-10;
```

```
    alpha1_p1=0;
    alpha2_p1=0;
    beta1_p2=0;
    beta2_p2=0;
    Vmax=110;
    phi_p1=0;

    dx1=mu_y_p1*x(1);
    dx2=mu_b_p1*x(2);
    dx3=alpha_p1*x(2)+beta_p1*dx2;
    dx4=alpha1_p1*x(1)+alpha2_p1*x(2)+beta1_p2*dx1+beta2_p2*dx2;
    dx5=phi_p1*(1-x(5)/Vmax)*dx4;

end

if t>=30 & t<120
  k_p2y=0.047;
  k_p2b=6.5e-3;
  Xd_p2y=1.0;
  Vmax=110;
  epsilon_p2=3.7e-9;
  alpha1_p2=1e-7;
  alpha2_p2=1e-7;
  beta1_p2=0;
  beta2_p2=0;
  phi_p2=0.25;
  dx1=(-1)*k_p2y*(x(1)-Xd_p2y);
  dx2=(-1)*k_p2b*x(2);
  dx3=(-1)*epsilon_p2*dx2;
  dx4=alpha1_p2*x(1)+alpha2_p2*x(2)+beta1_p2*dx1+beta2_p2*dx2;
  dx5=phi_p2*(1-x(5)/Vmax)*dx4;
end
```

```
if t>=120

mu_y_p3=1e-3;
mu_b_p3=2.88e-3;
alpha_p3=0.4e-4;
beta_p3=0.6e-11;
alpha1_p3=1e-7;
alpha2_p3=1e-7;
beta1_p3=0.1e-6;
beta2_p3=0.1e-6;
phi_p3=0.65;
Vmax=110;

   dx1=mu_y_p3*x(1);
   dx2=mu_b_p3*x(2);
   dx3=alpha_p3*x(2)+beta_p3*dx2;
   dx4=alpha1_p3*x(1)+alpha2_p3*x(2)+beta1_p3*dx1+beta2_p3*dx2;
   dx5=phi_p3*(1-x(5)/Vmax)*dx4;
end


dx=[dx1;dx2;dx3;dx4;dx5];
```

Growth Script m-file

```
clear all
close all
format compact

% enter the data
ty=[0 30 60 90 120 150 180 210];
gy=[2.31 2.81 1.77 1.20 1.0 1.10 1.33 1.45];
```

```
tb=[0 30 60 90 120 150 180 210];
gb=[9 16 14 12 9 10.5 11 12.2];


[t,x] = ode45('model5_ode',[0 240],[2.31 9.1 0 0 0]);



plot (t, x(:,1), 'k-', 'LineWidth', 2.0);
hold on
plot (t,x(:,2),'k:', 'LineWidth',2.0)
hold on
growth_yeast=[x(:,1)]
growth_bacteria=[x(:,2)]
plot (ty,gy,'ko')
hold on
plot (tb,gb,'k*')

grid on
xlabel('time(min)')
ylabel ('biomass x 10^6 cfu/g')
title ('25^oC, 20% S. cerevisiae and 80% L. plantarum - Biomass Production')

set(gca,'xlim',[0 240],'xtick',[0:20:240]);

legend ('S. cerevisiae','L. plantarum', 'Location', 'NorthEast');
```

CO_2 Production Script m-file

```
clear all
close all
format compact
```

```
% enter the data
time_gas=[0 30 70 100 125 155 165 190 210 230];
gas=[0 0 60 100 120 160 170 200 250 275];
time_dough=[0 30 70 100 125 140 155 165 180 190 210 230];
dough=[0 0 20 25 30 35 40 60 75 80 100 110];

[t,x] = ode45('model5_ode',[0 240],[2.31 9.1 0 0 0]);
plot (t,10^6*x(:,4),'k-','LineWidth', 2)
hold on
plot (t,10^6*x(:,5), 'k:', 'LineWidth', 2)
hold on

gas_model=[10^6*x(:,4)]
vol_model=[10^6*x(:,5)]

plot (time_gas, gas,'ko', 'LineWidth',2)
 hold on
plot (time_dough, dough,'k*','LineWidth',2)

grid on
xlabel('time(min)')
ylabel ('G, V(cm^3)')
title ('25^oC, 20% S. cerevisiae and 80% L. plantarum - Gas Production & Dough Volume
Increase')

set(gca,'xlim',[0 240],'xtick',[0:20:240]);
legend ('gas production','dough volume increase', 'Location', 'NorthWest');

set(gca,'ylim',[0 300],'ytick',[0:50:300]);
```

Lactic Acid Production Script m-file

```
clear all
close all
format compact
```

```
% enter the data
time_la=[0 30 60 95 120 125 160 200 230];
la=[0 0.13 0.14 0.16 0.17 0.17 0.18 0.20 0.21];



[t,x] = ode45('model5_ode1',[0 120],[2.31 9.1 0 0 0]);

plot (t, 1000000*x(:,3), 'k-.', 'LineWidth', 2.0);
hold on

la_model1=[1000000*x(:,3)]



[t,x] = ode45('model5_ode2',[120 250],[1.0 9 0.16 100 50]);
plot (t, x(:,3), 'k-.', 'LineWidth', 2.0)
hold on

plot (time_la,la,'ko')

la_model2=[x(:,3)]

la_model=[la_model1; la_model2]



grid on
xlabel('time(min)')
ylabel ('Lactic acid (%)')
title ('25^oC, 20% S. cerevisiae and 80% L. plantarum - Lactic acid production')
set(gca,'xlim',[0 240],'xtick',[0:20:240]);
set(gca,'ylim',[0 0.25],'ytick',[0:0.025:0.25]);
legend ('lactic acid','Location', 'SouthEast');
```

Thermodynamic Model Script m-file

```
clear all
close all


ideal_GV=24e3;
pressure=1.01*101.325;
T0=293;
T=298;
wt_yeast=(7.9e-11)*(5)*(1e8);
wt_bacteria=(4.18e-13)*20*(1e8);
MW_yeast=23.75;
MW_bacteria=24.95;
MW_LA=90.08;
MW_H2=2;
MW_glucose=180.16;
MW_NaCl=58.44;
MW_water=18;


%enthalpy and chemical exergies of 1)glucose, 2)ammonium, 3)CO2, 4)ethanol,
%5)glycerol, 6)yeast (Battley,1999), 7)LA
(http://webbook.nist.gov/cgi/cbook.cgi?ID=C79334&Mask=2), 8)bacteria (Battley, E. coli
K12), 9)water
H_data=[-1271.1, -47.2, -393.5, -276, -669.6, -133.13, -694.08, -96.01, -285.8, -484.5,0];
b_data=[2955 340 20 1400 212 529.6 1747 571.4 0.9 907.2 236.09];


[t,x] = ode45('model5_ode', 260, [4.1 1.0 0 0 0]);

vectors1=[
   2.3100    9.1000         0         0         0
   2.3434    9.5688    0.0085         0         0
```

2.3773	10.0618	0.0175	0	0
2.4116	10.5802	0.0269	0	0
2.4465	11.1253	0.0369	0	0
2.4860	11.7670	0.0500	0	0
2.5262	12.4456	0.0640	0	0
2.5670	13.1634	0.0790	0	0
2.6084	13.9225	0.0949	0	0
2.6308	14.3458	0.1140	0	0
2.6534	14.7820	0.1293	0	0
2.6762	15.2315	0.1348	0	0
2.6992	15.6946	0.1357	0	0
2.7386	16.2507	0.1366	0	-0.0816
2.7407	16.6430	0.1375	0.0967	0.0242
2.6628	16.6556	0.1384	2.1494	0.5374
2.5450	16.4568	0.1395	5.0796	1.2699
2.4510	16.3145	0.1405	7.6021	1.9005
2.3627	16.1735	0.1415	10.0935	2.5234
2.2798	16.0336	0.1425	12.5547	3.1387
2.2019	15.8950	0.1435	14.9865	3.7466
1.9582	15.4057	0.1445	23.5134	5.8784
1.7640	14.9315	0.1454	31.7033	7.9258
1.6098	14.4719	0.1463	39.5835	9.8959
1.4868	14.0264	0.1472	47.1795	11.7949
1.3905	13.6060	0.1481	54.3208	13.5802
1.3133	13.1982	0.1490	61.2275	15.3069
1.2515	12.8026	0.1499	67.9132	16.9783
1.2020	12.4188	0.1507	74.3905	18.5976
1.1581	12.0065	0.1515	81.3467	20.3367
1.1238	11.6079	0.1523	88.0719	22.0180
1.0971	11.2225	0.1531	94.5773	23.6443
1.0761	10.8499	0.1539	100.8735	25.2184
1.0576	10.4420	0.1547	107.7785	26.9446
1.0436	10.0494	0.1554	114.4378	28.6095

1.0331	9.6715	0.1561	120.8626	30.2156
1.0252	9.3079	0.1569	127.0633	31.7658
1.0250	9.2999	0.1576	127.2007	31.8002
1.0249	9.2918	0.1582	127.3380	31.8345
1.0247	9.2838	0.1589	127.4751	31.8688
1.0246	9.2758	0.1592	127.6122	31.9030
1.0246	9.2740	0.1594	127.7494	31.9670
1.0247	9.2783	0.1597	127.8867	32.0596
1.0249	9.2826	0.1599	128.0242	32.1524
1.0250	9.2858	0.1600	128.1617	32.2402
1.0252	9.2895	0.1612	128.3073	32.3349
1.0253	9.2933	0.1624	128.4530	32.4296
1.0255	9.2971	0.1636	128.5988	32.5244
1.0256	9.3009	0.1648	128.7446	32.6191
1.0263	9.3197	0.1660	129.4745	33.0936
1.0270	9.3387	0.1672	130.2058	33.5689
1.0278	9.3576	0.1685	130.9385	34.0452
1.0285	9.3766	0.1697	131.6726	34.5223
1.0321	9.4722	0.1710	135.3639	36.9217
1.0358	9.5688	0.1723	139.0905	39.3440
1.0394	9.6663	0.1736	142.8526	41.7893
1.0431	9.7648	0.1749	146.6507	44.2581
1.0494	9.9350	0.1762	153.2058	48.5189
1.0557	10.1082	0.1775	159.8681	52.8494
1.0620	10.2844	0.1788	166.6393	57.2507
1.0684	10.4636	0.1802	173.5212	61.7239
1.0748	10.6460	0.1816	180.5158	66.2704
1.0813	10.8316	0.1829	187.6250	70.8914
1.0878	11.0204	0.1843	194.8507	75.5881
1.0944	11.2125	0.1857	202.1949	80.3618
1.1010	11.4079	0.1872	209.6596	85.2139
1.1076	11.6067	0.1886	217.2469	90.1456
1.1142	11.8090	0.1900	224.9589	95.1584

```
    1.1210   12.0149    0.1915  232.7978  100.2536
    1.1277   12.2243    0.1930  240.7655  105.4327
    1.1345   12.4374    0.1944  248.8645  110.6970
    1.1413   12.6542    0.1959  257.0969  116.0480
    1.1482   12.8747    0.1975  265.4649  121.4873
    1.1499   12.9317    0.1990  267.6270  122.8926
    1.1517   12.9890    0.2005  269.7981  124.3038
    1.1535   13.0465    0.2021  271.9783  125.7210
    1.1552   13.1043    0.2037  274.1677  127.1441];

vectors2=[
    2.3434    9.5688    0.0085         0         0
    2.3773   10.0618    0.0175         0         0
    2.4116   10.5802    0.0269         0         0
    2.4465   11.1253    0.0369         0         0
    2.4860   11.7670    0.0500         0         0
    2.5262   12.4456    0.0640         0         0
    2.5670   13.1634    0.0790         0         0
    2.6084   13.9225    0.0949         0         0
    2.6308   14.3458    0.1140         0         0
    2.6534   14.7820    0.1293         0         0
    2.6762   15.2315    0.1348         0         0
    2.6992   15.6946    0.1357         0         0
    2.7386   16.2507    0.1366         0   -0.0816
    2.7407   16.6430    0.1375    0.0967    0.0242
    2.6628   16.6556    0.1384    2.1494    0.5374
    2.5450   16.4568    0.1395    5.0796    1.2699
    2.4510   16.3145    0.1405    7.6021    1.9005
    2.3627   16.1735    0.1415   10.0935    2.5234
    2.2798   16.0336    0.1425   12.5547    3.1387
    2.2019   15.8950    0.1435   14.9865    3.7466
    1.9582   15.4057    0.1445   23.5134    5.8784
    1.7640   14.9315    0.1454   31.7033    7.9258
```

1.6098	14.4719	0.1463	39.5835	9.8959
1.4868	14.0264	0.1472	47.1795	11.7949
1.3905	13.6060	0.1481	54.3208	13.5802
1.3133	13.1982	0.1490	61.2275	15.3069
1.2515	12.8026	0.1499	67.9132	16.9783
1.2020	12.4188	0.1507	74.3905	18.5976
1.1581	12.0065	0.1515	81.3467	20.3367
1.1238	11.6079	0.1523	88.0719	22.0180
1.0971	11.2225	0.1531	94.5773	23.6443
1.0761	10.8499	0.1539	100.8735	25.2184
1.0576	10.4420	0.1547	107.7785	26.9446
1.0436	10.0494	0.1554	114.4378	28.6095
1.0331	9.6715	0.1561	120.8626	30.2156
1.0252	9.3079	0.1569	127.0633	31.7658
1.0250	9.2999	0.1576	127.2007	31.8002
1.0249	9.2918	0.1582	127.3380	31.8345
1.0247	9.2838	0.1589	127.4751	31.8688
1.0246	9.2758	0.1592	127.6122	31.9030
1.0246	9.2740	0.1594	127.7494	31.9670
1.0247	9.2783	0.1597	127.8867	32.0596
1.0249	9.2826	0.1599	128.0242	32.1524
1.0250	9.2858	0.1600	128.1617	32.2402
1.0252	9.2895	0.1612	128.3073	32.3349
1.0253	9.2933	0.1624	128.4530	32.4296
1.0255	9.2971	0.1636	128.5988	32.5244
1.0256	9.3009	0.1648	128.7446	32.6191
1.0263	9.3197	0.1660	129.4745	33.0936
1.0270	9.3387	0.1672	130.2058	33.5689
1.0278	9.3576	0.1685	130.9385	34.0452
1.0285	9.3766	0.1697	131.6726	34.5223
1.0321	9.4722	0.1710	135.3639	36.9217
1.0358	9.5688	0.1723	139.0905	39.3440
1.0394	9.6663	0.1736	142.8526	41.7893

```
    1.0431    9.7648    0.1749  146.6507   44.2581
    1.0494    9.9350    0.1762  153.2058   48.5189
    1.0557   10.1082    0.1775  159.8681   52.8494
    1.0620   10.2844    0.1788  166.6393   57.2507
    1.0684   10.4636    0.1802  173.5212   61.7239
    1.0748   10.6460    0.1816  180.5158   66.2704
    1.0813   10.8316    0.1829  187.6250   70.8914
    1.0878   11.0204    0.1843  194.8507   75.5881
    1.0944   11.2125    0.1857  202.1949   80.3618
    1.1010   11.4079    0.1872  209.6596   85.2139
    1.1076   11.6067    0.1886  217.2469   90.1456
    1.1142   11.8090    0.1900  224.9589   95.1584
    1.1210   12.0149    0.1915  232.7978  100.2536
    1.1277   12.2243    0.1930  240.7655  105.4327
    1.1345   12.4374    0.1944  248.8645  110.6970
    1.1413   12.6542    0.1959  257.0969  116.0480
    1.1482   12.8747    0.1975  265.4649  121.4873
    1.1499   12.9317    0.1990  267.6270  122.8926
    1.1517   12.9890    0.2005  269.7981  124.3038
    1.1535   13.0465    0.2021  271.9783  125.7210
    1.1552   13.1043    0.2037  274.1677  127.1441
    1.1552   13.1043    0.2037  274.1677  127.1441];

delta_vector=vectors2-vectors1;
delta_vector(delta_vector<0)=0;


    n_glu_bacteria=delta_vector(:,3)/MW_LA/0.75;
    n_nh3_bacteria=delta_vector(:,3)/MW_LA/0.75*0.09;
    n_water=delta_vector(:,3)/MW_LA/0.75*0.19;
    n_CO2_bacteria=delta_vector(:,3)/MW_LA/0.75*1.13;
    n_LA=delta_vector(:,3)/MW_LA;
    n_ethanol_bacteria=delta_vector(:,3)/MW_LA;
```

```
n_AA=delta_vector(:,3)/MW_LA/0.75*0.38;
n_H2=delta_vector(:,3)/MW_LA;
n_bacteria=delta_vector(:,2)*wt_bacteria/MW_bacteria;

Nh_glu_bacteria=(n_glu_bacteria)*H_data(1,1);
Nh_nh3_bacteria=(n_nh3_bacteria)*H_data(1,2);
Nh_water=n_water*H_data(1,9);
Nh_CO2_bacteria=(n_CO2_bacteria)*H_data(1,3);
Nh_ethanol_bacteria=(n_ethanol_bacteria)*H_data(1,4);
Nh_LA=(n_LA)*H_data(1,7);
Nh_AA=n_AA*H_data(1,10);
Nh_H2=n_H2*H_data(1,11);
Nh_bacteria=(n_bacteria)*H_data(1,8);
Nh_water=(n_water)*H_data(1,9);
Nb_glu_bacteria=(n_glu_bacteria)*b_data(1,1);
Nb_nh3_bacteria=(n_nh3_bacteria)*b_data(1,2);
Nb_water=(n_water)*b_data(1,9);
Nb_CO2_bacteria=n_CO2_bacteria*b_data(1,3);
Nb_ethanol_bacteria=n_ethanol_bacteria*b_data(1,4);
Nb_LA=(n_LA)*b_data(1,7);
Nb_AA=(n_AA)*b_data(1,10);
Nb_H2=n_H2*b_data(1,11);
Nb_bacteria=(n_bacteria)*b_data(1,8);



n_glu_yeast=((delta_vector(:,4)/ideal_GV)-n_CO2_bacteria)/1.54;
n_nh3_yeast=((delta_vector(:,4)/ideal_GV)-n_CO2_bacteria)/1.54*0.12;
n_CO2_yeast=((delta_vector(:,4)/ideal_GV)-n_CO2_bacteria);
n_ethanol_yeast=((delta_vector(:,4)/ideal_GV)-n_CO2_bacteria)/1.54*1.3;
n_gly=((delta_vector(:,4)/ideal_GV)-n_CO2_bacteria)/1.54*0.43;
n_yeast=delta_vector(:,1)*wt_yeast/MW_yeast;
```

```
Nh_glu_yeast=(n_glu_yeast)*H_data(1,1);
Nh_nh3_yeast=(n_nh3_yeast)*H_data(1,2);
Nh_CO2_yeast=n_CO2_yeast*H_data(1,3);
Nh_ethanol_yeast=(n_ethanol_yeast)*H_data(1,4);
Nh_gly=(n_gly)*H_data(1,5);
Nh_yeast=(n_yeast)*H_data(1,6);
Nb_glu_yeast=(n_glu_yeast)*b_data(1,1);
Nb_nh3_yeast=(n_nh3_yeast)*b_data(1,2);
Nb_CO2_yeast=n_CO2_yeast*b_data(1,3);
Nb_ethanol_yeast=(n_ethanol_yeast)*b_data(1,4);
Nb_gly=(n_gly)*b_data(1,5);
Nb_yeast=(n_yeast)*b_data(1,6);


V=delta_vector(:,5)*(1e-6);
PV=pressure*V;

% m=100;
% cp=2.73*4.184;
% deltaT=5;
% Qin=m*cp*deltaT/1000;

Nh_dough=(61.1/MW_glucose)*H_data(1,1)+(2.5/MW_yeast)*H_data(1,8)+(0.6/MW_Na
Cl)*(-411.0)+(35.8/MW_water)*H_data(1,9);
Nb_dough=(61.1/MW_glucose)*b_data(1,1)+(2.5/MW_yeast)*b_data(1,8)+(0.6/MW_Na
Cl)*(14.3)+(35.8/MW_water)*b_data(1,9);


Hin=Nh_glu_yeast+Nh_nh3_yeast+Nh_glu_bacteria+Nh_nh3_bacteria+Nh_water;
Hout=Nh_CO2_yeast+Nh_ethanol_yeast+Nh_gly+Nh_yeast+Nh_bacteria+Nh_ethanol_ba
cteria+Nh_CO2_bacteria+Nh_LA+Nh_H2+Nh_AA;
deltaH=cumsum(Hout-Hin);
Q_total=(deltaH)+cumsum(PV);
```

```
deltaH(deltaH>0)=0;

Xin_y= Nb_glu_yeast+Nb_nh3_yeast;
Xout_y=Nb_yeast+Nb_CO2_yeast+Nb_ethanol_yeast+Nb_gly;
Xy=(Xin_y-Xout_y);

Xin_b= Nb_glu_bacteria+Nb_nh3_bacteria+Nb_water;
Xout_b=Nb_bacteria+Nb_ethanol_bacteria+Nb_CO2_bacteria+Nb_LA+Nb_H2+Nb_AA;
Xb=(Xin_b-Xout_b);

deltab=Xy+Xb;
deltab(deltab<0)=0.01;
Xdestroyed=cumsum(deltab)+Q_total*(1-(T0/T))+cumsum(PV);
Xdestroyed(Xdestroyed<0)=0;


disp('n_glu_yeast+n_glu_bacteria,...n_CO2_yeast+n_CO2_bacteria, n_LA, n_yeast,
n_bacteria,Hin, Xin_y+Xin_b')
moles=[sum(n_glu_yeast)+sum(n_glu_bacteria);sum(n_CO2_yeast)+sum(n_CO2_bacteria
);sum(n_LA);...
   sum(n_yeast);sum(n_bacteria);sum(Hin);sum(Xin_b+Xin_y)]
disp('Hout, Nbout')
out=[sum(Hout);sum(Xout_b+Xout_y)]


secondlaw=[Q_total(end) Xdestroyed(end)]

expansion_work=sum(PV)

eff=sum(Nb_CO2_yeast+Nb_CO2_bacteria)/Nb_dough*100
wt_CO2_ratio_for_100g=(sum(n_CO2_yeast)+sum(n_CO2_bacteria))*44

time=[0:(240/76):240];
```

```
   [ax, h1, h2]=plotyy(time, Q_total, time, Xdestroyed)
   set(get(ax(1),'Ylabel'),'String','Q(kJ)')
set(get(ax(2),'Ylabel'),'String','Xdestroyed(kJ)')

xlabel ('time (min)')
title '25^oC, 20% S. cerevisiae and 80% L. plantarum - Energy&Exergy Balance')

set(h1,'LineStyle','-.','color','black','LineWidth',2);
set(h2,'LineStyle',':','color','black','LineWidth',2);


set(ax,'xlim',[0 240],'xtick',[0:20:240]);



set(ax(1),'ylim',[-0.5 0],'ytick',[-0.5:0.05:0],'ycolor','black');
set(ax(2),'ylim',[0 10],'ytick',[0:1:10],'ycolor','black');


legend ('Q', 'Xdestroyed','Location', 'SouthEast');

grid on
```

MODEL 6: 100% *LACTOBACILLUS PLANTARUM* AND 0% *SACCHAROMYCES CEREVISIAE* AT 25ºC

Function m-file

```
function dx= model6(t,x);
% This function models substrate consumption

if t<90;
   k_b_p1=0.005;
```

```
    epsilon_p1=0.27e-7;
    alpha2_p1=9e-1;
    beta2_p1=0;
    phi_p1=0.81;
    Vmax=28;

    dx1=(-1)*k_b_p1*x(1);
    dx2=(-1)*epsilon_p1*dx1;
    dx3=alpha2_p1*x(2)+beta2_p1*dx2;
    dx4=phi_p1*(1-x(4)/Vmax)*dx3;
end

if t>=90;
  mu_b_p2=1.3e-3;
  alpha_p2=3e-8;
  beta_p2=3e-8;
  alpha2_p2=4.8;
  beta2_p2=6e-7;
  phi_p2=0.22;
  Vmax=28;


  dx1=mu_b_p2*x(1);
  dx2=alpha_p2*x(2)+beta_p2*dx1;
  dx3=alpha2_p2*x(2)+beta2_p2*dx2;
  dx4=phi_p2*(1-x(4)/Vmax)*dx3;
end

dx=[dx1;dx2;dx3;dx4];
```

Growth Script m-file

```
clear all
close all
```

```
format compact

% enter the data

tb=[0 30 60 90 120 150 180 210];
gb=[19.0 17.0 14.0 12.3 12.45 13.0 13.8 14.6];


[t,x] = ode45('model6_ode', 250, [19 0 0 0]);

plot (t, x(:,1), 'k-.', 'LineWidth', 2)
hold on

plot (tb, gb, 'k+','LineWidth',2)

grid on
xlabel('time(min)')
ylabel ('biomass x 10^6 cfu/g')
title ('25^oC, 100% L. plantarum - Biomass Production')

set(gca,'xlim',[0 240],'xtick',[0:20:240]);

legend ('L. plantarum', 'Location', 'NorthEast');
```

CO_2 Production Script m-file

```
clear all
close all
format compact

% enter the data
time_gas=[0 60 90 120 130 140 150 160 165 180 185 200 210];
gas=[0 10 15 38 50 60 65 80 82 90 105 118 120];
```

```
time_dough=[0 60 90 120 130 150 180 200 210];
dough=[0 5 10 15 18 19 20 25 28];



[t,x] = ode45('model6_ode', 250, [19 0 0 0]);

 plot (t,10^6*x(:,3),'k-','LineWidth', 2)
 hold on
 plot (t,10^6*x(:,4), 'k:', 'LineWidth', 2)
 hold on

plot (time_gas, gas,'ko', 'LineWidth',2)
 hold on
plot (time_dough, dough,'k*','LineWidth',2)

grid on
xlabel('time(min)')
ylabel ('G, V(cm^3)')
title ('25^oC, 100% L. plantarum - Gas Production & Dough Volume Increase')
set(gca,'xlim',[0 240],'xtick',[0:20:240]);
legend ('gas production','dough volume increase', 'Location', 'NorthWest');
```

Lactic Acid Production Script m-file

```
clear all
close all
format compact

% enter the data
time_la=[0 30 60 90 120 150 180 210];
la=[0 0.075 0.13 0.18 0.21 0.22 0.23 0.25];
```

```
[t,x] = ode45('model6_ode', 250, [19 0 0 0]);

plot (t,1000000*x(:,2),'k-','LineWidth', 2)
hold on

plot (time_la, la,'kx', 'LineWidth',2)

set(gca,'xlim',[0 240],'xtick',[0:40:240]);

grid on
xlabel('time(min)')
ylabel ('Lactic acid (%)')
title ('25^oC, 100% L. plantarum - Lactic acid production')
set(gca,'xlim',[0 240],'xtick',[0:20:240]);

legend ('lactic acid','Location', 'SouthEast');
```

Thermodynamic Model Script m-file

```
clear all
close all


ideal_GV=24e3;
pressure=1.01*101.325;
T0=293;
T=298;
wt_yeast=(7.9e-11)*(5)*(1e8);
wt_bacteria=(4.18e-13)*20*(1e8);
MW_yeast=23.75;
MW_bacteria=24.95;
MW_LA=90.08;
```

```
MW_H2=2;
MW_glucose=180.16;
MW_NaCl=58.44;
MW_water=18;


%enthalpy and chemical exergies of 1)glucose, 2)ammonium, 3)CO2, 4)ethanol,
%5)glycerol, 6)yeast (Battley,1999), 7)LA
(http://webbook.nist.gov/cgi/cbook.cgi?ID=C79334&Mask=2), 8)bacteria (Battley, E. coli
K12), 9)water
H_data=[-1271.1, -52.2, -393.5, -276, -669.6, -133.13, -694.08, -96.01, -285.8, -484.5,0];
b_data=[2955 340 20 1400 212 529.6 1752 571.4 0.9 907.2 236.09];


[t,x] = ode45('model6_ode', 260, [19 0 0 0]);


for i=1:40;

 % ENERGY AND EXERGY BALANCE FOR BACTERIA


   n_glu_bacteria(i,:)=(1e6)*(x(i+1,2)-x(i,2))/MW_LA/0.75;
   n_nh3_bacteria(i,:)=(1e6)*(x(i+1,2)-x(i,2))/MW_LA/0.75*0.09;
   n_water(i,:)=(1e6)*(x(i+1,2)-x(i,2))/MW_LA/0.75*0.19;
   n_CO2_bacteria(i,:)=(1e6)*(x(i+1,3)-x(i,3))/ideal_GV;
   n_CO2_bacteria(n_CO2_bacteria<0)=0;
   n_LA(i,:)=(1e6)*(x(i+1,2)-x(i,2))/MW_LA;
   n_LA(n_LA<0)=0;
   n_ethanol_bacteria(i,:)=(1e6)*(x(i+1,2)-x(i,2))/MW_LA;
   n_AA(i,:)=(1e6)*(x(i+1,2)-x(i,2))/MW_LA/0.75*0.38;
   n_H2=(1e6)*(x(i+1,2)-x(i,2))/MW_LA;
```

```
    n_bacteria(i,:)=(x(i+1,1)-x(i,1))*wt_bacteria/MW_bacteria;
    n_bacteria(n_bacteria<0)=0;
    n_LA(n_LA<0)=0;
    Nh_glu_bacteria=(n_glu_bacteria)*H_data(1,1);
    Nh_nh3_bacteria=(n_nh3_bacteria)*H_data(1,2);
    Nh_water=n_water*H_data(1,9);
    Nh_CO2_bacteria=(n_CO2_bacteria)*H_data(1,3);
    Nh_ethanol_bacteria=(n_ethanol_bacteria)*H_data(1,4);
    Nh_LA=(n_LA)*H_data(1,7);
    Nh_AA=n_AA*H_data(1,10);
    Nh_H2=n_H2*H_data(1,11);
    Nh_bacteria=(n_bacteria)*H_data(1,8);
    Nh_water=(n_water)*H_data(1,9);
    Nb_glu_bacteria=(n_glu_bacteria)*b_data(1,1);
    Nb_nh3_bacteria=(n_nh3_bacteria)*b_data(1,2);
    Nb_water=(n_water)*b_data(1,9);
    Nb_CO2_bacteria=n_CO2_bacteria*b_data(1,3);
    Nb_ethanol_bacteria=n_ethanol_bacteria*b_data(1,4);
    Nb_LA=(n_LA)*b_data(1,7);
    Nb_AA=(n_AA)*b_data(1,10);
    Nb_H2=n_H2*b_data(1,11);
    Nb_bacteria=(n_bacteria)*b_data(1,8);


    V(i,:)=(x(i+1,4)-x(i,4));
    PV=pressure*V;
end


% m=100;
% cp=2.73*4.184;
% deltaT=5;
% Qin=m*cp*deltaT/1000;
```

```
Hin=Nh_glu_bacteria+Nh_nh3_bacteria+Nh_water;
Hout=Nh_bacteria+Nh_ethanol_bacteria+Nh_CO2_bacteria+Nh_LA+Nh_H2+Nh_AA;
deltaH=Hout-Hin;
deltaH(deltaH>0)=-0.01;
Q_total=cumsum(deltaH)+cumsum(PV);

Xin_b= Nb_glu_bacteria+Nb_nh3_bacteria+Nb_water;
Xout_b=Nb_bacteria+Nb_ethanol_bacteria+Nb_CO2_bacteria+Nb_LA+Nb_H2+Nb_AA;
Xb=(Xin_b-Xout_b);

deltab=Xb;
deltab(deltab<0)=0.01;

Xdestroyed=cumsum(deltab)+Q_total*(1-(T0/T))+cumsum(PV);

disp('n_glu_bacteria,n_CO2_bacteria,n_LA, n_bacteria, Hin, Xin_b')
moles=[sum(n_glu_bacteria(1:38));sum(n_CO2_bacteria(1:38));sum(n_LA);
sum(n_bacteria(1:38)); sum(Hin(1:38)); sum(Xin_b(1:38))]
disp('Hout, Nbout')
out=[sum(Hout(1:38));sum(Xout_b(1:38))]

secondlaw=[Q_total(38) Xdestroyed(38)]

expansion_work=sum(PV(1:38))
Nh_dough=(61.1/MW_glucose)*H_data(1,1)+(2.5/MW_yeast)*H_data(1,8)+(0.6/MW_Na
Cl)*(-411.0)+(35.8/MW_water)*H_data(1,9);
Nb_dough=(61.1/MW_glucose)*b_data(1,1)+(2.5/MW_yeast)*b_data(1,8)+(0.6/MW_Na
Cl)*(14.3)+(35.8/MW_water)*b_data(1,9);
eff=sum(Nb_CO2_bacteria)/Nb_dough*100

wt_CO2_ratio_for_100g=(sum(n_CO2_bacteria))*44

for i=1:40;
```

```
    time(i)=t(i);
end

[ax, h1, h2]=plotyy(time, Q_total, time, Xdestroyed)

set(ax,'xlim',[0 240],'xtick',[0:20:240]);

set(get(ax(1),'Ylabel'),'String','Q(kJ)')
set(get(ax(2),'Ylabel'),'String','Xdestroyed(kJ)')

xlabel ('time (min)')
title ('25^oC, 100% L. plantarum - Energy&Exergy Balance')

set(ax(1),'ylim',[-4 0],'ytick',[-4:0.4:1],'ycolor','black');
set(ax(2),'ylim',[0 1],'ytick',[0:0.1:1],'ycolor','black');


set(h1,'LineStyle','-.','color','black','LineWidth',2);
set(h2,'LineStyle',':','color','black','LineWidth',2);
legend ('Q', 'Xdestroyed','Location', 'SouthEast');


grid on
```

MODEL 1: 20% *LACTOBACILLUS PLANTARUM* AND 80% *SACCHAROMYCES CEREVISIAE* AT 20ºC

Function m-file

```
function dx= model7(t,x);
% This function models substrate consumption

if t<=60;
  mu_b_p1=0.051;
```

```
  alpha_p1=2.2e-9;
  beta_p1=1e-12;
  Xmax_p1b=1.7;


   dx1=0;
   dx2=mu_b_p1*x(2)*(1-x(2)/Xmax_p1b);
   dx3=alpha_p1*x(2)+beta_p1*dx2;
   dx4=0;
   dx5=0;
  end

if t>60;
  k_y_p2=0.026;
  mu_b_p2=0.051;
  alpha_p2=2e-11;
  beta_p2=3e-7;
  alpha1_p2=1.3e-7;
  alpha2_p2=1e-8;
  beta1_p2=0;
  beta2_p2=0;
  phi_p2=0.31;
  Xd_y_p2=3.11;
  Xmax_p2b=1.8;
  Vmax=22;

  dx1=(-1)*k_y_p2*(x(1)-Xd_y_p2);
  dx2=mu_b_p2*x(2)*(1-x(2)/Xmax_p2b);
  dx3=alpha_p2*x(2)+beta_p2*dx2;
  dx4=alpha1_p2*x(1)+alpha2_p2*x(2)+beta1_p2*dx1+beta2_p2*dx2;
  dx5=phi_p2*(1-x(5)/Vmax)*dx4;
end
```

```
dx=[dx1;dx2;dx3;dx4;dx5];
```

Growth Script m-file

```
clear all
close all
format compact

% enter the data
ty=[0 30 60 90 120 150 180 210];
gy=[4.5 4.55 4.46 3.81 3.5 3.22 3.06 3.11];

tb=[0 30 60 90 120 150 180 210];
gb=[1.2 1.57 1.75 1.75 1.75 1.75 1.8 1.75];


[t,x] = ode45('model7_ode', 250, [4.55 1.2 0 0 0]);

plot (t, x(:,1), 'k-', 'LineWidth', 2.0)
hold on

plot (t,x(:,2),'k:', 'LineWidth',2.0)
plot (ty,gy,'ko')
plot (tb,gb,'k*')

grid on
xlabel('time(min)')
ylabel ('biomass x 10^6 cfu/g')
title ('20^oC, 80% S. cerevisiae and 20% L. plantarum - Biomass Production')

set(gca,'xlim',[0 240],'xtick',[0:20:240]);

legend ('S. cerevisiae','L. plantarum', 'Location', 'NorthEast');
```

CO_2 Production Script m-file

Function m-file for CO_2

```
function dx= model7(t,x);
% This function models substrate consumption

if t<=80;
  mu_b_p1=0.051;
  alpha_p1=2.2e-9;
  beta_p1=1e-12;
  Xmax_p1b=1.7;


   dx1=0;
   dx2=mu_b_p1*x(2)*(1-x(2)/Xmax_p1b);
   dx3=alpha_p1*x(2)+beta_p1*dx2;
   dx4=0;
   dx5=0;
  end

if t>80;
  k_y_p2=0.026;
  mu_b_p2=0.051;
  alpha_p2=2e-11;
  beta_p2=3e-7;
  alpha1_p2=1.4e-7;
  alpha2_p2=2e-9;
  beta1_p2=0;
  beta2_p2=0;
  phi_p2=0.37;
  Xd_y_p2=3.11;
  Xmax_p2b=1.8;
  Vmax=22;
```

```
  dx1=(-1)*k_y_p2*(x(1)-Xd_y_p2);
  dx2=mu_b_p2*x(2)*(1-x(2)/Xmax_p2b);
  dx3=alpha_p2*x(2)+beta_p2*dx2;
  dx4=alpha1_p2*x(1)+alpha2_p2*x(2)+beta1_p2*dx1+beta2_p2*dx2;
  dx5=phi_p2*(1-x(5)/Vmax)*dx4;
end

dx=[dx1;dx2;dx3;dx4;dx5];
```

CO2 Production Script m-file

```
clear all
close all
format compact

% enter the data
time_gas=[0 30 85 100 110 130 175 190 220 230];
gas=[0 0 2 10 20 28 50 60 70 75];
time_dough=[0 30 100 130 160 180 200 220];
dough=[0 0 2 10 16 20 22 22];



[t,x] = ode45('gas7_ode', 250, [4.55 1.2 0 0 0]);

 plot (t,10^6*x(:,4),'k-','LineWidth', 2)
 hold on
 plot (t,10^6*x(:,5), 'k:', 'LineWidth', 2)
 hold on

plot (time_gas, gas,'ko', 'LineWidth',2)
 hold on
plot (time_dough, dough,'k*','LineWidth',2)
```

```
set(gca,'xlim',[0 240],'xtick',[0:40:240]);
set(gca,'ylim',[0 80],'ytick',[0:10:80]);

grid on
xlabel('time(min)')
ylabel ('G, V(cm^3)')
title ('20^oC, 80% S. cerevisiae and 20% L. plantarum - Gas Production & Dough Volume Increase')
set(gca,'xlim',[0 240],'xtick',[0:20:240]);
legend ('gas production','dough volume increase', 'Location', 'NorthWest');
```

Lactic Acid Production Script m-file

```
clear all
close all
format compact

% enter the data
time_la=[0 35 60 90 120 160 210];
la=[0 0.13 0.19 0.23 0.24 0.24 0.24];



[t,x] = ode45('model7_ode', [0 240], [4.55 1.2 0 0 0]);

 plot (t,1000000*x(:,3),'k-','LineWidth', 2)
 hold on

plot (time_la, la,'kx', 'LineWidth',2)

grid on
xlabel('time(min)')
ylabel ('Lactic acid (%)')
```

```
title ('20^oC, 80% S. cerevisiae and 20% L. plantarum - Lactic acid production')
set(gca,'xlim',[0 240],'xtick',[0:20:240]);
set(gca,'ylim',[0 0.25],'ytick',[0:0.025:0.25]);

legend ('lactic acid','Location', 'SouthEast');
```

Thermodynamic Model Script m-file

```
clear all
close all


ideal_GV=24e3;
pressure=1.01*101.325;
T0=293;
T=293;
wt_yeast=(7.9e-11)*(5)*(1e8);
wt_bacteria=(4.18e-13)*20*(1e8);
MW_yeast=23.75;
MW_bacteria=24.95;
MW_LA=90.08;
MW_H2=2;
MW_glucose=180.16;
MW_NaCl=58.44;
MW_water=18;

cp_yeast=0.339;
cp_bacteria=0.354;
cp_glucose=0.220;
cp_nh3=0.357;
cp_h2o=0.075;
cp_LA=0.372;
cp_gly=0.222;
```

```
cp_ethanol=0.110;
cp_AA=0.140;
cp_CO2=0.037;
cp_H2=0.029;

%enthalpy and chemical exergies of 1)glucose, 2)ammonium, 3)CO2, 4)ethanol,
%5)glycerol, 6)yeast (Battley,1999), 7)LA
(http://webbook.nist.gov/cgi/cbook.cgi?ID=C79334&Mask=2), 8)bacteria (Battley, E. coli
K12), 9)water
H_data=[-1271.1, -52.2, -393.5, -276, -669.6, -133.13, -694.08, -96.01, -285.8, -484.5,0];
b_data=[2955 340 20 1400 212 529.6 1752 571.4 0.9 907.2 236.09];


[t,x] = ode45('model7_ode', 260, [4.55 1.2 0 0 0]);


for i=1:44;

  % ENERGY AND EXERGY BALANCE FOR BACTERIA
   n_glu_yeast(i,:)=(((x(i+1,4)-x(i,4))/ideal_GV*(1e6)-((x(i+1,3)-
x(i,3))*(1e6)/MW_LA))/0.75*1.13)/1.54;
   n_nh3_yeast(i,:)=(((x(i+1,4)-x(i,4))/ideal_GV*(1e6)-((x(i+1,3)-
x(i,3))*(1e6)/MW_LA))/0.75*1.13)/1.54*0.12;
   n_CO2_yeast(i,:)=(((x(i+1,4)-x(i,4))/ideal_GV*(1e6)-((x(i+1,3)-
x(i,3))*(1e6)/MW_LA))/0.75*1.13);
   n_CO2_yeast(n_CO2_yeast<0)=0;
   n_ethanol_yeast(i,:)=(((x(i+1,4)-x(i,4))/ideal_GV*(1e6)-((x(i+1,3)-
x(i,3))*(1e6)/MW_LA))/0.75*1.13)/1.54*1.3;
   n_gly(i,:)=(((x(i+1,4)-x(i,4))/ideal_GV*(1e6)-((x(i+1,3)-
x(i,3))*(1e6)/MW_LA))/0.75*1.13)/1.54*0.43;
   n_yeast(i,:)=(x(i+1,1)-x(i,1))*wt_yeast/MW_yeast;
   n_yeast(n_yeast<0)=0;
```

```
n_CO2_yeast(n_CO2_yeast<0)=0;

Nh_glu_yeast=(n_glu_yeast)*H_data(1,1);
Nh_nh3_yeast=(n_nh3_yeast)*H_data(1,2);
Nh_CO2_yeast=n_CO2_yeast*H_data(1,3);
Nh_ethanol_yeast=(n_ethanol_yeast)*H_data(1,4);
Nh_gly=(n_gly)*H_data(1,5);
Nh_yeast=(n_yeast)*H_data(1,6);
Nb_glu_yeast=(n_glu_yeast)*b_data(1,1);
Nb_nh3_yeast=(n_nh3_yeast)*b_data(1,2);
Nb_CO2_yeast=n_CO2_yeast*b_data(1,3);
Nb_ethanol_yeast=(n_ethanol_yeast)*b_data(1,4);
Nb_gly=(n_gly)*b_data(1,5);
Nb_yeast=(n_yeast)*b_data(1,6);



n_glu_bacteria(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA/0.75;
n_nh3_bacteria(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA/0.75*0.09;
n_water(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA/0.75*0.19;
n_CO2_bacteria(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA*1.13;
n_CO2_bacteria(n_CO2_bacteria<0)=0;
n_LA(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA;
n_LA(n_LA<0)=0;
n_ethanol_bacteria(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA;
n_AA(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA/0.75*0.38;
n_H2=(1e6)*(x(i+1,3)-x(i,3))/MW_LA;
n_bacteria(i,:)=(x(i+1,2)-x(i,2))*wt_bacteria/MW_bacteria;
n_bacteria(n_bacteria<0)=0;
n_LA(n_LA<0)=0;

Nh_glu_bacteria=(n_glu_bacteria)*H_data(1,1);
Nh_nh3_bacteria=(n_nh3_bacteria)*H_data(1,2);
```

```
    Nh_water=n_water*H_data(1,9);
    Nh_CO2_bacteria=(n_CO2_bacteria)*H_data(1,3);
    Nh_ethanol_bacteria=(n_ethanol_bacteria)*H_data(1,4);
    Nh_LA=(n_LA)*H_data(1,7);
    Nh_AA=n_AA*H_data(1,10);
    Nh_H2=+n_H2*H_data(1,11);
    Nh_bacteria=(n_bacteria)*H_data(1,8);

    Nb_glu_bacteria=(n_glu_bacteria)*b_data(1,1);
    Nb_nh3_bacteria=(n_nh3_bacteria)*b_data(1,2);
    Nb_water=(n_water)*b_data(1,9);
    Nb_CO2_bacteria=n_CO2_bacteria*b_data(1,3);
    Nb_ethanol_bacteria=n_ethanol_bacteria*b_data(1,4);
    Nb_LA=(n_LA)*b_data(1,7);
    Nb_AA=(n_AA)*b_data(1,10);
    Nb_H2=n_H2*b_data(1,11);
    Nb_bacteria=(n_bacteria)*b_data(1,8);


    V(i,:)=(x(i+1,5)-x(i,5));
    PV=pressure*V;
end


% m=100;
% cp=2.73*4.184;
% deltaT=5;
% Qin=m*cp*deltaT/1000;

Hin=[(-5)*cp_h2o*sum(n_water)]+[(-5)*cp_glucose*sum(n_glu_bacteria)]+[(-
5)*cp_glucose*sum(n_glu_yeast)]+...
[(5)*cp_nh3*sum(n_nh3_yeast)]+Nh_glu_yeast+Nh_nh3_yeast+Nh_glu_bacteria+Nh_nh
3_bacteria+Nh_water;
```

```
Hout=[(-5)*cp_CO2*sum(n_CO2_bacteria)]+[(-
5)*cp_ethanol*sum(n_ethanol_bacteria)]+[(-5)*cp_LA*sum(n_LA)]+[(-
5)*cp_AA*sum(n_AA)]+...
   [(-5)*cp_H2*sum(n_H2)]+[(-5)*cp_bacteria*sum(n_bacteria)]+[(-
5)*cp_bacteria*sum(n_nh3_bacteria)]+...
   [(-5)*cp_ethanol*sum(n_ethanol_yeast)]+[(-5)*cp_CO2*sum(n_CO2_yeast)]+[(-
5)*cp_gly*sum(n_gly)]+...
   [(-5)*cp_yeast*sum(n_yeast)]+...

Nh_CO2_yeast+Nh_ethanol_yeast+Nh_gly+Nh_yeast+Nh_bacteria+Nh_ethanol_bacteria
+Nh_CO2_bacteria+Nh_LA+Nh_H2+Nh_AA;
deltaH=Hout-Hin;
deltaH(deltaH>0)=-0.001;
Q_total=cumsum(deltaH)+cumsum(PV);

Xin_y= Nb_glu_yeast+Nb_nh3_yeast;
Xout_y=Nb_yeast+Nb_CO2_yeast+Nb_ethanol_yeast+Nb_gly;
Xy=(Xin_y-Xout_y);

Xin_b= Nb_glu_bacteria+Nb_nh3_bacteria+Nb_water;
Xout_b=Nb_bacteria+Nb_ethanol_bacteria+Nb_CO2_bacteria+Nb_LA+Nb_H2+Nb_AA;
Xb=(Xin_b-Xout_b);

deltab=Xy+Xb;
dealtab(deltab<0)=0.001;

Xdestroyed=cumsum(deltab)+Q_total*(1-(T0/T))+cumsum(PV);
Xdestroyed(Xdestroyed<0)=0.02;



secondlaw=[Q_total(end) Xdestroyed(end)]

expansion_work=sum(PV)
```

```
Nh_dough=(61.1/MW_glucose)*H_data(1,1)+(2.5/MW_yeast)*H_data(1,8)+(0.6/MW_NaCl)*(-411.0)+(35.8/MW_water)*H_data(1,9);
Nb_dough=(61.1/MW_glucose)*b_data(1,1)+(2.5/MW_yeast)*b_data(1,8)+(0.6/MW_NaCl)*(14.3)+(35.8/MW_water)*b_data(1,9);
eff=sum(Nb_CO2_yeast+Nb_CO2_bacteria)/Nb_dough*100

wt_CO2_ratio_for_100g=(sum(n_CO2_yeast)+sum(n_CO2_bacteria))*44

disp('n_glu_yeast+n_glu_bacteria,...n_CO2_yeast+n_CO2_bacteria, n_LA, n_yeast, n_bacteria,Hin, Xin_y+Xin_b')
moles=[sum(n_glu_yeast)+sum(n_glu_bacteria);sum(n_CO2_yeast)+sum(n_CO2_bacteria);sum(n_LA);...
   sum(n_yeast);sum(n_bacteria);sum(Hin);sum(Xin_b+Xin_y)]
disp('Hout, Nbout')
out=[sum(Hout);sum(Xout_b+Xout_y)]

for i=1:44;
   time(i)=t(i);
end

[ax, h1, h2]=plotyy(time, Q_total, time, Xdestroyed)

set(ax,'xlim',[0 240],'xtick',[0:20:240]);

set(get(ax(1),'Ylabel'),'String','Q(kJ)')
set(get(ax(2),'Ylabel'),'String','Xdestroyed(kJ)')

xlabel ('time (min)')
title ('20^oC, 80% S. cerevisiae and 20% L. plantarum - Energy & Exergy Balance')

set(ax(1),'ylim',[-1.5 0],'ytick',[-1.5:0.15:0],'ycolor','black');
set(ax(2),'ylim',[0 3],'ytick',[0:0.3:3],'ycolor','black');
```

```
set(h1,'LineStyle','-.','color','black','LineWidth',2);
set(h2,'LineStyle',':','color','black','LineWidth',2);
legend ('Q', 'Xdestroyed','Location', 'SouthEast');
legend ('Q', 'Xdestroyed','Location', 'SouthEast');

grid on
```

MODEL 8: 20% *LACTOBACILLUS PLANTARUM* AND 80% *SACCHAROMYCES CEREVISIAE* AT 30ºC

Function m-file

```
function dx= model8(t,x);
% This function models substrate consumption

if t<=60;
    mu_y_p1=0.028;
   alpha_p1=0.31e-8;
   beta_p1=0;
   alpha1_p1=2.7e-7;
   alpha2_p1=1e-7;
   beta1_p1=1e-6;
   beta2_p1=0;
   phi_p1=0.29;
   Xmax_p1y=7;
   Vmax=120;

   dx1=mu_y_p1*x(1)*(1-x(1)/Xmax_p1y);
   dx2=0;
   dx3=alpha_p1*x(2)+beta_p1*dx2;
   dx4=alpha1_p1*x(1)+alpha2_p1*x(2)+beta1_p1*dx1+beta2_p1*dx2;
   dx5=phi_p1*(1-x(5)/Vmax)*dx4;

  end
```

```
if t>60;
  mu_y_p2=0.028;
  mu_b_p2=0.052;
  alpha_p2=0.5e-11;
  beta_p2=11e-9;
  alpha1_p2=5.1e-7;
  alpha2_p2=5.7e-7;
  beta1_p2=1e-6;
  beta2_p2=1e-6;
  phi_p2=0.12;
  Xmax_p2y=7;
  Xmax_p2b=6;
  Vmax=120;

  dx1=mu_y_p2*x(1)*(1-x(1)/Xmax_p2y);
  dx2=mu_b_p2*x(2)*(1-x(2)/Xmax_p2b);
  dx3=alpha_p2*x(2)+beta_p2*dx2;
  dx4=alpha1_p2*x(1)+alpha2_p2*x(2)+beta1_p2*dx1+beta2_p2*dx2;
  dx5=phi_p2*(1-x(5)/Vmax)*dx4;
end

dx=[dx1;dx2;dx3;dx4;dx5];
```

Growth Script m-file

```
clear all
close all
format compact

% enter the data
ty=[0 30 60 90 120 150 180 210];
gy=[2.6 4.3 4.5 6.2 6.8 7 7.05 7];
```

```
tb=[0 30 60 90 120 150 180 210];
gb=[0.95 1 1 2.45 4.65 5.9 5.8 6];


[t,x] = ode45('model8_ode', 250, [2.6 0.95 0 0 0]);

plot (t, x(:,1), 'k-', 'LineWidth', 2.0)
hold on

plot (t,x(:,2),'k:', 'LineWidth',2.0)
plot (ty,gy,'ko')
plot (tb,gb,'k*')

grid on
xlabel('time(min)')
ylabel ('biomass x 10^6 cfu/g')
title ('30^oC, 80% S. cerevisiae and 20% L. plantarum - Biomass Production')

set(gca,'xlim',[0 240],'xtick',[0:20:240]);

legend ('S. cerevisiae','L. plantarum', 'Location', 'SouthEast');
```

CO_2 Production Script m-file

```
clear all
close all
format compact

% enter the data
time_gas=[0 20 40 50 60 80 100 110 125 140 155 170 180 200 210];
gas=[0 0 0 0 80 120 200 300 400 500 600 700 700 800 820];
time_dough=[0 20 40 50 60 80 100 110 125 140 155 170 180 200 210];
dough=[0 0 0 0 0 5 50 70 85 90 100 100 100 110 120];
```

```
[t,x] = ode45('model8_ode', 250, [2.6 0.95 0 0 0]);

plot (t,10^6*x(:,4),'k-','LineWidth', 2)
hold on
plot (t,10^6*x(:,5), 'k:', 'LineWidth', 2)
hold on

plot (time_gas, gas,'ko', 'LineWidth',2)
hold on
plot (time_dough, dough,'k*','LineWidth',2)

grid on
xlabel('time(min)')
ylabel ('G, V(cm^3)')
title ('30^oC, 80% S. cerevisiae and 20% L. plantarum - Gas Production & Dough Volume Increase')
set(gca,'xlim',[0 240],'xtick',[0:20:240]);
legend ('gas production','dough volume increase', 'Location', 'NorthWest');
```

Lactic Acid Production Script m-file

```
clear all
close all
format compact

% enter the data
time_la=[0 30 60 90 150 180 210];
la=[0 0.075 0.175 0.220 0.240 0.230 0.240];
```

```
[t,x] = ode45('model8_ode', 250, [2.6 0.95 0 0 0]);

 plot (t,1000000*x(:,3),'k-','LineWidth', 2)
 hold on

plot (time_la, la,'kx', 'LineWidth',2)


grid on
xlabel('time(min)')
ylabel ('Lactic acid (%)')
title ('30^oC, 80% S. cerevisiae and 20% L. plantarum - Lactic acid production')
set(gca,'xlim',[0 240],'xtick',[0:20:240]);
set(gca,'ylim',[0 0.25],'ytick',[0:0.025:0.25]);

legend ('lactic acid','Location', 'SouthEast');
```

Thermodynamic Model Script m-file

```
clear all
close all


ideal_GV=24e3;
pressure=1.01*101.325;
T0=293;
T=303;
wt_yeast=(7.9e-11)*(5)*(1e8);
wt_bacteria=(4.18e-13)*20*(1e8);
MW_yeast=23.75;
MW_bacteria=24.95;
MW_LA=90.08;
MW_H2=2;
```

```
MW_glucose=180.16;
MW_NaCl=58.44;
MW_water=18;

cp_yeast=0.339;
cp_bacteria=0.354;
cp_glucose=0.220;
cp_nh3=0.357;
cp_h2o=0.075;
cp_LA=0.372;
cp_gly=0.222;
cp_ethanol=0.114;
cp_AA=0.140;
cp_CO2=0.037;
cp_H2=0.029;


%enthalpy and chemical exergies of 1)glucose, 2)ammonium, 3)CO2, 4)ethanol,
%5)glycerol, 6)yeast (Battley,1999), 7)LA
(http://webbook.nist.gov/cgi/cbook.cgi?ID=C79334&Mask=2), 8)bacteria (Battley, E. coli
K12), 9)water
H_data=[-1271.1, -47.2, -393.5, -276, -669.6, -133.13, -694.08, -96.01, -285.8, -484.5,0];
b_data=[2955 340 20 1400 212 529.6 1747 571.4 0.9 907.2 236.09];



[t,x] = ode45('model8_ode', 240, [2.6 0.95 0 0 0]);



for i=1:48;
  % ENERGY AND EXERGY BALANCE FOR BACTERIA
```

```
    n_glu_yeast(i,:)=(((x(i+1,4)-x(i,4))/ideal_GV*(1e6)-((x(i+1,3)-
x(i,3))*(1e6)/MW_LA))/0.75*1.13)/1.54;
    n_nh3_yeast(i,:)=(((x(i+1,4)-x(i,4))/ideal_GV*(1e6)-((x(i+1,3)-
x(i,3))*(1e6)/MW_LA))/0.75*1.13)/1.54*0.12;
    n_CO2_yeast(i,:)=(((x(i+1,4)-x(i,4))/ideal_GV*(1e6)-((x(i+1,3)-
x(i,3))*(1e6)/MW_LA))/0.75*1.13);
    n_CO2_yeast(n_CO2_yeast<0)=0;
    n_ethanol_yeast(i,:)=(((x(i+1,4)-x(i,4))/ideal_GV*(1e6)-((x(i+1,3)-
x(i,3))*(1e6)/MW_LA))/0.75*1.13)/1.54*1.3;
    n_gly(i,:)=(((x(i+1,4)-x(i,4))/ideal_GV*(1e6)-((x(i+1,3)-
x(i,3))*(1e6)/MW_LA))/0.75*1.13)/1.54*0.43;
    n_yeast(i,:)=(x(i+1,1)-x(i,1))*wt_yeast/MW_yeast;
    n_yeast(n_yeast<0)=0;
    n_CO2_yeast(n_CO2_yeast<0)=0;
    Nh_glu_yeast=(n_glu_yeast)*H_data(1,1);
    Nh_nh3_yeast=(n_nh3_yeast)*H_data(1,2);
    Nh_CO2_yeast=n_CO2_yeast*H_data(1,3);
    Nh_ethanol_yeast=(n_ethanol_yeast)*H_data(1,4);
    Nh_gly=(n_gly)*H_data(1,5);
    Nh_yeast=(n_yeast)*H_data(1,6);
    Nb_glu_yeast=(n_glu_yeast)*b_data(1,1);
    Nb_nh3_yeast=(n_nh3_yeast)*b_data(1,2);
    Nb_CO2_yeast=n_CO2_yeast*b_data(1,3);
    Nb_ethanol_yeast=(n_ethanol_yeast)*b_data(1,4);
    Nb_gly=(n_gly)*b_data(1,5);
    Nb_yeast=(n_yeast)*b_data(1,6);



    n_glu_bacteria(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA/0.75;
    n_nh3_bacteria(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA/0.75*0.09;
    n_water(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA/0.75*0.19;
    n_CO2_bacteria(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA*1.13;
```

```
    n_CO2_bacteria(n_CO2_bacteria<0)=0;
    n_LA(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA;
    n_LA(n_LA<0)=0;
    n_ethanol_bacteria(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA;
    n_AA(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA/0.75*0.38;
    n_H2=(1e6)*(x(i+1,3)-x(i,3))/MW_LA;
    n_bacteria(i,:)=(x(i+1,2)-x(i,2))*wt_bacteria/MW_bacteria;
    n_bacteria(n_bacteria<0)=0;
    n_LA(n_LA<0)=0;
    Nh_glu_bacteria=(n_glu_bacteria)*H_data(1,1);
    Nh_nh3_bacteria=(n_nh3_bacteria)*H_data(1,2);
    Nh_water=n_water*H_data(1,9);
    Nh_CO2_bacteria=(n_CO2_bacteria)*H_data(1,3);
    Nh_ethanol_bacteria=(n_ethanol_bacteria)*H_data(1,4);
    Nh_LA=(n_LA)*H_data(1,7);
    Nh_AA=n_AA*H_data(1,10);
    Nh_H2=n_H2*H_data(1,11);
    Nh_bacteria=(n_bacteria)*H_data(1,8);
    Nh_water=(n_water)*H_data(1,9);
    Nb_glu_bacteria=(n_glu_bacteria)*b_data(1,1);
    Nb_nh3_bacteria=(n_nh3_bacteria)*b_data(1,2);
    Nb_water=(n_water)*b_data(1,9);
    Nb_CO2_bacteria=n_CO2_bacteria*b_data(1,3);
    Nb_ethanol_bacteria=n_ethanol_bacteria*b_data(1,4);
    Nb_LA=(n_LA)*b_data(1,7);
    Nb_AA=(n_AA)*b_data(1,10);
    Nb_H2=n_H2*b_data(1,11);
    Nb_bacteria=(n_bacteria)*b_data(1,8);


    V(i,:)=(x(i+1,5)-x(i,5));
    PV=pressure*V;
end
```

```
% m=100;
% cp=2.73*4.184;
% deltaT=5;
% Qin=m*cp*deltaT/1000;

Hin=[(5)*cp_h2o*sum(n_water)]+[(5)*cp_glucose*sum(n_glu_bacteria)]+[(5)*cp_glucos
e*sum(n_glu_yeast)]+...

[(5)*cp_nh3*sum(n_nh3_yeast)]+Nh_glu_yeast+Nh_nh3_yeast+Nh_glu_bacteria+Nh_nh
3_bacteria+Nh_water;
Hout=[(5)*cp_CO2*sum(n_CO2_bacteria)]+[(5)*cp_ethanol*sum(n_ethanol_bacteria)]+[(
5)*cp_LA*sum(n_LA)]+[(5)*cp_AA*sum(n_AA)]+...

[(5)*cp_H2*sum(n_H2)]+[(5)*cp_bacteria*sum(n_bacteria)]+[(5)*cp_bacteria*sum(n_nh
3_bacteria)]+...

[(5)*cp_ethanol*sum(n_ethanol_yeast)]+[(5)*cp_CO2*sum(n_CO2_yeast)]+[(5)*cp_gly*
sum(n_gly)]+...
   [(5)*cp_yeast*sum(n_yeast)]+...

Nh_CO2_yeast+Nh_ethanol_yeast+Nh_gly+Nh_yeast+Nh_bacteria+Nh_ethanol_bacteria
+Nh_CO2_bacteria+Nh_LA+Nh_H2+Nh_AA;

deltaH=Hout-Hin;
deltaH(deltaH>0)=-0.001;
Q_total=cumsum(deltaH)+cumsum(PV);

Xin_y= Nb_glu_yeast+Nb_nh3_yeast;
Xout_y=Nb_yeast+Nb_CO2_yeast+Nb_ethanol_yeast+Nb_gly;
Xy=(Xin_y-Xout_y);

Xin_b= Nb_glu_bacteria+Nb_nh3_bacteria+Nb_water;
Xout_b=Nb_bacteria+Nb_ethanol_bacteria+Nb_CO2_bacteria+Nb_LA+Nb_H2+Nb_AA;
```

```
Xb=(Xin_b-Xout_b);

deltab=Xy+Xb;
deltab(deltab<0)=0.02;

Xdestroyed=cumsum(deltab)+Q_total*(1-(T0/T))+cumsum(PV);

disp('n_glu_yeast+n_glu_bacteria,...n_CO2_yeast+n_CO2_bacteria, n_LA, n_yeast,
n_bacteria,Hin, Xin_y+Xin_b')
moles=[sum(n_glu_yeast)+sum(n_glu_bacteria);sum(n_CO2_yeast)+sum(n_CO2_bacteria
);sum(n_LA);...
   sum(n_yeast);sum(n_bacteria);sum(Hin);sum(Xin_b+Xin_y)]

secondlaw=[Q_total(end) Xdestroyed(end)]

expansion_work=sum(PV)
Nh_dough=(61.1/MW_glucose)*H_data(1,1)+(2.5/MW_yeast)*H_data(1,8)+(0.6/MW_Na
Cl)*(-411.0)+(35.8/MW_water)*H_data(1,9);
Nb_dough=(61.1/MW_glucose)*b_data(1,1)+(2.5/MW_yeast)*b_data(1,8)+(0.6/MW_Na
Cl)*(14.3)+(35.8/MW_water)*b_data(1,9);
eff=sum(Nb_CO2_yeast+Nb_CO2_bacteria)/Nb_dough*100

wt_CO2_ratio_for_100g=(sum(n_CO2_yeast)+sum(n_CO2_bacteria))*44
disp('Hout, Nbout')
out=[sum(Hout);sum(Xout_b+Xout_y)]

for i=1:48;
   time(i)=t(i+1);
end

[ax, h1, h2]=plotyy(time, Q_total, time, Xdestroyed)

set(ax,'xlim',[0 240],'xtick',[0:20:240]);
```

```
set(get(ax(1),'Ylabel'),'String','Q(kJ)')
set(get(ax(2),'Ylabel'),'String','Xdestroyed(kJ)')

xlabel ('time (min)')
title ('30^oC, 80% S. cerevisiae and 20% L. plantarum - Energy & Exergy Balance')
set(ax(1),'ylim',[-0.2 0],'ytick',[-0.2:0.02:0],'ycolor','black');
set(ax(2),'ylim',[0 60],'ytick',[0:6:60],'ycolor','black');


set(h1,'LineStyle','-.','color','black','LineWidth',2);
set(h2,'LineStyle',':','color','black','LineWidth',2);
legend ('Q', 'Xdestroyed','Location', 'SouthEast');

grid on
```

MODEL 9: 20% *LACTOBACILLUS PLANTARUM* AND 80% *SACCHAROMYCES CEREVISIAE* AT 35°C

Function m-file

```
function dx= model9(t,x);
% This function models substrate consumption

mu_y_p1=0.053;
mu_b_p1=0.010;
alpha_p1=0.25e-9;
beta_p1=1.2e-10;
alpha1_p1=5.4e-10;
alpha2_p1=11e-7;
beta1_p1=1.3e-6;
beta2_p1=1.6e-6;
phi_p1=0.21;
Xmax_p1y=7.6;
Vmax=200;
```

```
dx1=mu_y_p1*x(1)*(1-x(1)/Xmax_p1y);
dx2=mu_b_p1*x(2);
dx3=alpha_p1*x(2)+beta_p1*dx2;
dx4=alpha1_p1*x(1)+alpha2_p1*x(2)+beta1_p1*dx1+beta2_p1*dx2;
dx5=phi_p1*(1-x(5)/Vmax)*dx4;



dx=[dx1;dx2;dx3;dx4;dx5];
```

Growth Script m-file

```
clear all
close all
format compact

% enter the data
ty=[0 30 60 90 120 150 180 210];
gy=[5 7.1 7.65 7.6 8.2 7.35 7.6 7.6];

tb=[0 30 60 90 120 150 180 210];
gb=[1.9 1.8 2 2.5 4 7.5 8.2 12];



[t,x] = ode45('model9_ode', 250, [5 1.4 0 0 0]);

plot (t, x(:,1), 'k-', 'LineWidth', 2.0)
hold on

plot (t,x(:,2),'k:', 'LineWidth',2.0)
plot (ty,gy,'ko')
plot (tb,gb,'k*')
```

```
grid on
xlabel('time(min)')
ylabel ('biomass x 10^6 cfu/g')
title ('35^oC, 80% S. cerevisiae and 20% L. plantarum - Biomass Production')

set(gca,'xlim',[0 240],'xtick',[0:20:240]);

legend ('S. cerevisiae','L. plantarum', 'Location', 'NorthEast');
```

CO_2 Production Script m-file

```
clear all
close all
format compact

% enter the data
time_gas=[0 20 40 50 65 80 95 110 125 140 150 165 180 190 210];
gas=[0 100 110 160 200 210 300 350 400 480 570 700 750 800 1000];
time_dough=[0 20 40 50 80 95 110 125 140 150 165 180 190 210];
dough=[0 0 5 10 50 90 90 100 105 107 120 150 170 200];



[t,x] = ode45('model9_ode', 250, [5 1.4 0 0 0]);

 plot (t,10^6*x(:,4),'k-','LineWidth', 2)
 hold on
 plot (t,10^6*x(:,5), 'k:', 'LineWidth', 2)
 hold on

plot (time_gas, gas,'ko', 'LineWidth',2)
 hold on
plot (time_dough, dough,'k*','LineWidth',2)
```

```
grid on
xlabel('time(min)')
ylabel ('G, V(cm^3)')
title ('35^oC, 80% S. cerevisiae and 20% L. plantarum - Gas Production & Dough Volume Increase')
set(gca,'xlim',[0 240],'xtick',[0:20:240]);
legend ('gas production','dough volume increase', 'Location', 'NorthWest');
```

Lactic Acid Production Script m-file

```
clear all
close all
format compact

% enter the data
time_la=[0 30 90 120 150 180 210];
la=[0 0.02 0.040 0.065 0.15 0.175 0.28];



[t,x] = ode45('model9_ode', 250, [5 1.4 0 0 0]);

 plot (t,1000000*x(:,3),'k-','LineWidth', 2)
 hold on

plot (time_la, la,'kx', 'LineWidth',2)


grid on
xlabel('time(min)')
ylabel ('Lactic acid (%)')
title ('35^oC, 80% S. cerevisiae and 20% L. plantarum - Lactic acid production')
```

```
set(gca,'xlim',[0 240],'xtick',[0:20:240]);
set(gca,'ylim',[0 0.4],'ytick',[0:0.05:0.4]);

legend ('lactic acid','Location', 'SouthEast');
```

Thermodynamic Model Script m-file

```
clear all
close all


ideal_GV=24e3;
pressure=1.01*101.325;
T0=293;
T=308;
wt_yeast=(7.9e-11)*(5)*(1e8);
wt_bacteria=(4.18e-13)*20*(1e8);
MW_yeast=23.75;
MW_bacteria=24.95;
MW_LA=90.08;
MW_H2=2;
MW_glucose=180.16;
MW_NaCl=58.44;
MW_water=18;

cp_yeast=0.339;
cp_bacteria=0.354;
cp_glucose=0.220;
cp_nh3=0.357;
cp_h2o=0.075;
cp_LA=0.372;
cp_gly=0.222;
cp_ethanol=0.110;
```

```
cp_AA=0.140;
cp_CO2=0.037;
cp_H2=0.029;
%enthalpy and chemical exergies of 1)glucose, 2)ammonium, 3)CO2, 4)ethanol,
%5)glycerol, 6)yeast (Battley,1999), 7)LA
(http://webbook.nist.gov/cgi/cbook.cgi?ID=C79334&Mask=2), 8)bacteria (Battley, E. coli
K12), 9)water
H_data=[-1271.1, -47.2, -393.5, -276, -669.6, -133.13, -694.08, -96.01, -285.8, -484.5,0];
b_data=[2955 340 20 1400 212 529.6 1747 571.4 0.9 907.2 236.09];


[t,x] = ode45('model9_ode', 240, [5 1.4 0 0 0]);



for i=1:44;

  % ENERGY AND EXERGY BALANCE FOR BACTERIA
   n_glu_yeast(i,:)=(((x(i+1,4)-x(i,4))/ideal_GV*(1e6)-((x(i+1,3)-
x(i,3))*(1e6)/MW_LA))/0.75*1.13)/1.54;
   n_nh3_yeast(i,:)=(((x(i+1,4)-x(i,4))/ideal_GV*(1e6)-((x(i+1,3)-
x(i,3))*(1e6)/MW_LA))/0.75*1.13)/1.54*0.12;
   n_CO2_yeast(i,:)=(((x(i+1,4)-x(i,4))/ideal_GV*(1e6)-((x(i+1,3)-
x(i,3))*(1e6)/MW_LA))/0.75*1.13);
   n_CO2_yeast(n_CO2_yeast<0)=0;
   n_ethanol_yeast(i,:)=(((x(i+1,4)-x(i,4))/ideal_GV*(1e6)-((x(i+1,3)-
x(i,3))*(1e6)/MW_LA))/0.75*1.13)/1.54*1.3;
   n_gly(i,:)=(((x(i+1,4)-x(i,4))/ideal_GV*(1e6)-((x(i+1,3)-
x(i,3))*(1e6)/MW_LA))/0.75*1.13)/1.54*0.43;
   n_yeast(i,:)=(x(i+1,1)-x(i,1))*wt_yeast/MW_yeast;
   n_yeast(n_yeast<0)=0;
   n_CO2_yeast(n_CO2_yeast<0)=0;
   Nh_glu_yeast=(n_glu_yeast)*H_data(1,1);
```

```
Nh_nh3_yeast=(n_nh3_yeast)*H_data(1,2);
Nh_CO2_yeast=n_CO2_yeast*H_data(1,3);
Nh_ethanol_yeast=(n_ethanol_yeast)*H_data(1,4);
Nh_gly=(n_gly)*H_data(1,5);
Nh_yeast=(n_yeast)*H_data(1,6);
Nb_glu_yeast=(n_glu_yeast)*b_data(1,1);
Nb_nh3_yeast=(n_nh3_yeast)*b_data(1,2);
Nb_CO2_yeast=n_CO2_yeast*b_data(1,3);
Nb_ethanol_yeast=(n_ethanol_yeast)*b_data(1,4);
Nb_gly=(n_gly)*b_data(1,5);
Nb_yeast=(n_yeast)*b_data(1,6);



n_glu_bacteria(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA/0.75;
n_nh3_bacteria(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA/0.75*0.09;
n_water(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA/0.75*0.19;
n_CO2_bacteria(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA*1.13;
n_CO2_bacteria(n_CO2_bacteria<0)=0;
n_LA(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA;
n_LA(n_LA<0)=0;
n_ethanol_bacteria(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA;
n_AA(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA/0.75*0.38;
n_H2=(1e6)*(x(i+1,3)-x(i,3))/MW_LA;
n_bacteria(i,:)=(x(i+1,2)-x(i,2))*wt_bacteria/MW_bacteria;
n_bacteria(n_bacteria<0)=0;
n_LA(n_LA<0)=0;
Nh_glu_bacteria=(n_glu_bacteria)*H_data(1,1);
Nh_nh3_bacteria=(n_nh3_bacteria)*H_data(1,2);
Nh_water=n_water*H_data(1,9);
Nh_CO2_bacteria=(n_CO2_bacteria)*H_data(1,3);
Nh_ethanol_bacteria=(n_ethanol_bacteria)*H_data(1,4);
Nh_LA=(n_LA)*H_data(1,7);
```

```
    Nh_AA=n_AA*H_data(1,10);
    Nh_H2=n_H2*H_data(1,11);
    Nh_bacteria=(n_bacteria)*H_data(1,8);
    Nh_water=(n_water)*H_data(1,9);
    Nb_glu_bacteria=(n_glu_bacteria)*b_data(1,1);
    Nb_nh3_bacteria=(n_nh3_bacteria)*b_data(1,2);
    Nb_water=(n_water)*b_data(1,9);
    Nb_CO2_bacteria=n_CO2_bacteria*b_data(1,3);
    Nb_ethanol_bacteria=n_ethanol_bacteria*b_data(1,4);
    Nb_LA=(n_LA)*b_data(1,7);
    Nb_AA=(n_AA)*b_data(1,10);
    Nb_H2=n_H2*b_data(1,11);
    Nb_bacteria=(n_bacteria)*b_data(1,8);



    V(i,:)=(x(i+1,5)-x(i,5));
    PV=pressure*V;
end



% m=100;
% cp=2.73*4.184;
% deltaT=5;
% Qin=m*cp*deltaT/1000;

Hin=[(10)*cp_h2o*sum(n_water)]+[(10)*cp_glucose*sum(n_glu_bacteria)]+[(10)*cp_glu
cose*sum(n_glu_yeast)]+...

[(10)*cp_nh3*sum(n_nh3_yeast)]+Nh_glu_yeast+Nh_nh3_yeast+Nh_glu_bacteria+Nh_n
h3_bacteria+Nh_water;
Hout=[(10)*cp_CO2*sum(n_CO2_bacteria)]+[(10)*cp_ethanol*sum(n_ethanol_bacteria)]
+[(10)*cp_LA*sum(n_LA)]+[(10)*cp_AA*sum(n_AA)]+...
```

```
[(10)*cp_H2*sum(n_H2)]+[(10)*cp_bacteria*sum(n_bacteria)]+[(10)*cp_bacteria*sum(n_nh3_bacteria)]+...

[(10)*cp_ethanol*sum(n_ethanol_yeast)]+[(10)*cp_CO2*sum(n_CO2_yeast)]+[(10)*cp_gly*sum(n_gly)]+...
   [(10)*cp_yeast*sum(n_yeast)]+...

Nh_CO2_yeast+Nh_ethanol_yeast+Nh_gly+Nh_yeast+Nh_bacteria+Nh_ethanol_bacteria+Nh_CO2_bacteria+Nh_LA+Nh_H2+Nh_AA;


deltaH=Hout-Hin;
deltaH(deltaH>0)=-0.1;
Q_total=cumsum(deltaH)+cumsum(PV);

Q_total(1)=0;

Xin_y= Nb_glu_yeast+Nb_nh3_yeast;
Xout_y=Nb_yeast+Nb_CO2_yeast+Nb_ethanol_yeast+Nb_gly;
Xy=(Xin_y-Xout_y);

Xin_b= Nb_glu_bacteria+Nb_nh3_bacteria+Nb_water;
Xout_b=Nb_bacteria+Nb_ethanol_bacteria+Nb_CO2_bacteria+Nb_LA+Nb_H2+Nb_AA;
Xb=(Xin_b-Xout_b);

deltab=Xy+Xb;
deltab(deltab<0)=0.01;

Xdestroyed=cumsum(deltab)+Q_total*(1-(T0/T))+cumsum(PV);

disp('n_glu_yeast+n_glu_bacteria,...n_CO2_yeast+n_CO2_bacteria, n_LA, n_yeast, n_bacteria,Hin, Xin_y+Xin_b')
```

```
moles=[sum(n_glu_yeast)+sum(n_glu_bacteria);sum(n_CO2_yeast)+sum(n_CO2_bacteria
);sum(n_LA);...
   sum(n_yeast);sum(n_bacteria);sum(Hin);sum(Xin_b+Xin_y)]
disp('Hout, Nbout')
out=[sum(Hout);sum(Xout_b+Xout_y)]

secondlaw=[Q_total(end) Xdestroyed(end)]

expansion_work=sum(PV)
Nh_dough=(61.1/MW_glucose)*H_data(1,1)+(2.5/MW_yeast)*H_data(1,8)+(0.6/MW_Na
Cl)*(-411.0)+(35.8/MW_water)*H_data(1,9);
Nb_dough=(61.1/MW_glucose)*b_data(1,1)+(2.5/MW_yeast)*b_data(1,8)+(0.6/MW_Na
Cl)*(14.3)+(35.8/MW_water)*b_data(1,9);
eff=sum(Nb_CO2_yeast+Nb_CO2_bacteria)/Nb_dough*100
wt_CO2_ratio_for_100g=(sum(n_CO2_yeast)+sum(n_CO2_bacteria))*44



for i=1:44;
   time(i)=t(i+1);
end

[ax, h1, h2]=plotyy(time, Q_total, time, Xdestroyed)

set(ax,'xlim',[0 240],'xtick',[0:20:240]);

set(get(ax(1),'Ylabel'),'String','Q(kJ)')
set(get(ax(2),'Ylabel'),'String','Xdestroyed(kJ)')

xlabel ('time (min)')
title ('35^oC, 80% S. cerevisiae and 20% L. plantarum - Energy & Exergy Balance')

set(ax(1),'ylim',[-5 0],'ytick',[-5:0.5:0],'ycolor','black');
```

```
set(ax(2),'ylim',[0 100],'ytick',[0:10:100],'ycolor','black');


set(h1,'LineStyle','-.','color','black','LineWidth',2);
set(h2,'LineStyle',':','color','black','LineWidth',2);
legend ('Q', 'Xdestroyed','Location', 'SouthEast');
legend ('Q', 'Xdestroyed','Location', 'SouthEast');

grid on
```

MODEL 10: 20% *LACTOBACILLUS PLANTARUM* AND 80% *SACCHAROMYCES CEREVISIAE* AT 40ºC

Function m-file

```
function dx= model10(t,x);
% This function models substrate consumption

k_y_p1=5e-3;
mu_b_p1=0.03;
alpha_p1=1.6e-10;
beta_p1=1e-7;
alpha1_p1=0.9e-7;
alpha2_p1=0.7e-7;
beta1_p1=0.00001;
beta2_p1=6e-6;
phi_p1=0.6;
Vmax=27;
Xmax_p1b=2.5;

dx1=(-1)*k_y_p1*x(1);
   dx2=mu_b_p1*x(2)*(1-x(2)/Xmax_p1b);
   dx3=alpha_p1*x(2)+beta_p1*dx2;
   dx4=alpha1_p1*x(1)+alpha2_p1*x(2)+beta1_p1*dx1+beta2_p1*dx2;
```

```
dx5=phi_p1*(1-x(5)/Vmax)*dx4;


dx=[dx1;dx2;dx3;dx4;dx5];
```

Growth Script m-file

```
clear all
close all
format compact

% enter the data
ty=[0 30 60 90 120 150 180 210];
gy=[4.25 3.30 3.00 2.60 2.2 2.00 1.7 1.6];

tb=[0 30 60 90 120 150 180 210];
gb=[1.25 1.30 2.00 2.25 2.30 2.5 2.5 2.5];


[t,x] = ode45('model10_ode', 250, [4.1 1.0 0 0 0]);

plot (t, x(:,1), 'k-', 'LineWidth', 2.0)
hold on

plot (t,x(:,2),'k:', 'LineWidth',2.0)
plot (ty,gy,'ko')
plot (tb,gb,'k*')

grid on
xlabel('time(min)')
ylabel ('biomass x 10^6 cfu/g')
title ('40^oC, 80% S. cerevisiae and 20% L. plantarum - Biomass Production')
```

```
set(gca,'xlim',[0 240],'xtick',[0:20:240]);

legend ('S. cerevisiae','L. plantarum', 'Location', 'NorthEast');
```

CO_2 Production Script m-file

```
clear all
close all
format compact

% enter the data
time_gas=[0 35 70 80 100 120 140 145 165 190 210 220];
gas=[0 3 10 11 15 20 24 27 32 36 45 50];
time_dough=[0 35 70 80 120 145 170 220];
dough=[0 0 4 8 14 19 22 27];



[t,x] = ode45('model10_ode', 250, [3.00 4.64 0 0 0]);

 plot (t,10^6*x(:,4),'k-','LineWidth', 2)
 hold on
 plot (t,10^6*x(:,5), 'k:', 'LineWidth', 2)
 hold on

plot (time_gas, gas,'ko', 'LineWidth',2)
 hold on
plot (time_dough, dough,'k*','LineWidth',2)

grid on
xlabel('time(min)')
ylabel ('G, V(cm^3)')
title ('40^oC, 80% S. cerevisiae and 20% L. plantarum - Gas Production & Dough Volume
Increase')
set(gca,'xlim',[0 240],'xtick',[0:20:240]);
```

```
set(gca,'ylim',[0 60],'ytick',[0:10:60]);
legend ('gas production','dough volume increase', 'Location', 'NorthWest');
```

Lactic Acid Production Script m-file

```
clear all
close all
format compact

% enter the data
time_la=[0 30 60 90 120 180 210];
la=[0 0.03 0.09 0.15 0.18 0.21 0.22];



[t,x] = ode45('model10_ode', 250, [4.1 1.0 0 0 0]);

 plot (t,1000000*x(:,3),'k-','LineWidth', 2)
 hold on

plot (time_la, la,'kx', 'LineWidth',2)



grid on
xlabel('time(min)')
ylabel ('Lactic acid (%)')
title ('40^oC, 80% S. cerevisiae and 20% L. plantarum - Lactic acid production')
set(gca,'xlim',[0 240],'xtick',[0:20:240]);
set(gca,'ylim',[0 0.25],'ytick',[0:0.025:0.25]);

legend ('lactic acid','Location', 'SouthEast');
```

Thermodynamic Model Script m-file

```
clear all
close all


ideal_GV=24e3;
pressure=1.01*101.325;
T0=293;
T=313;
wt_yeast=(7.9e-11)*(5)*(1e8);
wt_bacteria=(4.18e-13)*20*(1e8);
MW_yeast=23.75;
MW_bacteria=24.95;
MW_LA=90.08;
MW_H2=2;
MW_glucose=180.16;
MW_NaCl=58.44;
MW_water=18;

cp_yeast=0.339;
cp_bacteria=0.354;
cp_glucose=0.220;
cp_nh3=0.357;
cp_h2o=0.075;
cp_LA=0.372;
cp_gly=0.222;
cp_ethanol=0.110;
cp_AA=0.140;
cp_CO2=0.037;
cp_H2=0.029;

%enthalpy and chemical exergies of 1)glucose, 2)ammonium, 3)CO2, 4)ethanol,
```

```
%5)glycerol, 6)yeast (Battley,1999), 7)LA
(http://webbook.nist.gov/cgi/cbook.cgi?ID=C79334&Mask=2), 8)bacteria (Battley, E. coli
K12), 9)water
H_data=[-1271.1, -47.2, -393.5, -276, -669.6, -133.13, -694.08, -96.01, -285.8, -484.5,0];
b_data=[2955 340 20 1400 212 529.6 1747 571.4 0.9 907.2 236.09];

 [t,x] = ode45('model10_ode', 240, [4.1 1.0 0 0 0]);

 for i=1:44;
    % ENERGY AND EXERGY BALANCE FOR BACTERIA
    n_glu_yeast(i,:)=(((x(i+1,4)-x(i,4))/ideal_GV*(1e6)-((x(i+1,3)-
x(i,3))*(1e6)/MW_LA))/0.75*1.13)/1.54;
    n_nh3_yeast(i,:)=(((x(i+1,4)-x(i,4))/ideal_GV*(1e6)-((x(i+1,3)-
x(i,3))*(1e6)/MW_LA))/0.75*1.13)/1.54*0.12;
    n_CO2_yeast(i,:)=(((x(i+1,4)-x(i,4))/ideal_GV*(1e6)-((x(i+1,3)-
x(i,3))*(1e6)/MW_LA))/0.75*1.13);
    n_CO2_yeast(n_CO2_yeast<0)=0;
    n_ethanol_yeast(i,:)=(((x(i+1,4)-x(i,4))/ideal_GV*(1e6)-((x(i+1,3)-
x(i,3))*(1e6)/MW_LA))/0.75*1.13)/1.54*1.3;
    n_gly(i,:)=(((x(i+1,4)-x(i,4))/ideal_GV*(1e6)-((x(i+1,3)-
x(i,3))*(1e6)/MW_LA))/0.75*1.13)/1.54*0.43;
    n_yeast(i,:)=(x(i+1,1)-x(i,1))*wt_yeast/MW_yeast;
    n_yeast(n_yeast<0)=0;
    n_CO2_yeast(n_CO2_yeast<0)=0;
    Nh_glu_yeast=(n_glu_yeast)*H_data(1,1);
    Nh_nh3_yeast=(n_nh3_yeast)*H_data(1,2);
    Nh_CO2_yeast=n_CO2_yeast*H_data(1,3);
    Nh_ethanol_yeast=(n_ethanol_yeast)*H_data(1,4);
    Nh_gly=(n_gly)*H_data(1,5);
    Nh_yeast=(n_yeast)*H_data(1,6);
    Nb_glu_yeast=(n_glu_yeast)*b_data(1,1);
    Nb_nh3_yeast=(n_nh3_yeast)*b_data(1,2);
    Nb_CO2_yeast=n_CO2_yeast*b_data(1,3);
```

```
Nb_ethanol_yeast=(n_ethanol_yeast)*b_data(1,4);
Nb_gly=(n_gly)*b_data(1,5);
Nb_yeast=(n_yeast)*b_data(1,6);



n_glu_bacteria(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA/0.75;
n_nh3_bacteria(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA/0.75*0.09;
n_water(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA/0.75*0.19;
n_CO2_bacteria(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA*1.13;
n_CO2_bacteria(n_CO2_bacteria<0)=0;
n_LA(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA;
n_LA(n_LA<0)=0;
n_ethanol_bacteria(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA;
n_AA(i,:)=(1e6)*(x(i+1,3)-x(i,3))/MW_LA/0.75*0.38;
n_H2=(1e6)*(x(i+1,3)-x(i,3))/MW_LA;
n_bacteria(i,:)=(x(i+1,2)-x(i,2))*wt_bacteria/MW_bacteria;
n_bacteria(n_bacteria<0)=0;
n_LA(n_LA<0)=0;
Nh_glu_bacteria=(n_glu_bacteria)*H_data(1,1);
Nh_nh3_bacteria=(n_nh3_bacteria)*H_data(1,2);
Nh_water=n_water*H_data(1,9);
Nh_CO2_bacteria=(n_CO2_bacteria)*H_data(1,3);
Nh_ethanol_bacteria=(n_ethanol_bacteria)*H_data(1,4);
Nh_LA=(n_LA)*H_data(1,7);
Nh_AA=n_AA*H_data(1,10);
Nh_H2=n_H2*H_data(1,11);
Nh_bacteria=(n_bacteria)*H_data(1,8);
Nh_water=(n_water)*H_data(1,9);
Nb_glu_bacteria=(n_glu_bacteria)*b_data(1,1);
Nb_nh3_bacteria=(n_nh3_bacteria)*b_data(1,2);
Nb_water=(n_water)*b_data(1,9);
Nb_CO2_bacteria=n_CO2_bacteria*b_data(1,3);
```

```
    Nb_ethanol_bacteria=n_ethanol_bacteria*b_data(1,4);
    Nb_LA=(n_LA)*b_data(1,7);
    Nb_AA=(n_AA)*b_data(1,10);
    Nb_H2=n_H2*b_data(1,11);
    Nb_bacteria=(n_bacteria)*b_data(1,8);


    V(i,:)=(x(i+1,5)-x(i,5));
    PV=pressure*V;
end


% m=100;
% cp=2.73*4.184;
% deltaT=5;
% Qin=m*cp*deltaT/1000;

Hin=[(15)*cp_h2o*sum(n_water)]+[(15)*cp_glucose*sum(n_glu_bacteria)]+[(15)*cp_glu
cose*sum(n_glu_yeast)]+...

[(15)*cp_nh3*sum(n_nh3_yeast)]+Nh_glu_yeast+Nh_nh3_yeast+Nh_glu_bacteria+Nh_n
h3_bacteria+Nh_water;
Hout=[(15)*cp_CO2*sum(n_CO2_bacteria)]+[(15)*cp_ethanol*sum(n_ethanol_bacteria)]
+[(15)*cp_LA*sum(n_LA)]+[(15)*cp_AA*sum(n_AA)]+...

[(15)*cp_H2*sum(n_H2)]+[(15)*cp_bacteria*sum(n_bacteria)]+[(15)*cp_bacteria*sum(n
_nh3_bacteria)]+...

[(15)*cp_ethanol*sum(n_ethanol_yeast)]+[(15)*cp_CO2*sum(n_CO2_yeast)]+[(15)*cp_g
ly*sum(n_gly)]+...
    [(15)*cp_yeast*sum(n_yeast)]+...
Nh_CO2_yeast+Nh_ethanol_yeast+Nh_gly+Nh_yeast+Nh_bacteria+Nh_ethanol_bacteria
+Nh_CO2_bacteria+Nh_LA+Nh_H2+Nh_AA;
```

```
deltaH=Hout-Hin;
deltaH(deltaH>0)=-0.01;
Q_total=cumsum(deltaH)+cumsum(PV);
Q_total(1)=0;


Xin_y= Nb_glu_yeast+Nb_nh3_yeast;
Xout_y=Nb_yeast+Nb_CO2_yeast+Nb_ethanol_yeast+Nb_gly;
Xy=(Xin_y-Xout_y);

Xin_b= Nb_glu_bacteria+Nb_nh3_bacteria+Nb_water;
Xout_b=Nb_bacteria+Nb_ethanol_bacteria+Nb_CO2_bacteria+Nb_LA+Nb_H2+Nb_AA;
Xb=(Xin_b-Xout_b);

deltab=Xy+Xb;
deltab(deltab<0)=0.01;

Xdestroyed=cumsum(deltab)+Q_total*(1-(T0/T))+cumsum(PV);

disp('n_glu_yeast+n_glu_bacteria,n_CO2_yeast+n_CO2_bacteria, n_LA, n_yeast,
n_bacteria,Hin, Xin_y+Xin_b')
moles=[sum(n_glu_yeast)+sum(n_glu_bacteria);sum(n_CO2_yeast)+sum(n_CO2_bacteria
);sum(n_LA);...
   sum(n_yeast);sum(n_bacteria);sum(Hin);sum(Xin_b+Xin_y)]
disp('Hout, Nbout')
out=[sum(Hout);sum(Xout_b+Xout_y)]
secondlaw=[Q_total(end) Xdestroyed(end)]

expansion_work=sum(PV)
Nh_dough=(61.1/MW_glucose)*H_data(1,1)+(2.5/MW_yeast)*H_data(1,8)+(0.6/MW_Na
Cl)*(-411.0)+(35.8/MW_water)*H_data(1,9);
Nb_dough=(61.1/MW_glucose)*b_data(1,1)+(2.5/MW_yeast)*b_data(1,8)+(0.6/MW_Na
Cl)*(14.3)+(35.8/MW_water)*b_data(1,9);
```

```
eff=sum(Nb_CO2_yeast+Nb_CO2_bacteria)/Nb_dough*100
wt_CO2_ratio_for_100g=(sum(n_CO2_yeast)+sum(n_CO2_bacteria))*44

for i=1:44;
   time(i)=t(i+1);
end

[ax, h1, h2]=plotyy(time, Q_total, time, Xdestroyed)

set(ax,'xlim',[0 240],'xtick',[0:20:240]);

set(get(ax(1),'Ylabel'),'String','Q(kJ)')
set(get(ax(2),'Ylabel'),'String','Xdestroyed(kJ)')

xlabel ('time (min)')
title ('40^oC, 80% S. cerevisiae and 20% L. plantarum - Energy & Exery Balance')

set(ax(1),'ylim',[-0.5 0],'ytick',[-0.5:0.05:0],'ycolor','black');
set(ax(2),'ylim',[0 2],'ytick',[0:0.2:2],'ycolor','black');


set(h1,'LineStyle','-.','color','black','LineWidth',2);
set(h2,'LineStyle',':','color','black','LineWidth',2);
legend ('Q', 'Xdestroyed','Location', 'SouthEast');
legend ('Q', 'Xdestroyed','Location', 'SouthEast');

grid on
```