

T.R.
GEBZE TECHNICAL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

**GASIFICATION AND MATHEMATICAL MODELLING OF
SOLID FUELS IN A DOWNDRAFT GASIFIER**

EBUBEKİR SİDDİK AYDIN
A THESIS SUBMITTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
DEPARTMENT OF CHEMICAL ENGINEERING

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THESIS SUPERVISOR
PROF. DR. HASAN SADIKOĞLU

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T.C.
GEBZE TEKNİK ÜNİVERSİTESİ
FEN BİLİMLERİ ENSTİTÜSÜ

KATI YAKITLARIN AŞAĞI AKIŞLI
GAZLAŞTIRICIDA GAZLAŞTIRILMASI VE
MATEMATİKSEL MODELLENMESİ

EBUBEKİR SİDDİK AYDIN
DOKTORA TEZİ
KİMYA MÜHENDİSLİĞİ ANABİLİM DALI

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2019

 GEBZE TEKNİK ÜNİVERSİTESİ	DOKTORA JÜRİ ONAY FORMU
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GTÜ Fen Bilimleri Enstitüsü Yönetim Kurulu'nun 17/10/2019 tarih ve 2019/47 sayılı kararıyla oluşturulan jüri tarafından 13/11/2019 tarihinde tez savunma sınavı yapılan Ebubekir Sıddık Aydın'ın tez çalışması Kimya Mühendisliği Anabilim Dalında DOKTORA tezi olarak kabul edilmiştir.

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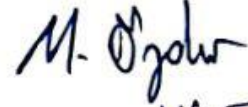
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SUMMARY

This thesis proposes a stoichiometric equilibrium model (SEM) to estimate the chemical composition of the syngas, tar and char yield produced by a downdraft gasifier for various wood-based fuels for different equivalence ratios (ER). Global stoichiometric equilibrium approach is used to model a downdraft gasifier. In order to estimate dry gas composition, three different SEM models have been constructed. Those models were validated and modified through comparison with a large amount of data collected from various sources. Two correction factors were introduced for altering the equilibrium constant of methanation and the water-gas shift reaction as a function of gasification temperature, equilibrium temperature, and ER. The modified model presents a clear enhancement in the prediction of the concentration for all gaseous species in the producer gas and tar yield. After that, the relation between hydrogen-rich syngas production and the gasification parameters such as ER, gasification temperature and biomass moisture content were studied. SEM that developed during this thesis was used to investigate the optimum hydrogen output generated from woody biomass in a fixed bed downdraft gasifier by considering the thermodynamic equilibrium limit. The effects of different oxidizing agents on the hydrogen concentration in the product gas as well as the effect of various air-biomass, oxygen-biomass, and steam-biomass ratios were investigated. The theoretical results clearly show that the gasification process especially that uses the air-steam mixture as the gasification medium can be used for hydrogen production. Finally, an investigation of gasification of pine cones particles and wood pellets in a pilot scale 10kW_{th} downdraft fixed bed gasifier using air as an oxidizing agent was carried out. It was found that syngas produced by gasification of pine cones particles would be a clean alternative energy carrier for the production of clean energy.

Key Words: Biomass, Gasification, Equilibrium modelling, Downdraft, Hydrogen, Oxidizing agent.

ÖZET

Bu tez, farklı eşdeğer hava yakıt oranı değerlerinde (ER) üretilen sentez gazının kimyasal bileşimini, katran ve çar verimini öngörmek için bir stokiyometrik denge modelini (SEM) önermektedir. Aşağı akışlı gazlaştırıcıyı modellemek için genel stokiyometrik denge yaklaşımı kullanılmıştır. Kuru sentez gazı bileşimini tahmin etmek için üç farklı sitokiyometrik denge modeli geliştirilmiştir. Bu modeller çeşitli kaynaklardan toplanan büyük miktarda veri ile karşılaştırılarak doğrulanmış ve modifiye edilmiştir. Metanasyon ve su-gaz kaydırma reaksiyonlarına ait denge sabitlerini değiştirmek için, gazlaştırma sıcaklığı, denge sıcaklığı ve eşdeğer hava yakıt oranının fonksiyonu olan iki düzeltme korelasyonu oluşturulmuştur. Modifiye edilmiş modeller, üretici gaz içerisinde yer alan tüm gaz türlerinin konantrasyonu ve katran miktarının tahmininde açık bir gelişme göstermektedir. Daha sonra, hidrojen bakımından zengin sentez gazı üretimi ile ER, gazlaştırma sıcaklığı ve biyokütle nem içeriği gibi gazlaştırma parametreleri arasındaki ilişki incelenmiştir. Bu tez sırasında geliştirilen stokiyometrik denge modeli, odunsu biyokütleden elde edilen optimum hidrojen üretimini, termodinamik denge limitlerini göz önünde tutarak sabit yataklı bir aşağı akışlı gazlaştırıcıda araştırmak için kullanılmıştır. Farklı oksitleyici maddelerin, üretici gazındaki hidrojen konsantrasyonu üzerindeki etkileri ile çeşitli hava biyokütle, oksijen-biyokütle ve buhar-biyokütle oranlarının etkisi incelenmiştir. Teorik sonuçlar, gazlaştırma işleminin, özellikle gazlaştırma ortamı olarak hava-buhar karışımını kullanıldığında, hidrojen üretimi için kullanılabileceğini açıkça göstermektedir. Son olarak, çam kozalak parçacıklarının ve odun peletlerinin, oksitleyici madde olarak hava kullanılarak, 10 kWh pilot ölçekli reaktörde gazlaştırılması araştırılmıştır. Çam kozalağı parçacıklarının gazlaştırılmasıyla üretilen sentez gazının, temiz enerji üretimi için alternatif enerji taşıyıcısı olabileceği bulunmuştur.

Anahtar Kelimeler: Biyokütle, Gazlaştırma, Denge modellemesi, Aşağı akış, Hidrojen, Oksitleyici ajan.

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LIST of ABBREVIATIONS and ACRONYMS

<u>Abbreviations and Acronyms</u>	<u>Explanations</u>
β	: Number of oxygen molecule in one mole biomass
γ	: Number of hydrogen molecule in one mole biomass
θ	: Molar ratio of nitrogen to oxygen gasification, mole N ₂ /mole O ₂
ϕ	: Molar carbon quantity is a function of equivalence ratio
A	: Ash mass fraction weight basis from proximate analysis
C	: Carbon mass fraction in weight basis from ultimate analysis
H	: Hydrogen (monoatomic) mass fraction in weight basis from ultimate analysis
K	: Thermodynamic equilibrium constant
l	: Liquid phase
m	: Amount of oxygen per kmol of biomass
N	: Nitrogen (monoatomic)
O	: Oxygen (monoatomic) mass fraction in weight basis from ultimate analysis
R	: Universal gas constant, 8.314 kJ/kmol K
S	: Mass fraction of sulfur from ultimate analysis
s	: Solid phase
T	: Temperature, K
X _j	: Mole fraction of component j with respect to biomass
ER	: Equivalence ratio
HHV	: Higher heating value, MJ/kg for biomass and MJ/Nm ³ for syngas
LHV	: Lower heating value, MJ/Nm ³
MC	: Moisture content, %

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1. INTRODUCTION

Biomass is the general name of all non-fossilized biological material obtained from living or recently living creatures. It refers to animal and vegetable-based products commonly used to produce biofuels and bio-chemicals. Biomass is a term consisting of bios which mean “life” in Greek and mass words and defined as all the materials that can be renewed in a shorter period than a century-long process, including land and water-related plants, animal residues, food industry wastes, forest by-products and urban wastes [1]. It is a continuous source of renewable and sustainable energy in nature, and every kind of energy such as electricity, heat, work and etc. obtained from biomass is called bioenergy. In addition, it is considered to be a strategic energy source not only it is renewable but also it can be grown or raised everywhere. Biomass can be used safely to generate electricity, chemicals, and fuel especially for vehicles by enhancing socio-economic development and contributing to environmental protection. Due to the limited availability and fluctuating high prices of fossil energy resources such as petroleum, natural gas and coal in the world as well as problems of environmental pollution based on fossil energy resources, biomass is becoming increasingly alternative to solve energy problems. The storage of energy, one of the main problems, can be eliminated by using biomass for electricity and heat energy.

Fossil-based energy resources such as natural gas, coal and petroleum are being spent at an accelerated rate and can be faced diminution in the near future. As a natural consequence of the energy demand and environmental awareness emerging in the world, developed countries use both biomass and non-recoverable parts for the production of the electric energy and heat energy by gasification. Today, the world's renewable energy needs play a key role in the revitalization of gasification systems, with the decline of petroleum. In order to solve energy demand and to reduce the level of air pollution, clean energy resources and technologies are crucial and gaining importance. One of the promising technologies, gasification is highly efficient and environmentally friendly and it has been received significant attention, recently [2]. Gasification is a thermochemical process that deals with the conversion of carbonaceous materials including biomass, fossil fuels, plastics, and coal into syngas through partial oxidation in a gasifier. It is also a successful option for waste

management, energy production from non-conventional feeds like forest waste, agricultural waste, poultry waste, and municipal solid waste and production of valuable chemicals. The low-value feedstocks could be converted into saleable products and fuels by the gasification process. During the gasification process, a combustible gaseous fuel consisting of CO, H₂, CH₄ and some saturated hydrocarbons is produced by partial oxidation of feedstocks. By means of gasification, the harmful substances contained in the fuel are removed from the fuel and SO₂ and NO_x emissions resulted from gasification are extremely low in the gaseous mixtures. For this reason, gasification is widely accepted as an environmentally friendly method. Typically, 15-20 percent of the mass of burned solid waste results in ash. Hence, the bottom ash yield of solid waste gasification is about 7%. Gasification process reduces volume (up to 90%) and weight (up to 75%) and breaks down hazardous substances such as dioxin or furans. Nevertheless, in the gasification, sulfur dioxide and nitrogen oxide do not form due to high temperatures and low oxygen levels. In addition, all the thermal efficiency of the gasification process is greater than the direct combustion process. One of the disadvantages of small scale energy production from gasification is the necessity of regular control of the gas cleaning system. Otherwise, internal combustion engines are damaged.

The product gas, obtained by partial oxidation of biomass can be supplied to the internal combustion engine, the gas turbine or the boilers to produce energy. [3]. When they burn in internal combustion engines, gas-fuels have lower emissions than petrol. Producer gas can be utilized in Diesel engines by introducing a spark ignition system with reduced compression ratio [4]. Generally, the syngas quality varies with the chosen oxidizing agent, such as steam, air, steam-oxygen, air-steam, and oxygen-enriched air [4]. Because of availability and simplicity, air is the most widely used oxidizing agent in laboratory and industrial applications. The syngas which is a mixture of hydrogen, methane, carbon monoxide and carbon dioxide has a calorific value of 3-5 MJ/m³ in the case of air and air/steam process, and 10-18 MJ/m³ in the case of oxygen and steam process [5, 6]. By further processing of syngas, it can be used to produce heat and electricity or directly as a gaseous fuel. In addition to energy production, syngas can be considered as a key intermediary product in the chemical industry to produce some crucial end products such as dimethyl ether (DME), methyl tert-butyl ether (MTBE) and methanol [7-9].

Gasifiers are classified three principal categories: fixed beds, fluidized and entrained suspension gasifiers. Among them, fixed bed gasifiers are the advanced and most popular reactors used to produce syngas. The fixed bed gasifiers are widely studied and used because of simple operation conditions and easy construction. Gasifiers also classified as updraft, downdraft and cross-draft depending upon the direction and entry of oxidizing agent flow. In a downdraft gasifier, the solid fuels and air move in the downward direction in the lower section of the gasifier. A sequence of temperature-dependent thermochemical conversions of carbonaceous material occurred inside the gasifier. The carbonaceous material passes through four different zones: drying, pyrolysis, combustion, and reduction. Each stage occurs in a specific temperature region. These temperature zones vary according to the type of gasifier. Figure 1.1 shows the different domains in the process of gasification in a downdraft gasifier.

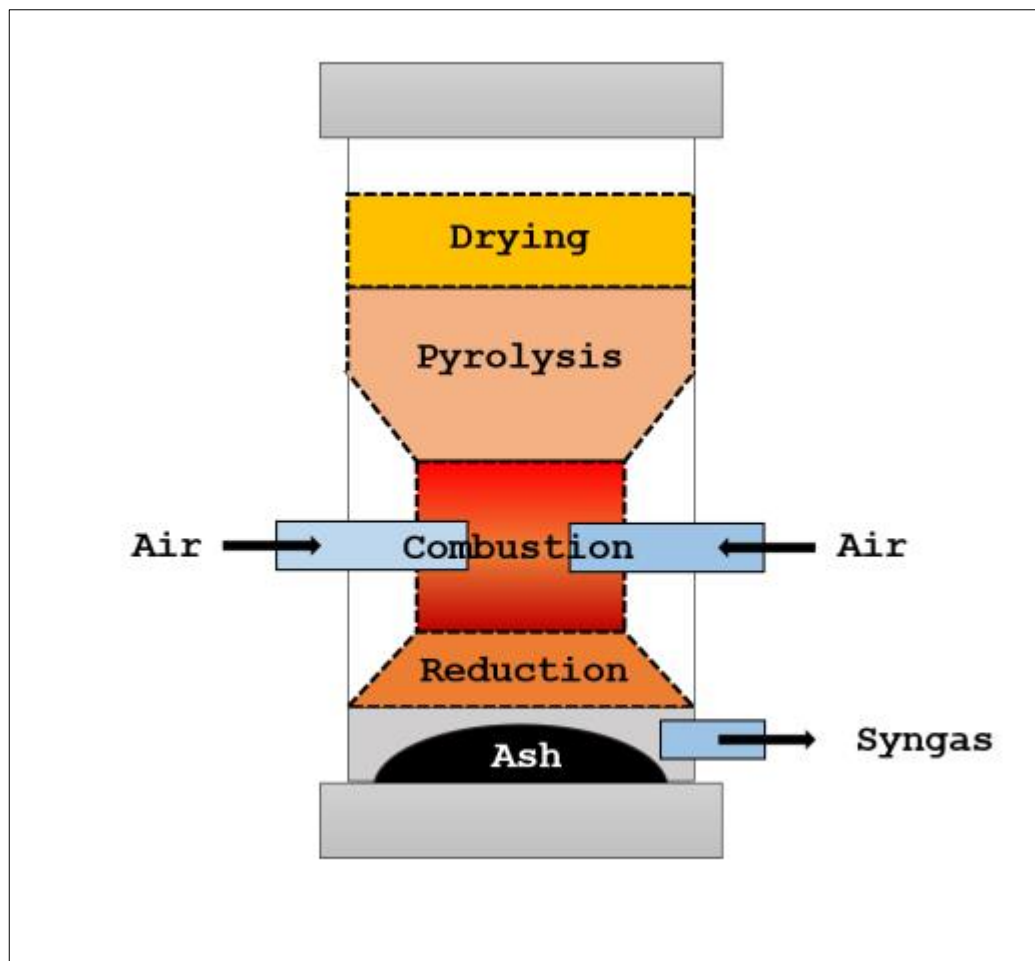


Figure 1.1: The different domains in the process of gasification in a downdraft gasifier.

These type of gasifiers are well qualified to manage solid fuels having moisture and ash content less than 20% and 5%, respectively [10]. The syngas produced from downdraft gasifier has higher temperature nearby 700 °C, less tar content (<1%), and more particulate matter than from an updraft gasifier [11]. The performance of the gasification process in terms of energy efficiency is affected by a number of factors and events such as the gasification temperature, feedstock composition, reactor geometry, the amount of oxidant and direction of gas-solid contact. Moreover, if the clean gas is desired, the downdraft gasifier is suitable [12]. The gasifier design can be optimized either based on experimental data or using mathematical models of the gasification process in the reactor. The experimental approach, though most reliable, is not always practical and satisfactory. Considering the variation in different design and operating parameters, the sensitivity of the gasifier performance could be identified and in addition to this, exploring operational limits and optimizing the operation of a reactor could be possible via an effective model. Mathematical models that represent the dynamic behavior of gasifiers can reduce the expense of time-consuming experiments and complicated by helping the cost-effective design of processes [13]. Equilibrium approach and kinetic approach can be used to represent the biomass downdraft gasification and due to its simplicity and effectiveness, the equilibrium approach is more applicable for gasification systems [14].

Processes depending on chemical reactions can be analyzed by chemical balance theory or by chemical-fluid models containing kinetic expressions. The models based on the chemical balance theory aim to calculate the best transformation and product distribution that can be achieved due to the thermodynamic constraints of the operating conditions of the system design. Moreover, this type of model does not calculate the period of time that the system reaches equilibrium and the residence time in the system during product flow, and all chemical reactions are assumed as in equilibrium. Otherwise, the heterogeneous char reactions are taken place in the gasification process. The dynamic mathematical models that obtained by using conservation of mass and energy along with kinetic equation can supply precious information related with reaction mechanism and give the more accurate concentration results in desired space and time within the system at any point [15]. The thermochemical equilibrium approach along with stoichiometric or non-stoichiometric model can be used to describe any gasification system [16]. However, equilibrium approaches are applicable under the high operating temperature and enough retention time for the complete

gasification reactions. Therefore, the results may show less accurate at a low operating temperature between 750-900 °C [17]. The stoichiometric method is based on a number of chosen chemical reactions to calculate the equilibrium constants. In the stoichiometric modeling, while important reactions are considered, other reactions are ignored and this makes the model less sensitive in the prediction of syngas compositions [18]. The non-stoichiometric approach based on minimization of Gibbs free energy gives the direct and general solution when a number of simultaneous reactions are required to determine equilibrium composition. Although this process is more complicated, it is advantageous because it does not require a chemical reaction [19].

1.1. Hypothesis

Gasification is a complicated and responsive process affected by feedstock properties such as chemical composition, size and moisture content. The gasifying agent flow rate, equivalence ratio (ER), gasifier temperature and pressure are other important parameters which influence the gasification dramatically. Modeling could be used for different purposes and extends from a preliminary design of industrial process to a complex simulation. If the impact of the operation conditions on the calorific value and syngas composition is determined via gasification model, the experimental effort and costs can be reduced and also used to facilitate preparation and optimization steps of experiments that carried out in a real gasification system.

1.2. Objectives

The objectives of this study are to:

- i) construct a thermodynamic equilibrium model for the fixed bed downdraft gasification process to determine operating conditions.
- ii) perform simulations on biomass gasification with air, air-steam, oxygen and obtain data on temperature profile, gas composition under various operating conditions to produce hydrogen-rich syngas.
- iii) investigate the gasification of pine cones particles and wood pellets in a pilot scale 10kW_{th} downdraft fixed bed gasifier using air as oxidizing agent.

2. METHODOLOGY

Details of the materials used and methods followed to:

- i) construct a thermodynamic equilibrium model for the fixed bed downdraft gasification process to determine operating conditions is explained in the “Materials and Methods for the Stoichiometric Equilibrium Gasification (SEM) Model”.
- ii) perform simulations on biomass gasification with air, air-steam, oxygen and acquire data on temperature distribution, gas composition under different operating conditions to produce hydrogen-rich syngas are explained in the “Materials and Methods for the Hydrogen Production”.
- iii) investigate the gasification of pine cones particles and wood pellets in a pilot scale 10kW_{th} downdraft fixed bed gasifier using air as oxidizing agent are explained in the “Materials and Methods for the Gasification Experiments”.

3. DEVELOPMENT of a MATHEMATICAL MODEL for DOWNDRAFT GASIFICATION SYSTEMS

Gasification is a thermochemical conversion process which transforms solid into gaseous fuel. Non-renewable resources such as coal, petroleum and natural gas are facing fear of depletion in near future. In order to meet the energy demand and reduce the gas emissions from fossil fuels, biomass gasification is a promising energy option [2]. The syngas, produced through partial oxidation of biomass, is mainly composed of hydrogen, carbon monoxide, carbon dioxide, methane and residual char; various contaminants such as tar and ash are also present [3]. Generally, the syngas quality differs with the supplied oxidizing agent, such as air, oxygen, steam, or mixture of them [4]. Depending upon the gasifying medium employed, the syngas has a dry calorific value of 3-5 MJ/Nm³ in the case of air and air/steam process, owing to the main presence of nitrogen in the syngas; and 10-18 MJ/Nm³ in the case of oxygen and steam or indirectly heated process [5-6]. Thus formed syngas can be used as a gaseous fuel to produce electricity and heat value-added chemicals [7].

Gasification process depends on various reactions, and includes four steps: drying of feedstock, pyrolysis, oxidation and reduction. In the drying step, the feedstock is heated and the water content of feedstock undergoes vaporization at a temperature below 150 °C. In the pyrolysis step, the feedstock is converted to char and volatile components. The volatile constituent is formed in the temperature range of 150–700 °C. A viscous, black, and corrosive liquid containing inorganic molecules and heavy organic known as tar is also occurred during the pyrolysis step. The oxidation process supplies the thermal energy required for the endothermic reduction reactions taking place inside the gasifier, by using some of the char or dry biomass. Reduction step is the result of numerous chemical reactions involving the reduction of H₂, CO₂, and H₂O with char in the temperature range of 800–1100 °C [8-10].

Gasifiers are principally classified various categories: fluidized bed, fixed bed, and entrained suspension gasifiers. The fixed bed gasifiers are categorized as downdraft, updraft, cross draft and multi-stage considering types of bed and direction of gas movement/oxidizing agent. Compared to other gasification systems, the downdraft gasifiers are the most preferable option for small-scale applications (<10

MW_{th}) due to the simple design, construction, and low tar content (1–2 g/Nm³) by syngas production [3, 11].

Gasification is a complicated and sensitive process affected by feedstock properties such as chemical composition, size and moisture content. The gasifying agent flow rate, equivalence ratio (ER), gasifier temperature and pressure are other important parameters which influence the gasification dramatically [7]. In order to evaluate the impact of the operation conditions on the syngas composition and calorific value, numerous mathematical models have been developed for the gasification process, including thermodynamic equilibrium, kinetic, computational fluid dynamic (CFD) and artificial neural networks [8, 12].

Equilibrium approaches are practical to predict the product streams of the gasification process in downdraft gasifiers [13]. These approaches are also appropriate for simulating fluidized gasifiers which are considered perfect mixing and uniform temperature. For equilibrium models, the reactions are assumed almost complete and the system is at steady state. But real conversion depends on kinetic factors and operation conditions. Thus, the equilibrium models overestimate the CO and H₂ yields and underestimate CH₄, CO₂, char and tar, relatively at lower gasification temperatures. Therefore, the models are inadequate to give eminently accurate results in many cases. Equilibrium models estimate the most obtainable conversion and the distribution of the desired products in the limit of thermodynamic constraints independent from reactor type and geometry. On the other hand, the equilibrium models are applicable mainly when the operating temperature is high and the residence time is longer than the time required for completion of all the gasification reactions. Fixed bed gasifiers have high overall carbon conversion, high residence time of solids and low gas velocity.

Thermodynamic equilibrium approach is divided into two sections: the non-stoichiometric and stoichiometric equilibrium methods. The non-stoichiometric method is based on expressions determining the thermodynamic potential of each compound, meanwhile the stoichiometric method on expressions specifying the equilibrium constant of particular reactions. The non-stoichiometric are faster but can have difficult to converge so are used for large problems and starting from stoichiometric solution. Thus, the paper develops a stoichiometric model. In order to calculate the equilibrium constant, several chemical reactions that take place in the gasification process must be chosen [13-15].

In previous studies in the literature, many researchers have focused on the thermochemical equilibrium models to analyze downdraft gasification [15-17]. In a downdraft gasifier, several authors [14-15, 18] predicted the syngas composition and calorific value from various biomass types using a thermodynamic stoichiometric equilibrium model at a fixed equivalence ratio. In the works of Azzone [19], Gagliano [12] and Dutta and Jarungthammachote [15] have qualified the equilibrium model via the correction factor in order to improve the accuracy of model.

Zainal et al [14] have developed a stoichiometric equilibrium model in order to predict the gasification process in a downdraft gasifier for the first time. The effect of initial moisture content in biomass and the temperature in the gasification zone on the calorific value had been investigated at a fixed equivalence ratio. Due to the nature of the stoichiometric equilibrium model, from the global reactions, they constructed the model for the six unknowns X_{H_2} , X_{CO} , X_{CO_2} , X_{H_2O} , X_{CH_4} and m , representing five unknown species of the syngas and the amount of oxygen supplied to the gasifier. In order to identify the gasification process, six independent equations were formulated by Azzone et al. [19]. They stated that in real conditions, the carbon conversion is not possible to achieve completely so the presence of char can be seen at the end of the process. Therefore, in order to consider the char ratio, the α factor which is a function of equivalence ratio has been identified. This factor represents the fraction of carbon involved in the equilibrium reactions, while the rest unreacted carbon bypasses the reaction zones. They also present a correlation for the calculation of the ER as a function of m , in other words ER remained as a unknown in the calculations of the gasification process. But the ER is one of the most important operating variables in biomass gasification and it must remain as an independent variable. In the study of Gagliano et al. [12], the authors have used a global gasification reaction mechanism including yields of char and tar as input parameters [6, 20]. According to typical product yield recommended by Bridgewater [21] and in accordance with the results of the study of Yamazaki et al. [22], the char and tar yield for the downdraft biomass gasification were observed 10.5% and 4.5% (mass percentage) respectively and same values were used as input parameters. The gasification temperature considered as an unknown. So a system of six unknowns (X_{H_2} , X_{CO} , X_{CO_2} , X_{H_2O} , X_{CH_4} and T) and equations were solved. They have used experimental data available from other literature studies but they did not mention the difference between calculated and

reported temperature. Jarungthammachote and Dutta [15] made some modifications in order to improve the performance of their stoichiometric model by multiplying the equilibrium constants with correction coefficients. They used the experimental data including eleven cases reported by Altafini et al. [23], Zainal et al. [14], and Jayah et al. [16]. Water-gas shift reaction equilibrium constant, K_2 , was multiplied with a correction factor of 11.28 in order to improve the accuracy of the model. This coefficient is a ratio of average methane value from eleven experimental data and methane model predictions. Similarly, a value 0.91 was defined as a correction factor to modify K_1 , the methanation reaction equilibrium constant. Although the modifications increased the accuracy of the model prediction, the absence of any correlation which is a function of gasification conditions makes the model less reliable.

A number of modelling and experimental works on fluidized bed gasification [24-27] have been reported in the scientific literature. However, the equilibrium models may not provide accurate results at low operating temperatures (750–900 °C) [28]. The equilibrium models for fluidized bed gasifier also has limitations when predicting light hydrocarbons and unconverted solid carbon content in the final product gas as well as fixed bed gasifiers [4].

In this paper, a stoichiometric equilibrium model has been proposed to predict the yields of tar, gas, and char released during the gasification process as well as the calorific value of the syngas. In order to improve the accuracy of the model, the equilibrium constants are multiplied by correction coefficients which are function of equivalence ratio, gasification temperature and equilibrium temperature. These are the main features that distinguish the semi-empirical equilibrium model for downdraft gasification systems from the other models. After that, the model was approved with published experimental data in the literature including gasification of wood, wood pellet, wood chip, rubber wood, polish pellet, torrefied pellet and bagasse. Finally, a sensitivity analysis had been carried out for investigating the influence of the higher heating value of woody biomass which takes place in the energy balance calculations.

3.1. Materials and Methods for the Stoichiometric Equilibrium Gasification (SEM) Model

The stoichiometric equilibrium model has been developed based on the following assumptions.

- i) The biomass consists of hydrogen, carbon, oxygen and nitrogen only.
- ii) Gasifier is in thermodynamic equilibrium.
- iii) Oxidizing agent is dry at a temperature of 25 °C and the system is at a pressure of 101.13 kPa.
- iv) The syngas includes CO, CO₂, H₂, CH₄, N₂, H₂O and Tar.
- v) Nitrogen is not involved in any chemical reaction inside the system.
- vi) The gasifier is completely adiabatic and there is no heat loss from the gasifier.
- vii) Gasification reaction rates are fast enough and residence time is sufficiently long to reach the equilibrium state.
- viii) Ash is inert.

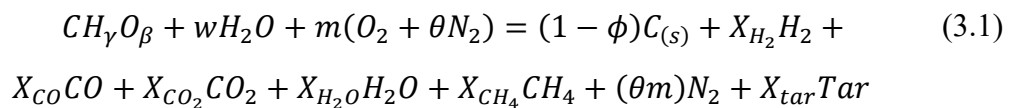
The stoichiometric equilibrium model utilizes several complex reactions of gasification and one global gasification reaction. The model reactions are listed in Table 3.1.

Table 3.1: Gasification reactions of equilibrium model.

Reaction	Reaction name	Heat of reaction (kJ/mol)
$C + CO_2 \leftrightarrow 2CO$	Boudouard reaction	+172.46
$C + H_2O \leftrightarrow CO + H_2$	Steam gasification	+131.29
$C + 2H_2 \rightarrow CH_4$	Methane formation	-74.52
$CO + H_2O \leftrightarrow CO_2 + H_2$	Water-gas shift reaction	-41.17

Boudouard and steam gasification reactions combine into water-gas shift reaction.

The global gasification reaction is given below:



In the global gasification reaction, the dry biomass can be stated in the form of generalized molecular formula $CH_\gamma O_\beta$. The subscripts γ and β are derived from the ultimate analysis of the biomass. The terms of $X_{H_2}, X_{CO}, X_{CO_2}, X_{H_2O}, X_{CH_4}, X_{tar}$ and $(1 - \phi)$ are the mole fractions of H_2 , CO , CO_2 , H_2O , CH_4 , tar and char (unreacted carbon). Tar is assumed to be C_6H_6 , because of benzene is the major tar component [29-31]. In real gasification conditions, the conversion of the carbon in the feedstock to gaseous form is not complete and char forms inside the gasifier. In order to consider the complete conversion of carbon, the ϕ factor has been identified [19]. This factor represents carbon fraction participates in the equilibrium reactions. The molar carbon quantity is a function of equivalence ratio and calculated from Eq. 3.2. below [32-33].

$$\phi = 0.32 + 0.82 \left(1 - e^{\frac{-ER}{0.229}} \right) \quad 0.21 < ER < 0.40 \quad (3.2)$$

The amount of water w is a function of the initial moisture content of the biomass with the unit of kmol per kmol of biomass and m is the amount of oxygen per kmol of biomass [18]. θ is the nitrogen to oxygen molar ratio in the oxidizing agent. Three elemental balances of carbon, hydrogen and oxygen are given below.

Carbon balance:

$$X_{CO} + X_{CO_2} + X_{CH_4} + X_{char} + 6X_{tar} = 1 \quad (3.3)$$

Hydrogen balance:

$$2w + \gamma = 2X_{H_2} + 2X_{H_2O} + 4X_{CH_4} + 6X_{tar} \quad (3.4)$$

Oxygen balance:

$$w + \beta + 2m = X_{CO} + 2X_{CO_2} + X_{H_2O} \quad (3.5)$$

The methane reaction and water-gas reaction are adequate for equilibrium modeling of the gasification process [20]. The equilibrium constants for those reactions can be written in terms of their molar composition. They are given below

$$K_{1, \text{methane}} = \frac{X_{CH_4}}{X_{H_2}^2} X_t \quad (3.6)$$

$$X_t = X_{H_2} + X_{CO} + X_{CO_2} + X_{H_2O} + X_{CH_4} \quad (3.7)$$

where X_t is the total molar concentration of the syngas excluding inerts.

$$K_{2, \text{wgs}} = \frac{X_{H_2} X_{CO_2}}{X_{CO} X_{H_2O}} \quad (3.8)$$

The equilibrium constant $K_{1, \text{methane}}$ and $K_{2, \text{wgs}}$ are functions of Gibbs free energy

$$\Delta G^0 = -RT \ln K(T) \quad (3.9)$$

and ΔG^0 can be defined in the terms of formation enthalpy, H_f^0 as

$$\ln K = \int \frac{H_f^0}{RT^2} dT \quad (3.10)$$

The formation enthalpy, H_f^0 which is a function of the temperature and specific heat at constant pressure is given in the following equation [3.14].

$$H_f^0 = \int C_p(T) dT \quad (3.11)$$

The specific heat capacity $C_p(T)$ can be expressed as

$$C_p = a + bT + cT^2 + dT^3 \quad (3.12)$$

The equilibrium constant K is calculated by integration of Eq.10 [12].

$$\ln K = \frac{1}{R} \left(-\frac{j}{T} + \Delta a \ln T + \frac{\Delta b}{2} T + \frac{\Delta c}{6} T^2 + \frac{\Delta d}{12} T^3 + i \right) \quad (3.13)$$

The value of $\Delta a, \Delta b, \Delta c$ and Δd are the coefficient for specific heat of chemical species and j, i are the integration constants in order to calculate the equilibrium constant. The energy balance for the gasification process at adiabatic condition is as follows

$$H_{reactants} = H_{products} \quad (3.14)$$

$$H_{reactants} = H_{f, biomass}^0 + w \left[H_{f, H_2O}^0 + \int_{298.15}^{T_i} C_{p, H_2O} dT_i \right] \quad (3.15)$$

$$H_{products} = \sum_{products} X_i \left[H_{fi}^0 + \int_{298.15}^{T_i} C_{pi} dT_i \right] \quad (3.16)$$

Considering $CH_\gamma O_\beta$ as a model for the composition of the biomass, equivalence ratio is defined as ratio of actual air supply to stoichiometric air requirement, dimensionless and determined by the following expression,

$$ER = \frac{m}{1 + \frac{\gamma}{4} - \frac{\beta}{2}} \quad (3.17)$$

The biomass formation enthalpy, $H_{f, biomass}^0$, is measured either experimentally or calculated using correlations as a function of biomass heating value. There are seven unknowns $X_{H_2}, X_{CO}, X_{CO_2}, X_{H_2O}, X_{CH_4}, X_{tar}$ and m , representing the six unknown product species and the amount of oxygen for the reaction. Therefore 7 equations are required, (three mass balance Eqs. (3.3), (3.4) and (3.5); two equilibrium reactions Eqs. (3.6) and (3.8); one energy balance Eq. (3.14) and one equivalence correlation as a function of biomass oxygen content Eq. (3.17)). The system of equations is solved using the Newton-Raphson iterative method. The algorithm of the stoichiometric equilibrium model is given in Figure 3.1.

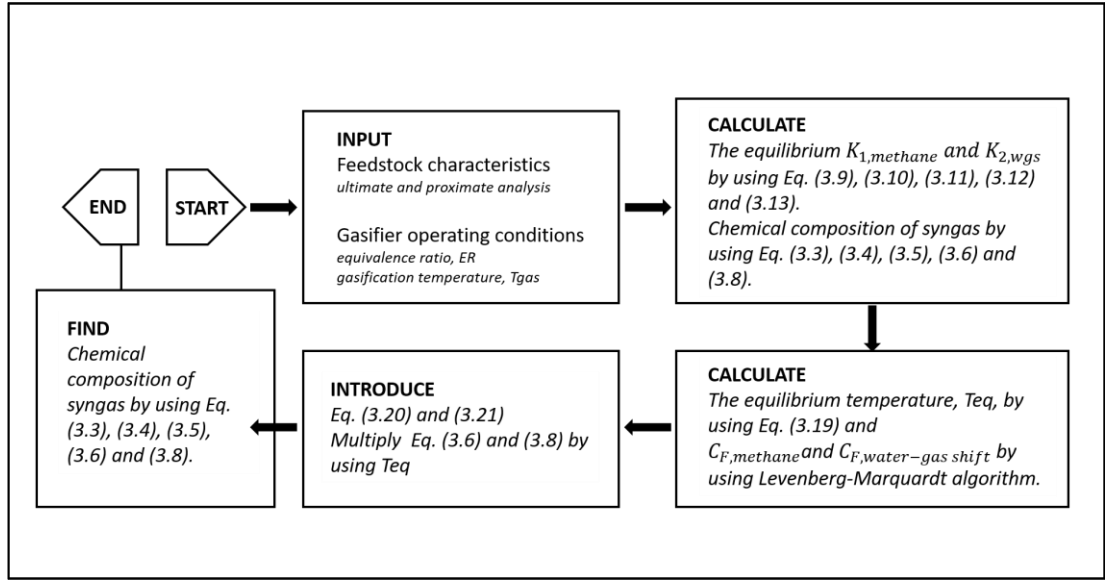


Figure 3.1: Algorithm of equilibrium model.

3.2. Results and Discussion for Development a Semi-Empirical Equilibrium Model

In order to analyze the performance of stoichiometric equilibrium gasification models (SEM), some biomass experiments which takes place in the literature were used. The ultimate and proximate analysis of the woody biomass given in Table 3.2 were used in the model. Biomass molecular formula $CH_\gamma O_\beta$ derived from the ultimate analysis of the biomass. It can be clearly seen that woody biomasses with different chemical compositions were used in this study.

The root mean square error (RMSE) as given in Eq. (3.18) is used for the comparison of the results obtained with each model and the experiments,

$$RMSE = \sqrt{\frac{\sum_{i=1}^N (\text{experimental}_i - \text{model}_i)^2}{N}} \quad (3.18)$$

Table 3.2. Ultimate and proximate analysis of feedstocks.

Ultimate analysis						
Component						
Feedstocks	C ^a	H ^a	O ^a	N ^a	S ^a	References
Wood pellet	50.70	6.90	42.40	<0.30	-	Barrio et al. [34]
Wood pellet	50.67	6.18	40.97	2.00	0.18	Yucel et al. [3]
Wood chips	45.60	5.90	48.40	<1.00	0.0762	Olgun et al. [35]
Wood chips	46.50	5.80	43.50	0.20	0.10	Son et al. [36]
Bagasse	48.20	6.10	44.30	0.30	0.03	Erlich et al. [37]
Wood	50.40	5.90	43.30	<0.10	<0.01	Erlich et al. [37]
Wood sawdust pellet	48.91	5.80	45.11	0.18	-	Simone et al. [38]
Rubber wood	50.60	6.50	42.00	0.20	-	Jayah et al. [16]
Polish pellet	52.60	5.90	41.30	0.30	-	Dudyński et al. [39]
Torrefied pellet	56.00	5.00	38.60	0.30	-	Dudyński et al. [39]
Proximate analysis						
Components						
Feedstocks	FC ^a	VM ^a	Ash ^a	HHV ^b	LHV ^b	References
Wood pellet	-	-	0.39	18.86	-	Barrio et al. [34]
Wood pellet	-	-	1.00	18.69	-	Yucel et al. [3]
Wood chips	12.30	77.50	1.50	20.50	19.10	Olgun et al. [35]
Wood chips	14.30	60.90	3.90	17.29	-	Son et al. [36]
Bagasse	-	-	1.1	19.26	17.93	Erlich et al. [37]
Wood	-	-	0.30	20.27	18.99	Erlich et al. [37]
Wood sawdust pellet	17.27	80.63	2.10	-	18.43	Simone et al. [38]
Rubber wood	19.20	80.10	0.70	19.60	-	Jayah et al. [16]
Polish pellet	19.50	70.00	0.50	-	17.00	Dudyński et al. [39]
Torrefied pellet	34.50	60.00	1.00	-	20.00	Dudyński et al. [39]
^a wt. % db ^b MJ/kg db						

3.2.1. Validation of the Model

Three models are constructed to predict dry gas composition produced from downdraft gasification of woody biomass. The detailed model structure is given in Table 3.3.

Table 3. 3: The detailed model structure.

Model	Equation set	Exception	Variables	Information
SEM1	Eqs.(3.2)-(3.6), (3.8), (3.16), (3.17)	-	$X_C, X_{H_2}, X_{CO}, X_{CO_2}, X_{H_2O},$ X_{CH_4}, X_{tar}, m	Full model
SEM2	Eqs. (3.3)-(3.6), (3.8), (3.16), (3.17)	$X_{tar} = 0$	$X_C, X_{H_2}, X_{CO}, X_{CO_2}, X_{H_2O},$ X_{CH_4}, m	Model without Tar
SEM3	Eqs. (3.3)-(3.6), (3.8), (3.16), (3.17)	$\phi = 1$ $X_c = 0$	$X_{H_2}, X_{CO}, X_{CO_2}, X_{H_2O},$ X_{CH_4}, X_{tar}, m	Model without Char

First model consists the global gasification reaction including char and tar components and is called SEM1. Model of SEM2 is based on global gasification reaction that includes only char component and SEM3 model includes only tar component. All three model are validated with experimental data presented in literature considering composition of the syngas produced by a downdraft gasifier. The predicted RMSE values of the models are given in Table 3.4. The comparisons were carried out for different gasification temperatures, equivalence ratios and moisture contents for a total of 32 cases. The experimental data sets and operating conditions of all cases is given in Table 3.5. The overall RMSE values of SEM1, SEM2 and SEM3 model are 4.34, 4.06 and 4.62 respectively so models exist within $\pm 4.34, 4.06$ and 4.62 vol.% in average. Considering the RMSE values from Table 3.4 and operating conditions given in Table 3.5, for the cases that have lower gasification temperature gave higher RMSE values as expected. At low temperature the reaction rates are slow so reactions takes longer to reach equilibrium state. Thus, the performance of equilibrium models reduces with the gasification temperature. For example, for the 3 cases with the lowest temperature, the largest error values were taken.

Table 3.4: The RMSE value of SEM models.

Ref.	Case ID	RMSE value		
		SEM1	SEM2	SEM3
Barrio et al. [34]	Case 1	4.546	5.154	5.697
	Case 2	5.285	4.492	6.477
	Case 3	4.647	3.775	5.435
	Case 4	4.718	3.765	5.530
	Case 5	4.076	3.856	4.960
	Case 6	5.466	4.587	6.636
	Case 7	5.037	4.703	6.339
	Case 8	6.925	4.238	8.158
Yucel et al. [3]	Case 9	4.588	4.263	5.573
	Case 10	4.363	3.962	5.075
	Case 11	3.517	3.390	4.068
	Case 12	4.989	4.388	5.435
Olgun et al. [35]	Case 13	5.496	6.108	4.800
	Case 14	4.528	4.615	3.981
	Case 15	4.113	3.601	3.846
	Case 16	4.679	3.553	4.659
Olgun et al. [35]	Case 17	5.846	4.179	5.846
	Case 18	6.805	4.753	6.805
Son et al. [36]	Case 19	1.411	2.301	1.323
Erlich et al. [37]	Case 20	9.114	9.070	8.442
	Case 21	7.090	7.112	6.426
Simone et al. [38]	Case 22	2.012	2.404	1.399
Jayah et al. [16]	Case 23	2.316	1.558	2.452
	Case 24	1.563	0.671	1.563
	Case 25	0.784	0.963	0.784
	Case 26	1.541	1.526	1.739
	Case 27	1.926	3.103	1.911
	Case 28	1.579	2.289	1.860
	Case 29	2.362	3.212	2.348
	Case 30	2.747	3.147	2.747
Dudyński et al. [39]	Case 31	9.521	9.809	8.916
	Case 32	5.203	5.501	6.722

RMSE values of cases 20, 21 and 31 are 9.114, 7.090,3 and 9.521 respectively for SEM1. The RMSE values of case 20 and 31 are the highest 2 values for all models (SEM1, SEM2 and SEM3). With the increase of equivalence ratio, oxidation zone

temperature increases because air promoted the combustion reaction. If ER is high while temperature is low, the heat loss is high and in such cases the RMSE values is also high (Cases 17, 18) because of adiabatic assumption. Also the RMSE values are high for the cases which combustion reaction is predominant. For instance, the RMSE value of case 8 which has high gasification temperature while ER is low is 6.925 for SEM1 model.

In reference to the comparison, results are given in Figure 3.2, equilibrium models tending to underestimate/overestimate the quantity of syngas component depending on operating condition of gasification. In order to reduce RMSE values caused by the difference between measured data and data predicted by the model, some correlations are introduced to calculate equilibrium constant.

Table 3.5: The experimental data sets and operational conditions of all cases.

Case ID	H ₂ ^a	CO ^a	CO ₂ ^a	CH ₄ ^a	N ₂ ^a	T _{gasification} ^b	ER	MC ^c	Gasifier Type
Case 1	16.1	24.7	9.7	1.6	47.9	1259	0.25	7.5	Downdraft
Case 2	16.8	25.8	9.1	1.5	46.8	1297	0.27	7.5	Downdraft
Case 3	16.5	25.3	9.3	1.5	47.3	1317	0.3	7.5	Downdraft
Case 4	16.4	25.2	9.4	1.5	47.5	1324	0.3	7.5	Downdraft
Case 5	15.6	23.9	10.1	1.7	48.7	1320	0.29	7.5	Downdraft
Case 6	17.2	26.4	8.8	1.4	46.3	1289	0.27	7.5	Downdraft
Case 7	16.4	25.2	9.4	1.5	47.5	1290	0.26	7.5	Downdraft
Case 8	16.4	25.3	9.4	1.5	47.4	1390	0.29	7.5	Downdraft
Case 9	17.88	23.9	8.77	2.97	46.48	1096.3	0.26	7.28	Downdraft
Case 10	18.02	24.74	8.3	2.96	45.98	1097.3	0.28	7.28	Downdraft
Case 11	17.97	23.76	8.86	2.99	46.42	1093.5	0.29	7.28	Downdraft
Case 12	18.32	27.6	6.71	2.75	44.62	1101.2	0.31	7.28	Downdraft
Case 13	13.44	22.96	10.64	2.48	50.48	1133	0.25	8.8	Downdraft
Case 14	13.6	23.44	10.96	2.72	49.28	1133	0.3	8.8	Downdraft
Case 15	13.68	24.08	10.88	2.64	48.72	1133	0.35	8.8	Downdraft
Case 16	13.44	22.56	11.52	2.72	49.76	1133	0.4	8.8	Downdraft
Case 17	13.28	20.8	12.24	2.88	50.8	1133	0.45	8.8	Downdraft
Case 18	13.04	20	12.16	2.64	52.16	1133	0.5	8.8	Downdraft
Case 19	16.5	15.9	15.3	2.1	50.2	1123	0.35	21.7	Downdraft
Case 20	9.4	23.4	11.5	2.8	53	973	0.285	11	Downdraft
Case 21	11	26.4	9.2	2.4	51.3	1023	0.29	7.5	Downdraft
Case 22	17.6	21.6	12	2.3	46	1123	0.3	9.5	Downdraft
Case 23	17.2	19.6	9.9	1.4	51.9	1300	0.38	18.5	Downdraft
Case 24	18.3	20.2	9.7	1.1	50.7	1300	0.42	6	Downdraft
Case 25	17.2	19.4	9.7	1.1	52.6	1300	0.45	14.7	Downdraft
Case 26	17	18.4	10.6	1.3	52.7	1300	0.37	16	Downdraft
Case 27	13.2	19.7	10.8	1.3	55	1300	0.4	15.2	Downdraft
Case 28	15.5	19.1	11.4	1.1	52.9	1300	0.35	14.7	Downdraft
Case 29	12.7	22.1	10.5	1.3	53.4	1300	0.39	13.8	Downdraft
Case 30	13	19.1	10.7	1.2	56	1300	0.45	12.5	Downdraft
Case 31	7.8	29.9	4.7	1.9	53.2	1023	0.277	10	Updraft
Case 32	10.3	29	6.7	2.4	48.3	1233	0.219	4.5	Updraft
^a (% vol), ^b (K), ^c (%)									

3.2.2. Modification of the Model

It can be observed from Figure 3.2 that there is a need to increase the reliability and accuracy of the stoichiometric equilibrium model. The basic problems of the equilibrium models are due to complex mechanisms of gasification process.

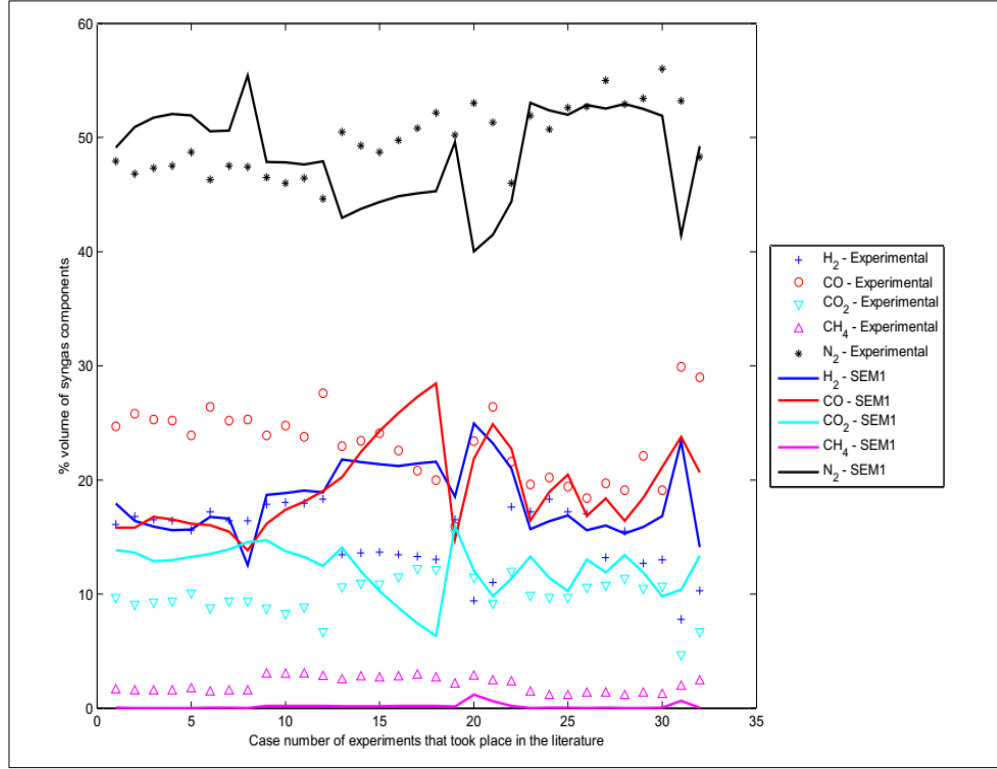


Figure 3.2: Comparison of SEM1 model with experimental data.

Model results mostly show that equilibrium calculations underestimate the N₂ and CH₄ content and overestimate the H₂ content. The modified equilibrium models can improve the prediction capability by combining empirical correlations. Applying a correction coefficient in order to predict syngas composition may be advisable but using them by disregarding the operating conditions is insufficient.

In this work, two correction correlations have been introduced that is dependent on gasification temperature, equilibrium temperature and ER for the methanation reaction and the water-gas shift reaction. The equilibrium temperature is calculated according to the following equation [24, 40] .

$$CO/CO_2 = 10^{3.4} e^{-\frac{12400}{1.98T_{eq}}} \quad (3.19)$$

In order to increase the accuracy of results, the equilibrium constants of the methanation and the water-gas shift reaction are multiplied by the following coefficients respectively.

$$C_{F, \text{methane}} = -778.4(ER) + 774.6e^{\frac{0.6639(ER)}{(T_{eq}/T_{gas}^*)^{-2}}} + 666.6 \quad (3.20)$$

$$C_{F, \text{water-gas shift}} = 3.194(ER) + 0.02912.6e^{\frac{4.23(ER)}{(T_{eq}/T_{gas}^*)^{-2}}} - 0.6354 \quad (3.21)$$

The terms of $C_{F, \text{methane}}$ and $C_{F, \text{water-gas shift}}$ are given in Eqs. (3.20-3.21) were obtained after fitting the SEM1 model with published experimental data [3, 16, 34-39] within the gasification temperature range 973 – 1390 K and the ER range 0.21 – 0.5. The fitting surfaces of $C_{F, \text{methane}}$ and $C_{F, \text{water-gas shift}}$ coefficients are presented in Figure 3.3. The small blue dots are data points represent correction coefficients which have been estimated from experimental data and model prediction data for the perfect agreement by using Levenberg-Marquadt algorithm. For the $C_{F, \text{methane}}$ and $C_{F, \text{water-gas shift}}$ correlations the R squared values are 0.9191 and 0.8260 respectively in the 95% confidence bounds.

Gasification temperature and its position on the gasifier are highly variable from case to case. In order to provide good fitting, we had to apply another correction for gasification temperature. For example, reported temperature for the cases come from Yucel and Barrio [3, 34, 41] is maximum gas temperature. For such cases we define $T_{gas}^* = 0.89T_{gas}$ in order to calculate $C_{F, \text{methane}}$ and $C_{F, \text{water-gas shift}}$. Also some author [35, 37] gives char gasification temperature as gasification temperature which is fairly low temperature from gasification temperature, for such cases we define $T_{gas}^* = 1.2T_{gas}$. For other 12 cases come from various researchers [16, 36, 38-39], reported temperature can be used directly in calculation of $C_{F, \text{methane}}$ and $C_{F, \text{water-gas shift}}$. Figure 3.4 shows the comparison for the syngas components between the result of modified SEM1 model and experimental data. In the simulations of SEM2 and SEM3 models, the correction correlations were recalculated and adopted to each model and their results also compared to experimental data. The aforementioned comparisons are listed in Table 3.6.

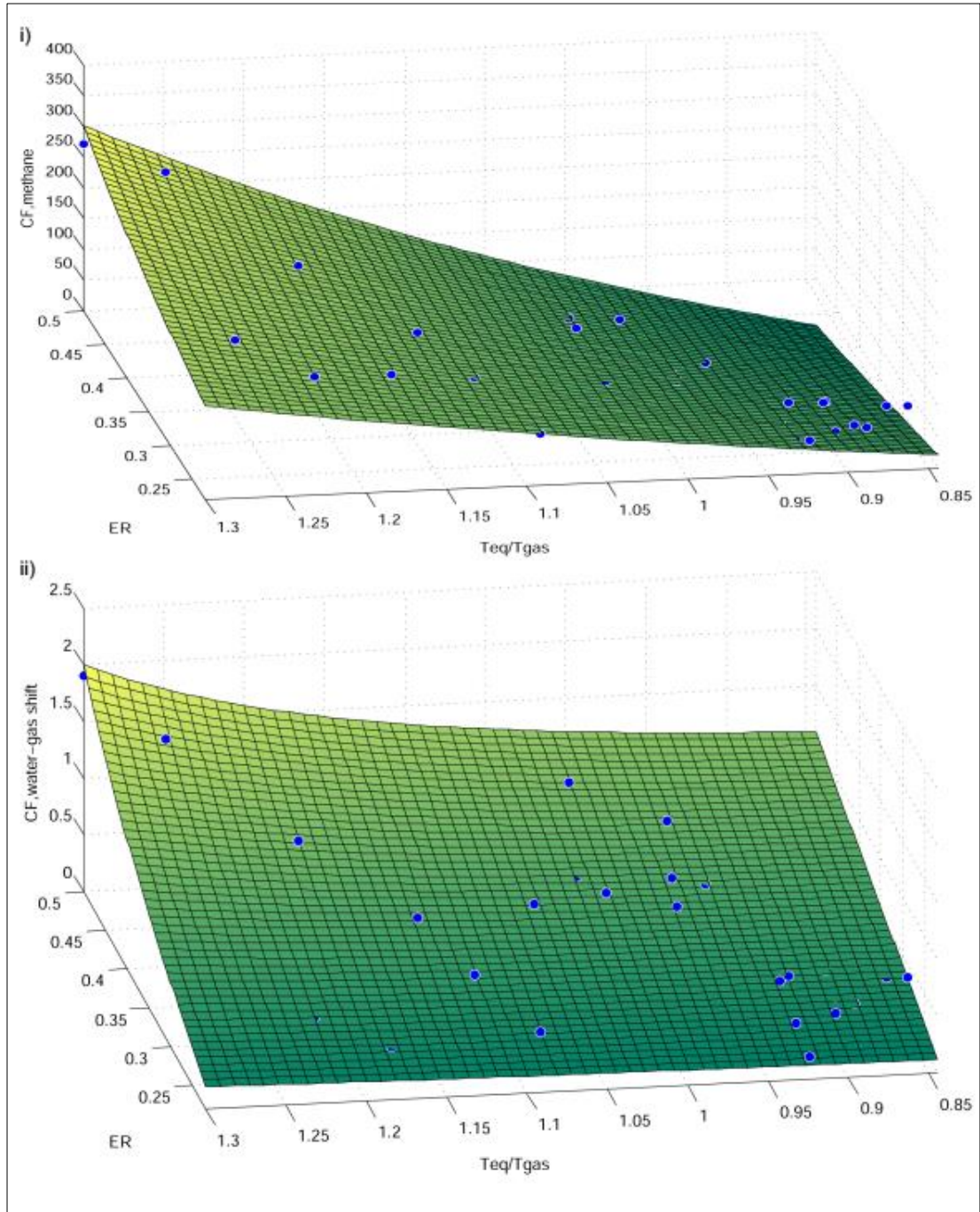


Figure 3.3: Surface fitting for determination $C_{F, \text{methane}}$ and $C_{F, \text{water-gas shift}}$ correction correlations.

Table 3.6: The RMSE value of SEM modified models.

Ref.	Case ID	RMSE value of modified models		
		SEM1	SEM2	SEM3
Barrio et al. [34]	Case 1	0.880	1.508	0.943
	Case 2	0.899	1.274	1.016
	Case 3	0.977	1.214	1.000
	Case 4	0.998	1.226	1.069
	Case 5	1.146	1.580	1.279
	Case 6	1.289	1.422	1.373
	Case 7	0.672	1.328	0.852
	Case 8	1.475	1.444	3.091
Yucel et al. [3]	Case 9	3.406	4.076	1.648
	Case 10	2.247	3.679	1.634
	Case 11	2.399	3.630	1.244
	Case 12	1.420	3.581	2.876
Olgun et al. [35]	Case 13	1.208	1.444	1.709
	Case 14	0.591	0.369	0.855
	Case 15	0.964	0.851	0.914
	Case 16	0.516	0.580	0.491
Olgun et al. [35]	Case 17	0.837	0.533	1.047
	Case 18	1.010	0.390	1.334
Son et al. [36]	Case 19	1.436	1.607	1.487
Erlich et al. [37]	Case 20	2.588	2.423	3.056
	Case 21	1.534	1.503	1.868
Simone et al. [38]	Case 22	2.814	2.954	2.628
Jayah et al. [16]	Case 23	1.042	0.743	1.159
	Case 24	1.626	1.698	1.807
	Case 25	1.031	1.050	1.202
	Case 26	1.139	0.762	1.441
	Case 27	1.495	1.441	1.272
	Case 28	0.714	0.714	0.942
	Case 29	1.391	1.607	1.016
	Case 30	1.609	1.418	1.567
	Case 31	4.477	4.348	5.069
	Case 32	1.167	1.240	1.398

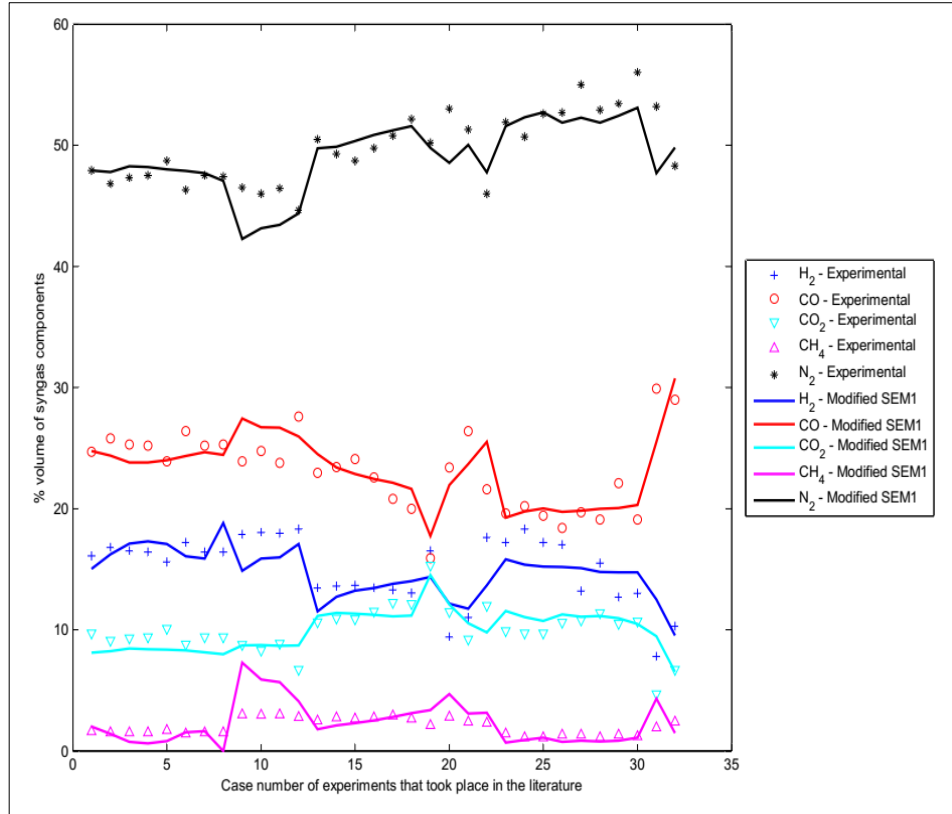


Figure 3.4: Comparison of modified SEM1 model with experimental data.

The RMSE value varies in the range of 0.516-4.477 for the modified SEM1 model and the summation of RMSE value were reduced from the 138.793 to 46.997 by modifying the model for the 32 cases. For the modified SEM2 model, the total RMSE value was reduced from 130.048 to 53.637 and for modified SEM3 model, it decreased from 147.952 to 50.287. The overall RMSE values of SEM1, SEM2 and SEM3 model are 1.46, 1.67 and 1.57 respectively. With the modification, the accuracy of the modified model SEM1 successfully increased in the prediction of concentration of syngas components. The results of modified SEM1 and SEM3 model are almost identical but, modified SEM2 model result is slightly lower than others. As mentioned earlier, SEM2 model is based on global gasification reaction including only char component, and it may be stated that the difference in RMSE value may come from char component. SEM2 model is constructed after excluding tar component from SEM1 model in order to resolve the equations. Thus, it was seen that the total RMSE value increased from 46.997 to 53.637 and overall RMSE value increased from 1.46 to 1.57. The RMSE value of case 20 which has the lowest gasification temperature is

still the highest for value for SEM1 and SEM2 model with the results of 5.124 and 5.250.

In addition to the information given above, a published experimental study by Dogru et al. [41] was tested externally from other 32 cases to validate modified SEM1 model. Figure 3.5 shows the comparison between SEM1 model, modified SEM1 model and experimental results. The accuracy and agreement seems fairly good except the methane concentration.

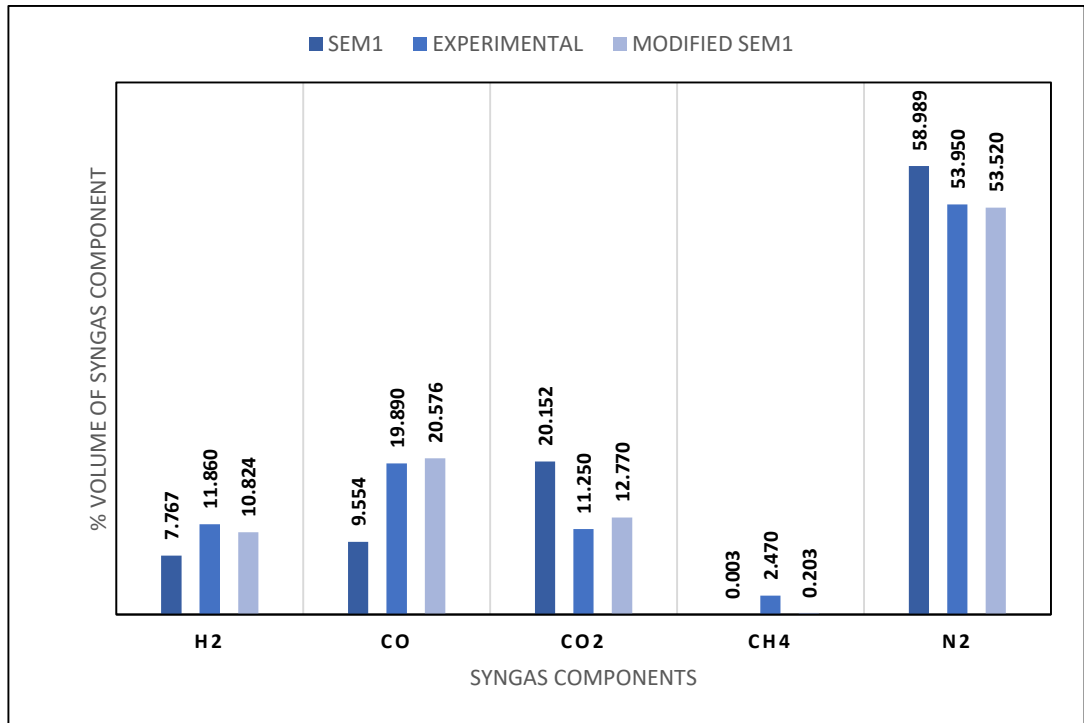


Figure 3.5: Validation of modified SEM1 model with experimental data of Dogru et al.

3.2.3. Tar Validation

Tar yield from biomass gasification usually causes operational challenges in internal combustion engines (IC). Downdraft gasifiers mostly produce less tar content than other types of gasifiers and are therefore suitable for small scale power generation. In addition to this, for electrical generation systems, the tar content in the syngas should not exceed the limit for IC engines [42-43]. In order to ensure the limit of tar content for IC, the tar concentration prediction capability should be integrated into the models. However, most of researchers did not take into account the tar content of syngas and ignored it in the construction of equilibrium gasification modelling. In this

work, SEM1 and SEM3 models include the tar content and benzene is assumed as a tar structure and its physical and chemical properties are used to determine the tar concentration. Firstly, the modified SEM1 model was tested in order to determine the yield of tar. It is clearly shown that results given in Figure 3.6 are not represent satisfactorily the variation of the tar yield with different ER values.

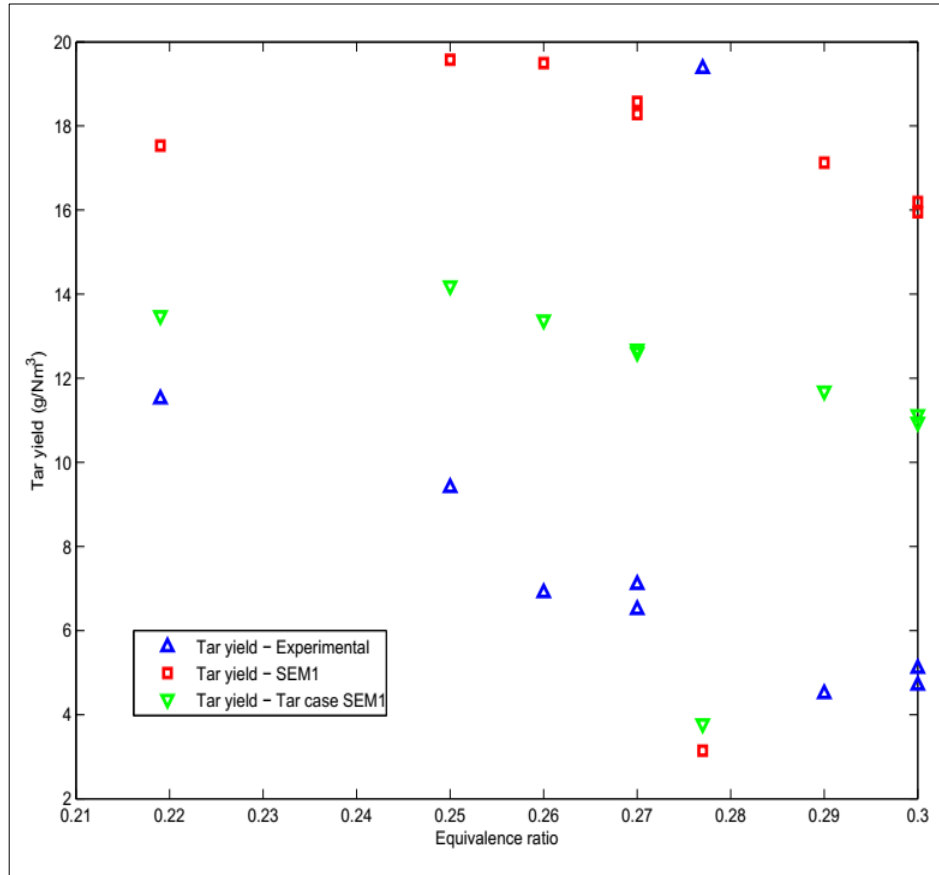


Figure 3.6: Comparison of experimental tar yield with SEM1 and modified SEM1 model.

To improve the prediction accuracy, the modified SEM3 model which applied a modification of the equilibrium equations is used by multiplying the equilibrium constants as indicated below, respectively:

$$\begin{aligned}
 C_{F, \text{methane}, \text{tar}} = & 2678 - 19920 (ER) - 441.3 (T_{eq}/T_{gas}^*) \\
 & + 23220 (ER) (T_{eq}/T_{gas}^*) - 3069 (T_{eq}/T_{gas}^*)^2
 \end{aligned} \quad (3.22)$$

$$\begin{aligned}
C_{F,water-gas\ shift,tar} &= 1.183 - 46.06 (ER) + 10.09 (T_{eq}/T_{gas}^*) \\
&+ 56.56(ER)(T_{eq}/T_{gas}^*) - 13.72(T_{eq}/T_{gas}^*)^2
\end{aligned} \tag{3.23}$$

Figure 3.7 shows the comparison of the tar yield (g/Nm^3) between the results of SEM3 model, modified SEM3 model and experimental data of Barrio and Dudynski [34, 39]. In Figure 3.8, the yield of tar has been represented versus ER. SEM3 model results show that equilibrium calculations underestimate the tar content. The total RMSE of SEM3 model prediction is 56.7116 for the 9 sets of experiments. The correction coefficients were developed within the gasification temperature range 1020 – 1160 K and the ER range 0.21 – 0.3. After modification, the total RMSE value reduced to 18.2212. Higher gasification temperature causes tar cracking and consequently reduces yield of tar. As can be seen the tar yield decreased as the ER value increased.

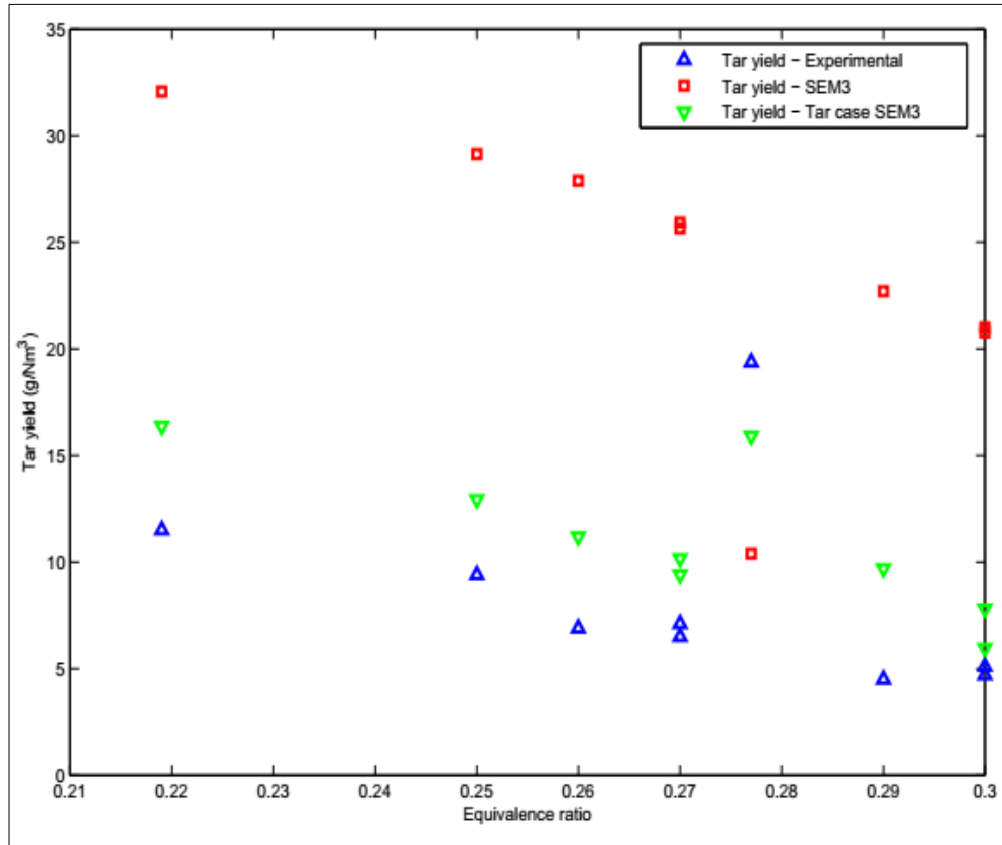


Figure 3.7: Comparison of experimental tar yield with SEM3 and modified SEM3 model.

3.2.4. Sensitivity Analysis of Biomass Heating Value by using HHV Correlations

In Eq. (3.15), H_f^0 representing the enthalpy of formation of feedstock, an expression is required in terms of HHV or LHV. In the gasification studies, sometimes LHV value or HHV value may be used to construct the energy balance. In our work, Eq. (3.24) below is used to determine the enthalpy of formation of feedstock in terms of HHV.

$$H_f^0 = HHV + H_{f_{CO_2}}^0 + \frac{\gamma}{2} H_{f_{H_2O(l)}}^0 \quad (3.24)$$

Energy balance is a key factor of equilibrium model, and it may affect the simulation results by increasing or decreasing RSME values. In the literature, there are many of HHV correlations using the mass percentages given in the ultimate analysis to obtain the enthalpy of formation of feedstock [44-53]. Some of these correlations are given in Table 3.7, used to perform a sensitivity analysis of biomass heating value.

Table 3.7: HHV correlations for feedstocks.

Cor. No.	Correlation	References
1	$HHV^* = 0.3414C^* + 1.4445H^* - (N^* - O^* - 1)/8 + 0.093S^* \quad MJ/kg$	Dulong-Berthelot [54-55]
2	$HHV^* = 0.3391\left(C^* - \frac{3}{8}O^*\right) + 0.2386\left(\frac{3}{8}O^*\right) + 1.444(H^* - \frac{1}{16}O^* + 0.1047S^* \quad MJ/kg$	Steuer [56]
3	$HHV^* = (0.373 - 0.00026C^*)C^* + 1.444\left(H^* - \frac{1}{10}O^*\right) + 0.1047S^* \quad MJ/kg$	Vondracek [57]
4	$HHV^* = 0.3391C^* + 1.4337H^* + 0.0931S^* - 1.273O^* \quad MJ/kg$	D'huart [58]
5	$HHV^* = 0.3403C^* + 1.2432H^* + 0.0628N^* + 1.909S^* - 0.0984O^* \quad MJ/kg$	Gumz [59]
6	$HHV = 0.341C + 1.323H + 0.0685 - 0.0153A - 0.1194(O + N) \quad MJ/kg$	IGT [50, 60]

Table 3.7: HHV correlations for feedstocks (continued).

Cor. No.	Correlation	References
7	$\text{HHV} = 0.328C + 1.4306H - 0.0237N + 0.0929S$ $- \left(1 - \frac{A}{100}\right) \left(40.11 \frac{H}{C}\right)$ $+ 0.3466 \text{ MJ/kg}$	Grabosky and Bain [61]
8	$\text{HHV}^* = 35.8368 + 0.7523H^* - 0.2674S^* - 0.4654O^*$ $- 0.3814Cl^* - 0.2802N^* \text{ MJ/kg}$	Chang [62]

After correlations were used in Eq. (3.24), the energy balance calculations were repeated and the comparison of the results of the RMSE values are listed in Table 3.8. According to SEM1 model results Dulong-Berthelot's correlation [49, 51] showed best accuracy among other correlations. In this work, we have benefited from IGT correlation [50] in order to determine RMSE values given in Tables 3.4. By changing the HHV correlation, overall RMSE value reduced from 4.34 to 3.85 and the total RMSE value reduced from 138.795 to 123.336 for 32 cases.

Table 3.8: The RMSE value of SEM1 model using HHV correlations.

Case ID	Correlation number							
	1	2	3	4	5	6	7	8
1	3.651	3.806	3.787	3.917	3.978	4.546	4.855	4.579
2	3.619	4.092	3.071	4.318	4.430	5.285	5.685	5.329
3	3.007	3.485	2.436	3.709	3.820	4.647	5.027	4.689
4	3.031	3.526	2.422	3.757	3.871	4.718	5.106	4.762
5	2.656	3.012	2.489	3.203	3.300	4.076	4.450	4.117
6	3.795	4.277	3.193	4.505	4.617	5.466	5.862	5.510
7	3.551	3.937	3.243	4.135	4.236	5.037	5.425	5.080
8	4.591	5.335	3.313	5.658	5.814	6.925	7.418	6.981
9	3.344	3.578	3.253	3.693	3.505	4.588	4.449	3.216
10	3.099	3.356	2.915	3.477	3.279	4.363	3.953	2.904
11	2.565	2.704	2.716	2.787	2.655	3.517	4.168	2.617
12	3.544	3.900	2.955	4.048	3.801	4.989	3.079	3.071
13	5.557	5.295	5.795	5.235	6.029	5.496	6.670	8.801
14	4.595	4.297	4.850	4.223	5.092	4.528	5.734	7.776
15	4.183	3.867	4.441	3.785	4.680	4.113	5.296	7.202
16	4.761	4.379	5.052	4.273	5.312	4.679	5.952	7.816
17	5.926	5.550	6.208	5.444	6.457	5.846	7.063	8.801
18	6.879	6.531	7.139	6.433	7.368	6.805	7.925	9.521
19	2.296	2.824	1.534	3.017	2.000	1.411	9.498	4.152
20	9.476	9.202	9.933	9.112	9.532	9.114	10.979	10.662
21	7.676	7.392	8.215	7.305	7.758	7.090	7.773	8.977
22	1.766	1.488	2.398	1.440	2.109	2.012	4.263	6.087
23	1.419	1.733	1.431	1.891	1.746	2.316	1.307	1.446
24	0.696	0.994	1.011	1.151	1.007	1.563	0.744	0.718
25	1.541	1.157	2.403	1.023	1.145	0.784	2.045	1.496
26	1.120	1.127	1.822	1.212	1.133	1.541	1.465	1.106
27	2.650	2.285	3.517	2.161	2.274	1.926	3.150	2.606
28	1.270	1.211	2.062	1.275	1.215	1.579	1.675	1.248
29	2.548	2.389	3.142	2.358	2.385	2.362	2.866	2.525
30	3.736	3.305	4.623	3.137	3.290	2.747	4.260	3.687
31	9.806	9.660	10.189	9.616	9.779	9.521	9.862	10.535
32	4.983	5.468	4.220	5.617	4.700	5.203	4.308	5.720
Total RMSE	123.336	125.161	125.776	126.917	132.318	138.793	162.312	163.737

4. NUMERICAL and EXPERIMENTAL INVESTIGATION of HYDROGEN-RICH SYNGAS PRODUCTION

Hydrogen is seen as an important fuel for the future that can help to diminish the growing environmental concern such as global warming and can be a replacement for fossil fuels [63-64]. The hydrogen demand increases as a reactant in hydro-processing units in refineries by the improvement of new process for sustainable hydrogen production [65]. Furthermore, hydrogen is expected to reduce dependence on oil as a clean energy carrier and meet a large part of the world's future energy needs [66-67]. Hydrogen can be industrially produced through a variety of processes such as ion exchange membranes, biomass gasification, natural gas steam reforming, electrolysis and thermochemical water splitting with a Cu-Cl and S-I cycles. Nowadays, about 90% of total hydrogen production is derived from fossil fuel reforming, particularly natural gas [63-65]. Gasification is one of the effective thermochemical conversion processes which transforms solid into hydrogen-rich gaseous fuel and can be combined with fuel cell systems, Fischer-Tropsch process (numerous chemical reactions that transform the mixture of hydrogen and carbon monoxide into liquid hydrocarbons) and methanol synthesis reactions [6]. The quality of the produced gas via gasification is higher in terms of hydrogen production, compared to other methods. Gasification process comprises drying, pyrolysis, oxidation, reduction steps and depends on various reactions. By partial oxidation, biomass is converted into the combustible gas mixture (H_2 , CH_4 , CO) in the range of 800-1100 °C [8-9, 68]. The gasification media which can be either steam, air, oxygen, or combination of them are used throughout the gasification process depending on the desired gas composition and the quality of syngas [69-70]. In gasification, depending upon the gasifying medium employed, the syngas dry calorific value varies between 3-5 MJ/Nm³ to 10-18 MJ/Nm³ for the case of air and air/steam process and the case of oxygen and steam or indirectly heated process, respectively [5, 71]. However, steam as an oxidizing agent is attracting more attention because it gives better results in terms of H_2/CO and hydrogen yield (% H_2 in syngas) in gasification processes. Hydrogen as a fuel with high calorific value and highly efficient energy source has become a renewed focus of interest in the industry thanks to its environmental advantages [72].

Since gasification is a sensitive and complex process, it is highly affected by the chemical composition, size and moisture content of feedstock materials. The type of gasifying agent, its flow rate, pressure, gasification temperature, and ER are other crucial parameters that dramatically have an impact on the gasification performance. The equivalence ratio is a critical operating variable in biomass gasification, and express the amount of excess air supplied to the gasifier. Several studies have been performed to produce hydrogen-rich syngas from biomass gasification [73-75]. Many investigations based on experimental and mathematical modelling approaches have been carried out to describe the gasification process and the impact of the operating conditions on the syngas composition [3, 17, 76-79]. Different feedstocks, gasifier inlet conditions and oxidizing agent types have been used to produce the high quality syngas. Sharma et al. performed a study using an air-steam gasifying medium to enhance the hydrogen content of the syngas at the outlet the gasifier. The furniture waste of *Dalbergia sissoo* generally accepted sesame wood was used as a biomass source for the gasification. The effect of operating parameters such as equivalence ratio (0.1288–0.303), steam to biomass ratio (0.76–1.21), and moisture content (0.015–0.042 wet basis) over the performance of gasification has been analyzed by altering the conditions. They also developed an equilibrium model in order to predict the composition of syngas and its calorific value. It is observed that hydrogen yield was enhanced by steam addition right in the reduction zone of the gasifier [80]. Wiinikka et al. have compared the syngas production, gasification efficiency and syngas composition performance of an 18 kW atmospheric fixed bed oxygen blown gasifier with a high temperature ($>1000\text{ }^{\circ}\text{C}$), a pressurized (2–7 bar). The results show that in their work, it can be achievable to obtain a syngas of similarly high quality (high concentration of CO and H_2 (70~80%), low concentration of CH_4) and gasification efficiency as well as entrained flow gasification during fixed-bed gasification. They also observed that the production of a high-quality syngas is not particular to the entrained flow gasification technology [81]. Guo et al. carried out corn straw gasification experiments under atmospheric pressure, using air as an oxidizing agent. Experimental runs were performed in a downdraft gasifier with three stage of air supply in order to obtain a uniform temperature through the reactor. The influence of operating parameters such as biomass feeding rate and equivalence ratio on the performance of the gasification process was researched. Hydrogen content of syngas firstly showed an increasing trend and reached its maximum value of 12.89% at

ER=0.25 and then decreased as a result of an increase in the combustion reaction [82]. As a different gas medium, some agricultural wastes such as wheat straw, walnut shell, and almond shells were gasified by Safari et al to investigate the non-catalytic effect on the production of hydrogen-rich gas in supercritical water media through a range of temperatures between 400 °C and 440 °C. Maximum hydrogen yield of 4.1 mmol/g was reported in 440 °C [79]. Zang et al. researched hydrogen production during the steam gasification of biomass using a novel sorbent. The sorbent was prepared using calcined dolomite, limestone and water. Their result showed that steam to biomass mass ratio of 0.5 and sorbent to biomass mass ratio of 0.7 is optimal gasification parameters for hydrogen-rich gas production [83].

Besides experimental works, numerous mathematical modeling studies have been performed to analyze the gasification process. Pala et al. have been developed an Aspen Plus model to investigate the effect of the shift reactions over the syngas improvement processes for biomass steam gasification. Their aim is to present the effect of steam to biomass ratio, gasification temperature, and water-gas shift reaction temperature on CO, H₂, CO₂ conversion and H₂/CO ratio in the syngas. As a result of simulations, syngas composition was predicted and the H₂/CO molar ratio in the syngas composition was found close to a value of 2.15 as required for FT synthesis by the water-gas shift reaction [84]. Tinaut et al. [85] presented a steady state kinetic model of biomass gasification in a fixed bed downdraft gasifier and Di Blasi [86] presented an unsteady mathematical model of fixed bed counter-current wood gasifiers. For the first time, Zainal et al. have developed a stoichiometric equilibrium model in order to evaluate the gasification process. Their study was focusing on the investigation of the effect of moisture content and gasification temperature at a fixed equivalence ratio [87]. A process model was developed to investigate effects of critical parameters on the composition of fuel gas using Aspen Plus simulator by Favas et al. [88]. The steam injection was found as a key factor to produce H₂-rich gas in the SBR range studied. Their results indicate that low temperatures have a positive effect on the production of hydrogen, while high ER has a negative effect. To test oxygen as an oxidizing agent, Wu et al. studied the co-gasification of wheat straw and bituminous coal [89]. In the study, the influences of gasification temperature (1100-1400 °C), biomass mixing ratio (0, 0.25, 0.5, 0.75, 1), and oxygen/carbon ratio (0.35-0.65) on H₂ and other syngas component were considered. As the increasing of oxygen-fuel ratio, the content of H₂ and CH₄ decreases gradually. The gasification temperature of 1300°C

and the oxygen-fuel ratio of 0.45 were found as the optimum operating parameters for co-gasification of wheat straw and bituminous coal. The percentage of H_2 and CH_4 in syngas decreased with the increasing of O_2 /Fuel ratio.

In this part of the present study, the aim is to produce hydrogen-rich syngas from wood pellet gasification in a fixed bed downdraft gasifier. The study investigates the influence the gasification temperature, equivalence ratio, air as a gasifying medium on syngas quality and hydrogen production. Then a stoichiometric model was developed to determine the limit of the hydrogen yield of conventional gasification and validation was performed to examine the performance of gasification process. In the last part of the study, the effect of the oxidizing agent on the production of hydrogen-rich syngas and gasification performance was numerically tested by using air, air-steam and oxygen, respectively.

4.1. Materials and Methods for Hydrogen Production

4.1.1. Feedstock Material and Characterization

The wood pellet used in this study was purchased from a local manufacturer of wood pellet in Ankara, Turkey. The ultimate and proximate analyses of wood pellet were determined using standard procedures. ASTM E1755-01 for ash, ASTM E871-72 for moisture content and ASTM D3175 for volatile matter methods were applied for proximate analysis by using ash furnace. Fixed carbon was determined by balance [90]. The ultimate analysis carried out by using CHONS Elemental Analyzer in TUBITAK.

4.1.2. Gasifier Set-Up

The scheme of the downdraft wood gasifier is shown in Figure 4.1.

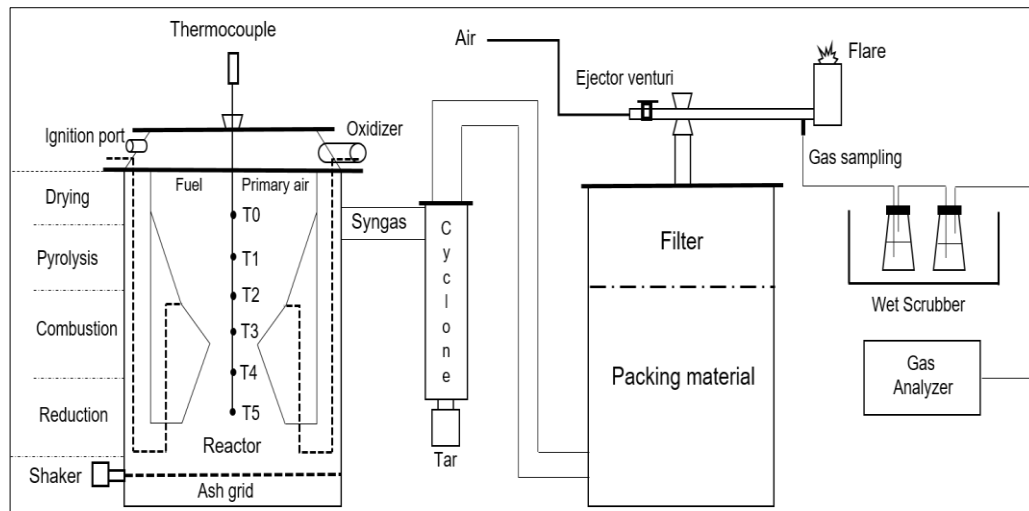


Figure 4.1: Gasification process in a fixed bed downdraft gasifier.

The total height of the gasification unit is 55 cm and it consists of two cylindrical coaxial structures that built using a stainless steel sheet. At the drying zone, the internal diameter is 28 cm while the height is 20 cm. In order to increase solid residence time in the zone of combustion and pyrolysis, the internal diameter of gasification unit reduced to 20 cm and finally to 7 cm gradually. The diameter of the unit enlarges to 19 cm than 23 cm and 38 cm respectively to decrease the gas velocity in the reduction zone. Designing gasification unit in this manner allows enough time for water-gas shift reaction to produce hydrogen. Also the volatile-char interaction can promote the Boudouard reaction to increase the concentration of carbon monoxide. The hot gas produced flows upward between the inner cylinder and the outer cylinder and provides the necessary energy as waste heat for drying and pyrolysis operations. The gas from the gasifier is passed through the inner and outer walls of the gasifier, then through the cyclone separator to remove the particles, and through the packed bed filter to collect the tar. A portable infrared syngas analyzer (Wuhan Cubic Syngas Analyzer Gas Board 3100P) equipped with a nondispersive infrared sensor, the thermal conductivity detector and electrochemical sensor was used for the measurement of H_2 , CO_2 , CO , CH_4 , and O_2 concentrations in sample syngas. The heating value of the producer gas is also calculated simultaneously via gas analyzer. Additionally, the clean, dry gas samples coming out of the moisture trap is then charged to the gas sample bags for further analysis by gas chromatograph (GC-7890A). In the last step, the flue gas is burned by a swirl burner. Also this gaseous mixture can be utilized in a gas engine to generate energy, or separated by a membrane to obtain CO , CH_4 , H_2 . Flue gas can also

be used to produce high added value chemicals such as ammonia, methanol, and other valuable chemicals.

A perforated iron grate is installed at the bottom of the gasifier to enable high ash-content fuels to be utilized. The grate can be shaken by a manual lever, or by a pneumatic or electric actuator in order to prevent dead zones and bridging inside the gasifier by disposing the ashes repeatedly from the gasifier. Our experimental set equipped a pneumatic shaking system that connected to the grate and controlled by a pneumatic directional control valve which is triggered by an adjustable time relay. For biomass gasification, the air is used as a gasifying medium and to prevent air inlet, the top of the gasifier is sealed. By the way, pressure drop prevents the primary air inlet to the filled gasifier. A venturi ejector provides the suction that enables air to enter the reactor to drive the gasifier via an orifice air flow meter. In the gasifier, there are 5 (secondary) air injection nozzles just above the center of the gasifier. Firstly, the inlet air pass through orifice plate flow meter then air flow is divided among the 5 air lines pass through the hot wood gas exiting the reactor to heat up. Then air is injected via 5 air nozzles to the combustion zone of gasifier. The standard nozzle inclination angle is zero in the Imbert design. The nozzle inclination angle is the angle between the radial line connecting the nozzle with the center and the center line of nozzle and angle being measured in the clockwise sense. But swirl flow can be generated by changing the angles of air nozzles in order to prevent local uniformities of temperature and concentrations in the combustion zones due to the mixing of air with the pyrolysis gases. Additionally, the residence time of the gas in the combustion zone increases with swirling flow. So efficiency of the thermal tar cracking inside the gasifier can be increased with the modification in the combustion chamber. But more experiments are required to determine the optimum angle to achieve maximum hydrogen yield.

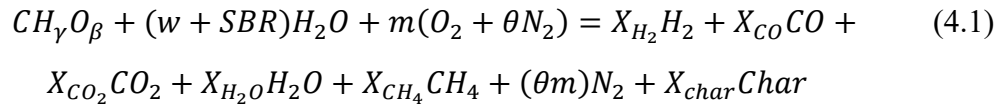
Several experiments are carried out for 3 or 4 hours with a 10 kW_{th} downdraft fixed-bed gasifier. During startup the gasification process, the gasifier is filled with wood charcoal batches from the grate up to air injection nozzles and then filled with the wood pellets. Then, a butane torch is used to ignite the charcoal from the ignition port until white flue gas is seen at the outlet in order to initiate the burning. To measure the temperature distribution within the reactor, six-point K-type thermocouples were placed in the system at predetermined heights in the center of the gasifier. Due to the high concentration of condensable gases in the flue gas, the gas analysis starts when the temperature in combustion zone reaches 1000 K or the time reaches around 500

seconds. Air and gas flows are measured with an orifice and differential manometer. Real-time values of flow rates, pressures and temperatures are monitored/recorded by an Arduino based system in the 1-second interval. The tar samples are collected with the cold trap along the gasification process.

Wood pellet was used for the gasification using air as a gasifying medium under the atmospheric pressure.

4.1.3. Mathematical Modelling for Hydrogen-Rich Syngas Production

In order to predict the limit of hydrogen-rich syngas production, a previously developed model was used [76]. The stoichiometric model was constructed based on following assumptions. The stoichiometric equilibrium model consists of a universal gasification reaction as outlined below:



In addition to Eq.4.1, several reactions are required to set up the model. The model reactions are listed in Table 4.1.

Table 4.1: Gasification reactions of equilibrium model for hydrogen-rich syngas production.

Reaction	Reaction name	Heat of reaction (kJ/mol)
$C + CO_2 \leftrightarrow 2CO$	Boudouard reaction	+172.46
$C + H_2O \leftrightarrow CO + H_2$	Steam gasification of carbon	+131.29
$C + 2H_2 \rightarrow CH_4$	Methane formation	-74.52
$CO + H_2O \leftrightarrow CO_2 + H_2$	Water-gas shift reaction	-41.17

Boudouard and steam gasification reactions can combine to form water-gas shift reaction. In the global gasification reaction, the dry biomass can be expressed as the molecular formula $CH_{\gamma}O_{\beta}$. The subscripts γ and β are were obtained from the ultimate analysis of the biomass. The terms of $X_{H_2}, X_{CO}, X_{CO_2}, X_{H_2O}, X_{CH_4}$ and X_{char} are the mole fractions of H_2 , CO , CO_2 , H_2O , CH_4 and char. Char formation occurs under real

conditions because of the carbon in the biomass structure cannot be transformed into gas form totally. The w term is the amount of water per kmol of wood pellet and a function of the initial moisture content of the biomass [87]. The term m serves as the amount of oxygen per kmol of biomass while θ is the nitrogen to oxygen molar ratio, in the gasifying medium [18]. The term of SBR is used to express the ratio of steam to biomass. In order to test the performance of different gasifying medium, the constraint limits of oxidizing agents are given in Table 4.2.

Table 4.2: Constraint limits of gasifying medium.

Gasifying medium	Constraint 1	Constraint 2
Air	SBR=0	$\theta=3.76$
O ₂	SBR=0	$\theta=0$
Air-Steam	SBR>0	$\theta=3.76$

The carbon, hydrogen and oxygen balance equations required for the model solution are as follows:

Carbon balance:

$$X_{CO} + X_{CO_2} + X_{CH_4} + X_{char} = 1 \quad (4.2)$$

Hydrogen balance:

$$2(w + SBR) + \gamma = 2X_{H_2} + 2X_{H_2O} + 4X_{CH_4} \quad (4.3)$$

Oxygen balance:

$$(w + SBR) + \beta + 2m = X_{CO} + 2X_{CO_2} + X_{H_2O} \quad (4.4)$$

Methane formation reaction and water-gas shift reaction are sufficient for equilibrium modeling of the gasification process. The equilibrium constants for these reactions are given below as molar composition.

$$K_{1, methane} = \frac{X_{CH_4}}{X_{H_2}^2} X_t \quad (4.5)$$

$$X_t = X_{H_2} + X_{CO} + X_{CO_2} + X_{H_2O} + X_{CH_4} \quad (4.6)$$

where X_t is given as the total molar concentration of the syngas except inerts.

$$K_{2, wgs} = \frac{X_{H_2} X_{CO_2}}{X_{CO} X_{H_2O}} \quad (4.7)$$

The equilibrium constant, $K_{1, methane}$ and $K_{2, wgs}$, can be expressed as a functions of Gibbs free energy

$$\Delta G^0 = -RT \ln K(T) \quad (4.8)$$

and ΔG^0 can be written in the terms of formation enthalpy, H_f^0 as

$$\ln K = \int \frac{H_f^0}{RT^2} dT \quad (4.9)$$

H_f^0 , the formation enthalpy which is a function of the specific heat and temperature at constant pressure is given in Eq. (4.10).

$$H_f^0 = \int C_p(T) dT \quad (4.10)$$

The specific heat capacity $C_p(T)$ can be defined as

$$C_p = a + bT + cT^2 + dT^3 \quad (4.11)$$

By integration of Eq. 4.9, the equilibrium constant K is calculated [12]. The value of j, i are the integration constants, and $\Delta a, \Delta b, \Delta c, \Delta d$ are the coefficient for specific heat of chemical species in order to calculate the equilibrium constant.

$$\ln K = \frac{1}{R} \left(-\frac{j}{T} + \Delta a \ln T + \frac{\Delta b}{2} T + \frac{\Delta c}{6} T^2 + \frac{\Delta d}{12} T^3 + i \right) \quad (4.12)$$

The energy balance for the gasification process at adiabatic condition is as follows

$$H_{reactants} = H_{products} \quad (4.13)$$

$$H_{reactants} = H_{f_{biomass}}^0 + w \left[H_{f_{H_2O}}^0 + \int_{298.15}^{T_i} C_{p_{H_2O}} dT_i \right] \quad (4.14)$$

$$H_{products} = \sum_{products} X_i \left[H_{fi}^0 + \int_{298.15}^{T_i} C_{pi} dT_i \right] \quad (4.15)$$

Equivalence ratio is defined as ratio of actual air supply to stoichiometric air requirement, dimensionless and obtained by the following expression,

$$ER = \frac{m}{1 + \frac{\gamma}{4} - \frac{\beta}{2}} \quad (4.16)$$

The biomass formation enthalpy, $H_{f_{biomass}}^0$, can be measured either experimentally or calculated using correlations as a function of carbon, hydrogen, oxygen elemental species. Six of the seven unknowns as $X_{H_2}, X_{CO}, X_{CO_2}, X_{H_2O}, X_{CH_4}, X_{char}$ in the model structure represent product species while one is the amount of oxygen needed for the gasification reaction. Therefore, for the solution three mass balance Eq. (4.2-4.5), two equilibrium reactions Eq. (4.5-4.7), one energy balance Eq. (4.13), and one equivalence correlation as a function of biomass oxygen content Eq. (4.16) are required. The equation dataset is solved using the Newton-Raphson iterative method. The algorithm of the stoichiometric equilibrium model is given in Figure 4.2.

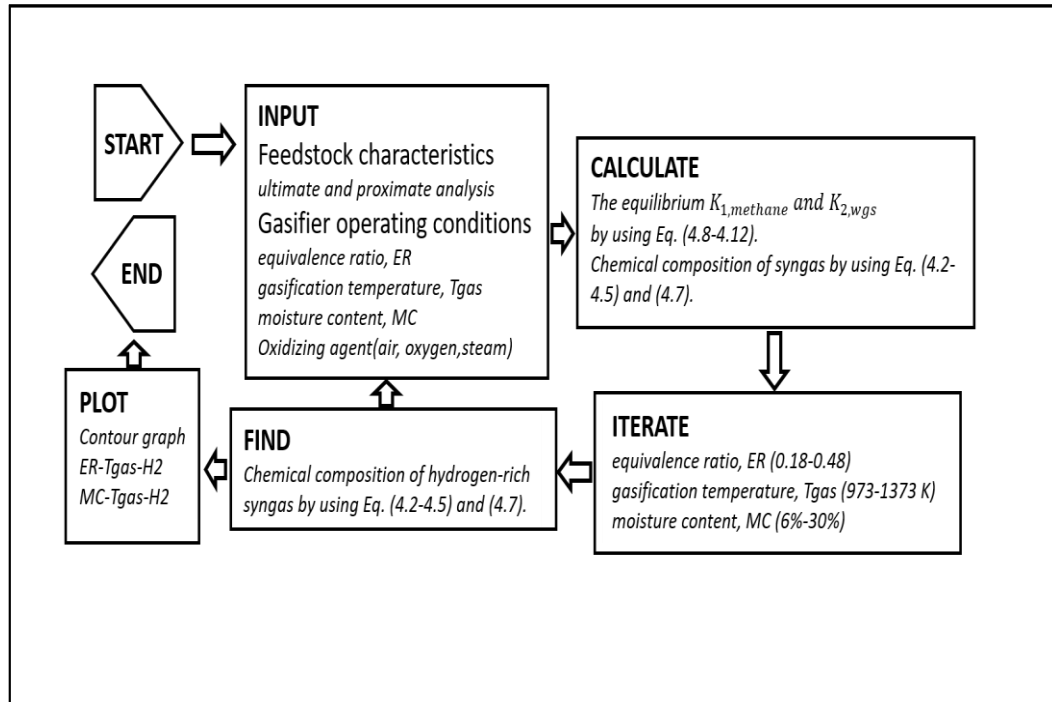


Figure 4.2: The algorithm of the stoichiometric equilibrium model for hydrogen-rich syngas production.

4.2. Results and Discussion for Hydrogen-Rich Syngas Production

4.2.1. Validation of the Model

To analyze the performance and to validate the equilibrium model, theoretical results that obtained from the solution the model equation compared with experimental data that obtained by using various air flow values and equilibrium ratios. The equilibrium model uses initial moisture content, biomass composition, reaction temperature and equivalence ratio as the input to predict the composition of syngas. Gasification temperature, syngas composition and equivalence ratio are found to vary with time. Hydrogen concentration of syngas is calculated by the model using real-time data of the equivalence ratio and temperature in the gasification zone. The ultimate and proximate analysis of the woody biomass given in Table 4.3 are used in the model.

Table 4.3: Physical and chemical characterization of the wood pellet.

Physical analysis (mm)	Wood pellet
Diameter	7
Length	20
Proximate analysis (wt%)	
Moisture	12
Volatile matter	79.17
Fixed carbon	7.83
Ash	1
Ultimate analysis (wt% db)	
Carbon	50.67
Hydrogen	6.18
Oxygen	40.97
Nitrogen	2.0
Sulphur	0.18
Calorimetric analysis (MJ/kg db)	
Lower heating value (LHV)	18.69

Figure 4.3 shows that the model predictions of hydrogen concentration are in good agreement with the experimental data. The variation of hydrogen concentration with the gasification temperature and ER is analyzed for different experimental runs. Effectively, the hydrogen concentration is found increasing with a decrease in the gasification temperature and ER. The equivalence ratio can be calculated with both the biomass combustion rate and the air feed rate known. To determine the consumption rate, the decrease in the level of biomass in the reactor is calculated. But this method doesn't give the exact biomass consumption due to channeling and bridging in the combustion zone. The total amount of biomass producer gas flow ratio also varies with time, and although this variation isn't too high it affects the syngas composition. In addition to all these, the uniform temperature distribution cannot be achieved in fixed bed gasifier with biomass pellets. The temperature in the gasifier increases along the length of the gasifier from the top to the combustion zone and also decreases along the reduction zone. Nevertheless, the results obtained from the model are in close agreement with the results obtained from our experiments.

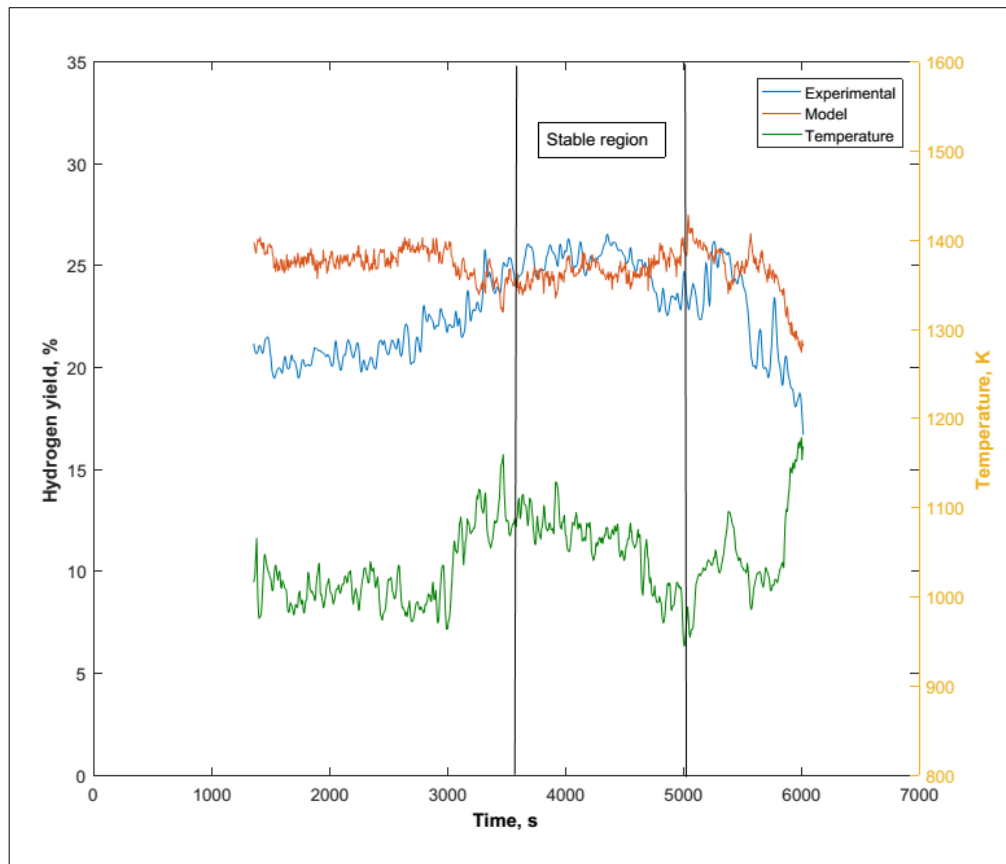


Figure 4.3: Validation of model with experimental data.

The fluctuations in the temperature are observed in Figure 4.3. The thermocouple can come in contact with solid or gas at a specific position. The iron grate installed at the bottom of the gasifier is shaken continuously to remove the ash and regulate the solid flow rate. The contact point of the thermocouple with either solid or gas could be changed due to the grate shaker and fuel consumption in the gasifier. So it is perhaps an important reason for the fluctuations observed in the temperature. Another reason may be inhomogeneous content of the biomass pellets and its low conductivity.

4.2.2. Effect of Air as a Gasifying Medium

Effect of using air as a gasifying medium for the production of hydrogen-rich syngas is shown in Figure 4.4.

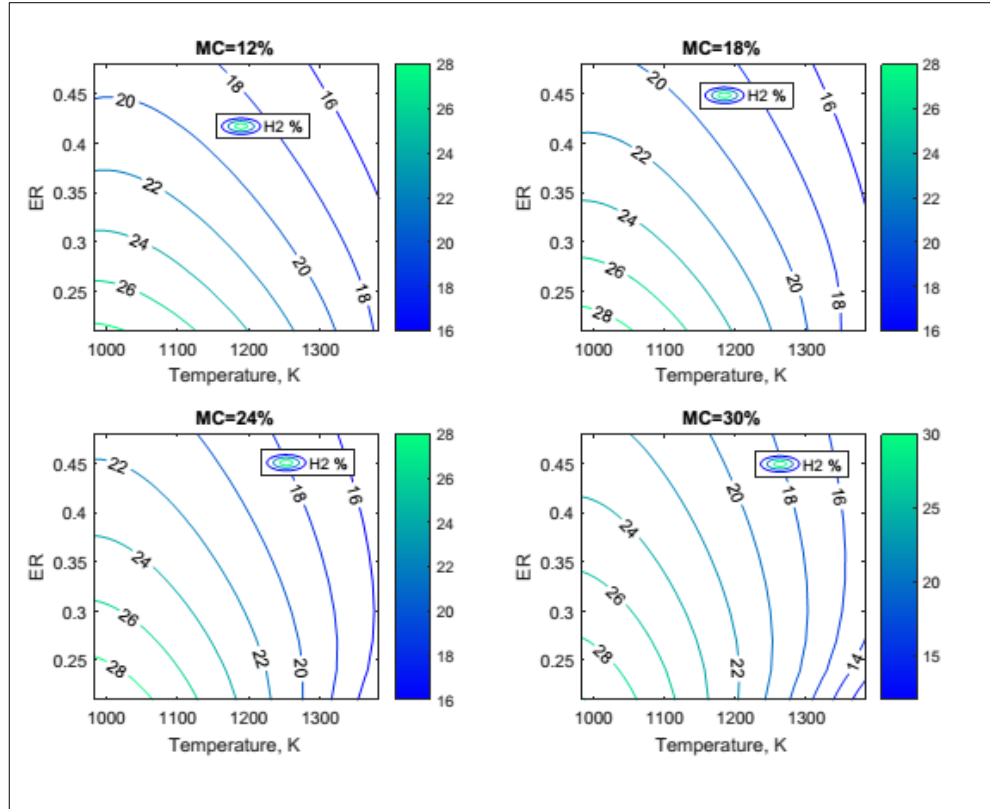


Figure 4.4: Effect of moisture content on hydrogen-rich syngas production.

As can be understood from the Figure 4.4., the effect of ER, gasification temperature and moisture content on hydrogen-rich syngas production was investigated by the model solution. As observed, increasing the temperature of fixed bed downdraft gasifier leads to diminished hydrogen yield. Since the water-gas shift reaction given in Table 4.1 is an exothermic reaction, the reaction direction shifted to the side of the products with increasing temperature. In addition, the value of hydrogen concentration increased with the decrease of ER. The concentration of hydrogen in the syngas increases as the moisture content of biomass increasing. The hydrogen content in syngas is about 16% to 30% for an increase in moisture content from 12% to 30% in the temperature interval 973-1373 K and $0.21 < ER < 0.48$. Operating conditions at $ER=0.21$ and $T_{gas}=973$ K, maximum hydrogen production was found to be 28.39%, 29.14%, 29.73% and 30.09% for moisture values of 12%, 18%, 24%, 30%, respectively. Due to the energy requirement for drying the biomass, feedstocks with relatively low moisture content may be preferred in the gasification process.

4.2.3. Effect of Oxygen as a Gasifying Medium

The general behavior and effect of oxygen as an oxidizer over gasification is shown in Figure 4.5.

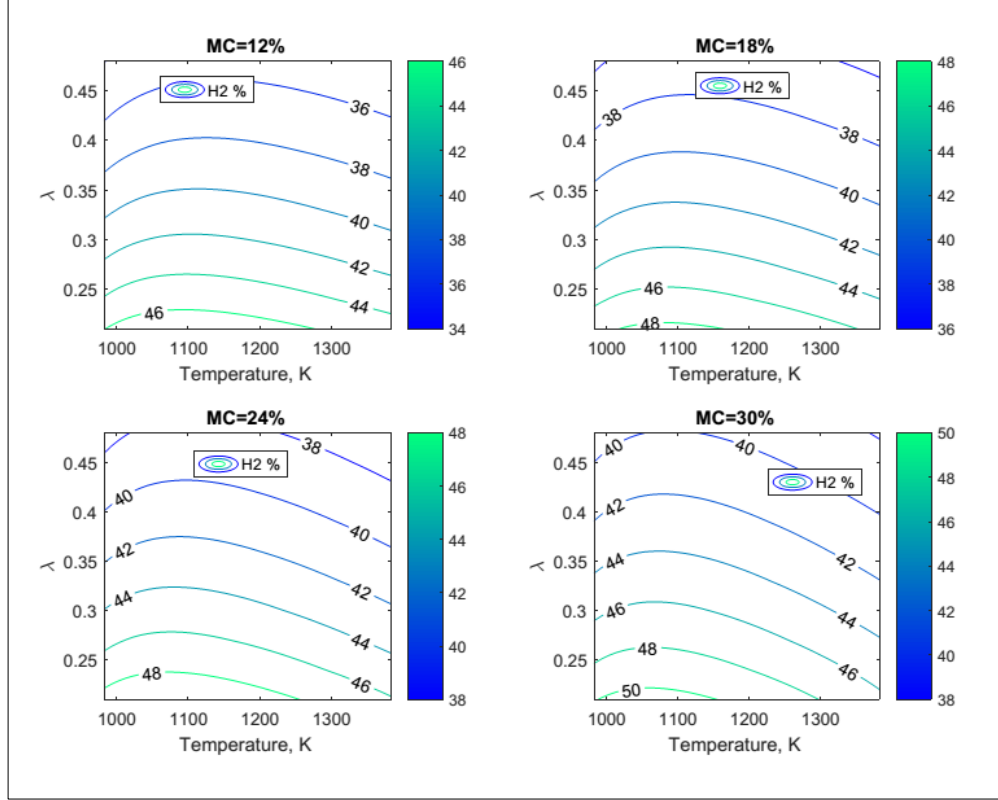


Figure 4.5: Effect of oxygen as an oxidizer on hydrogen-rich syngas production.

The term of λ is the ratio of the supplied O_2 to the stoichiometric O_2 demand for complete reaction. The graph is drawn by plotting the predicted hydrogen concentration against λ -gasification temperature for different biomass moisture content. The content of hydrogen for oxygen gasification is higher than that of air gasification. Because of the almost no nitrogen in the oxygen or vapor gasification condition, the gas flow is reduced, which results in a longer residence time. Consequently, the biomass gasification gas proceeds at a higher rate for cracking and reforming reactions to yield more H_2 . Contrary to using of air as an agent, hydrogen concentration firstly increased in the temperature range of 973-1073 K, and then slightly decreased in the temperature range of 1073-1373 K. Moreover, the decrease in λ value was effective on the increase of the hydrogen concentration. For $0.21 < \lambda < 0.48$, hydrogen yield increased as moisture content of biomass increasing from 12% to

30%. In the using oxygen as an oxidizer, maximum hydrogen production was found to be 50.62% at 1073 K, $\lambda=0.21$ and MC=30%. In the literature, Wiinikka et al. [81] reported that the amount of O₂ supplied should be $\lambda > 0.30$ to raise the temperature to 1000°C for tar destruction becomes complete, leading to a desirable gas composition. By considering this information, in order to reduce the weakness, the equilibrium model and stay in the thermodynamic limit, the optimum λ value interval can be taken $0.30 < \lambda < 0.48$ and gasification temperature 1373 K. Under this operating condition, the optimum hydrogen concentration is 43.05% at $\lambda=0.30$ and MC=30%. For the cases, which are selected the feedstocks with less moisture, hydrogen value decreases to 40.39% at MC=12%.

4.2.4. Effect of Air-Steam as a Gasifying Medium

In this section, the effects of steam addition to gasification system are discussed. The variation of initial biomass moisture content and gasification temperature were tested to observe hydrogen concentration changing in syngas at pre-determined steam to biomass ratio (S/B). The steam to biomass ratio varies from 0 to 1.5 and ER variation is 0.18 to 0.45. Figure 4.6 shows the simulation results of hydrogen concentration variation under specific operating conditions. The initial moisture content of biomass (%0-30) and gasification temperature (973-1200 K) for fixed equivalence ratio. It is difficult to carry out the biomass gasification using only steam. Steam gasification is an endothermic reaction so it is necessary to use air/oxygen to produce the heat required for the reactions. As the amount of steam injected into the system increases, the reaction rates in the gasifier decrease due to the low concentration of reactants and the high concentration of products. The gasifier should be large enough to compensate for slow kinetics in order to achieve high steam utilization. So to analyze that the effect of moisture content and the temperature, equivalence ratio is set to 0.28.

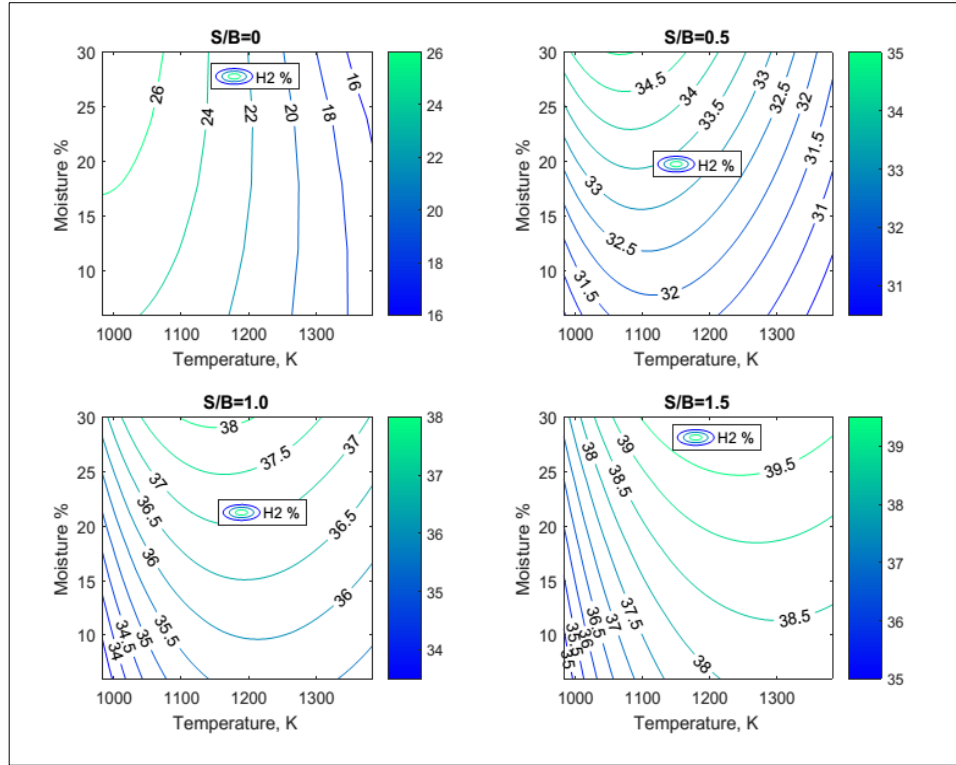


Figure 4.6: Effect of S/B ratio and moisture content of biomass using air-steam as an oxidizer on hydrogen-rich syngas production (ER=0.28).

It is clear from Figure 4.6 that hydrogen content in the syngas increases as the moisture content of biomass increasing. The increase in the amount of moisture reduces the efficiency of gasification while increasing the amount of energy required for drying and pyrolysis of the biomass. So the temperature of the injected steam should be increased to achieve higher hydrogen production. The hydrogen content is rapidly increasing due to the steam to biomass ratio for S/B value of 0–1.0. Nevertheless, this increasing trend gets slower after for S/B value of 1.0. The maximum H₂ values obtained between 0 and 1.5 of the S/B values are as follows. H₂ contents are 27.79%, 35.03%, 38.11, and 39.98%, respectively.

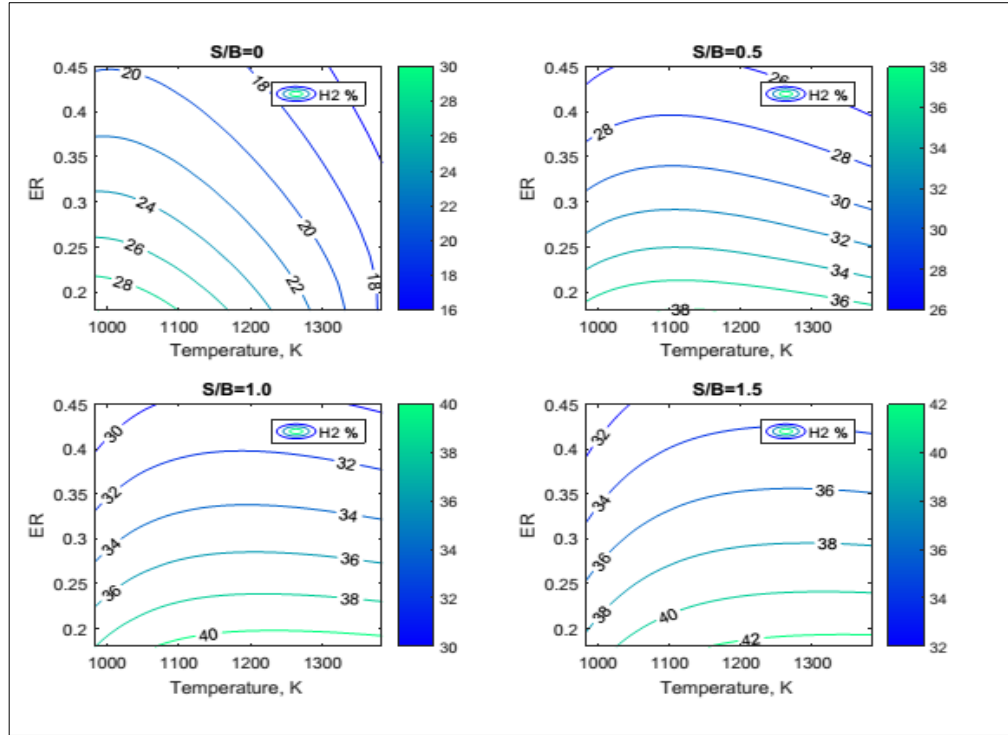


Figure 4.7: Effect of S/B ratio and ER using air-steam as an oxidizer on hydrogen-rich syngas production (MC=12%).

As can be seen from Figure 4.7, steam to biomass ratio has a significant effect on the gas composition due to the dominant water–gas shift reaction. Hydrogen output is found decrease with an increase in the ER. But especially for higher S/B ratios, hydrogen output increases with the temperature. Contrary, in the experiments conducted with air, hydrogen concentration improved at the higher temperature and lower ER. This hydrogen value is %42.59 at 1253 K, ER=0.18 and S/B=1.5. Hydrogen values for S/B=0, 0.5 and 1.0 are 30.04%, 38.08% and 40.93%, respectively. The results show that the steam gasification is a good option for hydrogen production. But on the other hand the high temperature steam gasification utilizes an external heat source. Another main problem of steam gasification is increasing solid formation due to steam gasification. There is not enough heat to completely convert all the carbon elements, since the heat of gasification is solely supplied by the steam. Therefore, the carbon based syngas components (CO, CO₂, and CH₄) decrease due to the carbon formation so hydrogen content of syngas increases.

5. GASIFICATION of PINE CONE PARTICLES and WOOD PELLETS for HYDROGEN-RICH SYNGAS PRODUCTION

The possible scarcity of the conventional fossil fuels in the future and environmental problems resulting from their excessive usage drive the countries to make effective policies and integration of renewable energy technologies [91]. In recent years, the use of biomass as a renewable energy source has found wide range of applications worldwide. The world energy consumption based on biomass energy has increased to 14% of total energy consumption [92]. Due to the low cost and high potential for chemicals and energy production, there is a growing trend towards biomass feed-stocks [93]. Many developed and industrialized countries are revising their view of biomass for its renewable nature and positive impact on carbon emissions [94]. As a primary biomass conversion process, gasification is regarded as an appropriate method to produce syngas consisting of high calorific gases like hydrogen and carbon monoxide [95-96]. Especially, hydrogen can reduce dependence on hydrocarbon based fuels as a clean energy carrier and compensate a large part of the world's future energy needs [66-67]. Many studies have focused on developing current and future technologies by taking into account factors such as raw material, technological feasibility, regional support and climate sensitivity for hydrogen production [97-100]. Hydrogen production via biomass gasification is a promising and economic technology and can be an energy solution due to rapid depletion of fossil fuels [101]. However, hydrogen would be the primary source of energy and transport on the future, directing the global energy system [102]. The produced syngas is necessary for synthetic fuels as a primary source and also can be used to generate electricity in power generation systems like boiler, engines, and fuel cells [103]. Focusing on the use of agricultural and forest wastes and residues in biomass energy production will help reduce to environmental problems. It is possible to find the several scientific studies [68, 104-106] in the literature that characterize the biomass gasification process using pilot and laboratory scale reactors. Wide variety of biomass and waste derivative feedstocks such as nutshells, olive husks, grape residues, beechwood, wood pellet were analysed to compare their gasification characteristics [3, 107-108]. Besides, the gasification performance of the pinecones as biomass has not been

investigated sufficiently. They are usually burned in the stove to provide heat in winter. Gasification is the process that converts biomass to energy in the presence of the oxidizing agent such as air, steam or the combination of air and steam [109]. The major syngas components that obtained by gasification are H_2 , CO, CO_2 , CH_4 and other higher hydrocarbons. Tar (consisting of heavy hydrocarbon residues) emerges as an undesirable by-product. Tar content formed in the gasification systems is highly dependent on operational parameters such as heating rate, gasifying medium and reactor temperature. Catalytic effects also are studied in addition to operational parameters to reduce the amount of tar in syngas. To enhance hydrogen production during biomass gasification, Ni-based catalyst have mostly been investigated [110-112]. Furthermore, natural materials such as dolomite, olivine, bio-char and hydro-char are also used as a catalyst or catalyst support in hydrogen production through gasification due to their relatively low price and high activity [113-114]. The use of dolomite as a direct catalyst instead of a support material has attracted considerable attention because it is both cheap and disposable [115-116]. Another factor affecting the gasification process is reactor types. Various reactor designs for biomass gasification have been developed and studied. Types of gasification reactors can be classified as fixed bed, fluidized bed and moving bed [117-119]. Recent studies on high-efficiency gas production with less tar have become major issue in biomass gasification [95-96, 120-121]. Downdraft gasifiers are more efficient in terms of tar destruction and compared to other gasification systems, the most preferable option for small-scale applications (<10 MWth) due to simple design, construction and syngas production with low tar content (1–2 g/Nm³) [11]. In the updraft gasifier, thermal efficiency is high as the temperatures in the gas exit are relatively low while in downdraft gasifier, the syngas leaves the gasifier at a high temperature as thermal efficiency is low according to updraft gasifier [122].

In order to determine the design and operational parameters, gasification of biomass originating from different sources has been studied extensively in the literature [82, 123-127]. Gasification characteristics of sawdust char at high temperature steam atmosphere in a fixed bed reactor, studied by Zhai et al. They observed that shifting the gasification temperature from 800 to 1200 °C resulted in increasing H_2 content in product gas from 53.08% to 60.01%. In the study of Soon et al. [124], rice husk and rice husk pellet gasification experiments were conducted using air, as a gasifying agent and bottom temperature of the gasifier was controlled in the

range of 650-850 °C with excess air ratio. They reported that H₂ content of the syngas composition were 13.6% and 18.6% for the rice husk and rice husk pellet respectively. In addition to this, they also found the optimum excess air ratio as 0.48-50 and 0.29 for the aforementioned biomasses. Gao and his colleagues focused [82] to study the effect of the designing and operating parameters such as reactor geometry, biomass feeding rate, equivalence ratio on the performance of corn straw gasification in a three air stage continuous fixed bed downdraft reactor. They have reported that bridging and channeling problems can be prevented by the designing of both the air supply system and rotation. By the way, increasing in the biomass feeding rate lead to reduce the lower heating value from 5455.5 kJ/Nm³ to 5253.2 kJ/Nm³ at ER, 0.27. Atnaw et al. [127] studied the gasification of oil palm fronds (24% of the total oil palm waste). In terms of concentration of the fuel components (CO, H₂ and CH₄), the oxidation zone temperature was found 850 °C to obtain favorable results. The cold gas efficiency (70.2%), calculated at optimum equivalence ratio of 0.37 showed that OPF has a high potential as a fuel for gasification.

The main purpose of this part of thesis is to contribute to the literature by making use of effective energy production of pinecones by examining the gasification performance. In this work, we compared the performance of pine cone and wood pellet as fuels for downdraft gasification under the catalytic effect of dolomite to reveals the influences of the operating parameters such as reactor temperature, equivalence ratio on the hydrogen rich-syngas composition, calorific value and cold gas efficiency. We carried out the experiments by measuring temperature zones throughout the reactor, syngas composition and heating value. Thus, we show that hydrogen rich-syngas can be achieved with pine cone and wood pellet gasification under the dolomite effect.

5.1. Materials and Methods for Gasification Experiments

5.1.1. Experimental Set-Up

Experimental setup consists of three different equipment: a 10 kWth fixed bed downdraft gasifier, data acquisition system and gas analyzer. A portable infrared syngas analyzer (Wuhan Cubic Syngas Analyzer Gas Board 3100P) was used to perform the measurement of CO, CO₂, CH₄, H₂ and O₂ concentrations in sample gases.

The scheme of the fixed bed downdraft gasifier is shown in Figure 4.1 adopted from [108].

The gasifiers can be theoretically divided into four zones as drying, pyrolysis, combustion and reduction zones. The total height of the gasification reactor is 55 cm and consists of two cylindrical coaxial structures constructed using stainless steel sheet. The initial diameter of drying zone is 28 cm and height is 20 cm. The internal diameter of the gasification reactor is reduced from 20 cm to 7 cm in order to ensure that the biomass remains more in the pyrolysis and combustion zones. The reduction zone diameter extends from 19 cm to 23 cm and 38 cm respectively to reduce gas velocity. The throat design of the gasification system allows sufficient time for the water-gas shift reaction to produce hydrogen. In addition, the increase of the hydrocarbon gas-char interaction can lead to the production of more carbon monoxide by the Boudouard reaction. The produced hot gas flows upward between the inner and outer cylinders and provides energy for drying and pyrolysis operations. The gas exiting the gasification reactor first passed through the cyclone separator to remove particulates contained in the produced gas, and then passed through the packed bed filter to collect the tar. Perforated grate added to the bottom of the gasifier in order to use high ash content fuels. Thus, the ash removed from the reduction zone of the gasifier to prevent the bridging in the system. The movement of the grate made with a pneumatic shaking system that connected to the grate and controlled by a pneumatic directional control valve that triggered by an adjustable time relay. Air used as an oxidizing agent for biomass gasification. The upper part of the gasifier sealed to prevent (primary) air inlet, and the pressure drop prevents the primary air from entering the incoming gases. A venturi ejector provides a driven suction and enables air to enter the gasifier by an orifice air flow meter. Before the inlet air reaches the combustion zone, the flow rate measured by passing through the perforated plate, then separated into five different air ducts and continuously injected by the air nozzles to burn the biomass.

5.1.2. Feedstock Material and Characterization

The pine cones used in this study were collected from Gebze Technical University campus in Kocaeli, Turkey. Pine cones were cut into small pieces known as cone scales for use in experiments. The ultimate and proximate analyses of

pinecones were determined using standard procedures. ASTM E1755-01 for ash, ASTM E871-72 for moisture content and ASTM D3175 for volatile matter methods were applied for proximate analysis by using ash furnace. Fixed carbon was determined by balance [90]. The ultimate analysis carried out by using LECO Truspec CHN-S Elemental Analyzer. The volume of oxygen was calculated using the Eq. (5.1).

$$O\% = 100 - C\% - H\% - N\% - S\% - Ash\% \quad (5.1)$$

The higher heating value calculated through empirical formula, given by Sheth and Babu [128].

$$HHV \text{ (MJ/kg)} = 0.3536FC + 0.1559VM - 0.0078ASH \quad (5.2)$$

where HHV = higher heating value; FC = fixed carbon content; VM = volatile meter content.

$$LHV \text{ (MJ/kg)} = HHV - 0.212(H\%) - 0.0245(MC\%) - 0.08(O\%) \quad (5.3)$$

where LHV=lower heating value; H=percent hydrogen; MC=percent moisture of biomass;

5.1.3. Experimental Procedure

Gasification experiments of pine cones and wood pellets performed for various airflow rates in a 10 kWth downdraft gasification system. During start up the gasification process, the gasifier is filled with approximately 1000 g of wood charcoal from the grate up to air injection nozzles and then followed by around 5000 g pine cone particles. The same process was also applied for wood pellet gasification experiment (5000 g wood pellet + 1000g dolomite). Charcoal for gasification experiments mixed with about 1000 g of dolomite. The necessary information about the ignition of the gasifier and placing the thermocouples inside the reactor is given in section 4.1.2. Gasifier set-up. Due to the high concentration of condensable gases in the flue gas, the gas analysis starts when the temperature in combustion zone reaches 1000 K or the time reaches around 500 seconds. Air and gas flows are measured with

an orifice and differential manometer. The heating value of the producer gas is also calculated simultaneously via gas analyzer. Finally, the flue gas burned with a swirl burner. In addition to burning obtained gaseous mixture can be utilized in a gas engine to generate energy, or separated by a membrane to obtain H_2 , CH_4 , CO or can be utilized to manufacture high added value chemicals such as ammonia, methanol, and other valuable chemicals. The challenges related to pine cones and wood pellet gasification can be categorized in three sections such as phenomena of channeling and bridging, gas cleaning, and catalytic destruction of tar. Downdraft stratified gasifiers seem to be the reactors which are most influenced by loading conditions [129]. The downdraft gasifiers have the high possibility of channeling and bridging phenomena, which occur more frequently as the gasifier size increases. However, the sudden collapse of the bed is prevented due to the activation of the pneumatic eccentric “grate shaking” mechanism and continuity is ensured in bed structure and operation. The syngas is first washed by three cold gas-washing bottles, which are immersed in an ice-water bath and then cleaned by a dust filter and dehumidifier. Dolomite is useful for tar removal and there is interest in using low cost dolomite catalysts to increase the production of H_2 . To clean-up and creating tar-free gas catalytic effect of dolomite is used.

5.1.4. Product Analysis

The chemical composition of syngas was measured at five seconds interval during gasification experiments by using Wuhan Cubic 3100P portable syngas analyzer. For the further analysis, gas samples were taken by tight syringes and injected into gas chromatograph's column. Gas chromatograph (Agilent 6890N) had been equipped with Carboxen®-1010 PLOT Capillary GC Column ($L \times I.D.$ 30 m $\times$ 0.53 mm, average thickness 30 μm), FID and TCD Detectors.

5.2. Result and Discussions for Gasification Experiments

The chemical reactions along with their enthalpy values that possible to occur in a gasification system are presented in Table 5.1. As reported by [130], the main reactions of gasification involve solid-solids, gas-liquid and gas-gas reactions, which are mainly affected by temperature and gasification medium. R1 is a highly complex reaction,

resulting in the production of char, tar and synthesis gas at varying proportions depending on the gasification temperature. R2 is the reaction that shows the cracking of the tar, while the R3-R5 reactions correspond to processes involving the steam reforming of hydrocarbons. R6-R11 represent the processes of oxidation reactions of carbon (which are called carbon gasification), shift reaction of carbon monoxide and steam (water-gas shift), reduction reaction of carbon dioxide, methanation reaction and methane dry reforming reaction, respectively.

Table 5.1: Reactions occurring in the reactor during gasification.

Reaction	Reaction number
$Dry\ material \rightarrow C + Tar + Gas$	R1
$Tar \rightarrow CH_4 + H_2 + H_2O + C_nH_m$	R2
$C_nH_m + 2nH_2O \rightarrow nCO_2 + (2n + m)/2H_2$	R3
$C_nH_m + nH_2O \rightarrow nCO + (n + m/2)/H_2$	R4
$CH_4 + H_2O \rightarrow CO + 3H_2 - 206.3\text{ kJ. mol}^{-1}$	R5
$C + H_2O \leftrightarrow CO + H_2 - 131.29\text{ kJ. mol}^{-1}$	R6
$C + 2H_2O \leftrightarrow CO_2 + 2H_2 - 90.2\text{ kJ. mol}^{-1}$	R7
$CO + H_2O \leftrightarrow CO_2 + H_2 + 41.17\text{ kJ. mol}^{-1}$	R8
$C + CO_2 \leftrightarrow 2CO - 172.46\text{ kJ. mol}^{-1}$	R9
$C + 2H_2 \rightarrow CH_4 + 74.52\text{ kJ. mol}^{-1}$	R10
$CH_4 + CO_2 \rightarrow 2CO + 2H_2 - 274\text{ kJ. mol}^{-1}$	R11

5.2.1. Effect of Gasification Temperature

The gasification temperature is an important parameter that determines whether the reactions occurring in the reactor are directed forward or backward directions. By increasing the temperature in the gasification processes, the interaction between steam and hydrocarbons increases and the reactions strengthened towards the products. In addition, the reactions of R3 and R4 produce more H_2 with increase in temperature. R6, R7 and R11 reactions are endothermic reactions and H_2 production is much easier for such reactions where heat is required. It has been observed that H_2 value is lower in some cases where the H_2 increase is expected together with the temperature increase. The main reason for this is that the shift reaction of carbon monoxide and steam (R8)

is an exothermic reaction. When the temperature starts to rise, the carbon monoxide and steam conversion reaction (R8) is inhibited at a certain rate. The R6 reaction plays an important role at temperatures above 850 °C, but at temperatures below 850 °C, the R7 reaction becomes active. When the temperature rises from 700 to 950 °C, at the beginning the R8 reaction takes place towards the substrates, which leads to CO consumption and CO₂ formation and causes decreasing the volume fraction of CO, then the CO fraction goes to a minimum level at 850 °C and then increase. The volume ratio of CO₂ tends to decrease gradually with increasing temperature. As the temperature increases, the volume fraction of CH₄ tends to decrease. The reason is that hydrocarbon gas and steam conversion reactions are endothermic reactions.

Figure 5.1 shows temperature distribution inside the gasifier during gasification of pine cones and wood pellets where it can be clearly seen that consumption time of gasification is different for the same amount of pine cones and wood pellets. The reason is pine cones and wood pellets have different sizes, porosities and densities. Despite the pine cones have lower energy content than wood pellets, pine cone gasifies at higher temperature in downdraft gasifier. In addition, channeling and bridging problems are more likely to occur during gasification of pine cones. In order to overcome these phenomena, the flame length is increased inside the gasifier for thermocouple come into contact with hot gases. In contrast to pinecone gasification, wood pellets cover the thermocouple and the average temperature in the wood pellet gasification drops.

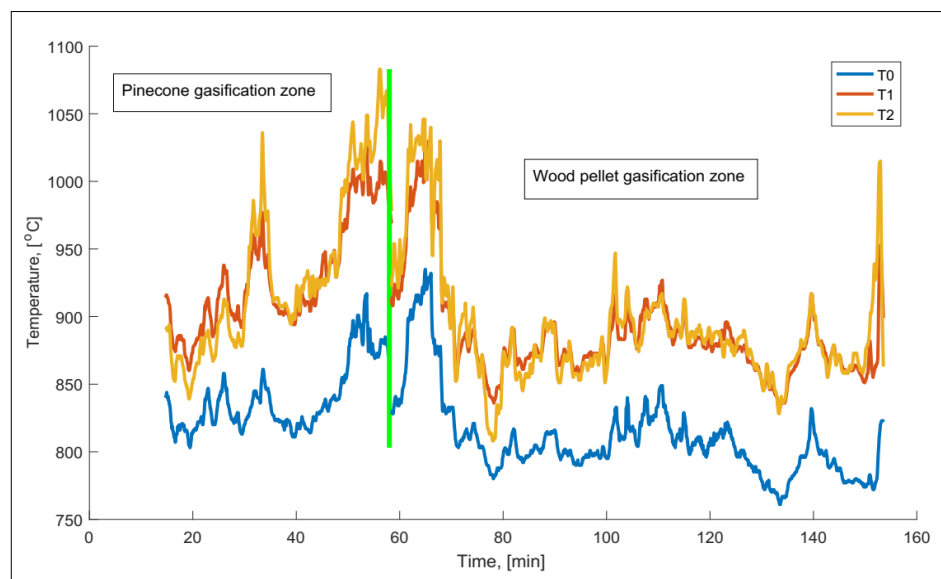


Figure 5.1: Temperature distribution inside the gasifier against time.

5.2.2. Syngas Composition

Figure 5.2 shows the syngas composition produced from pine cones and wood pellets gasification using air as a gasifying medium against time. Syngas was produced by gasification of pine cone particles with interaction of biomass water content and oxygen in the air. The volumetric syngas composition obtained from pinecones gasification varied from 18.21%, 6.39%, 0.20%, 7.4% to 30.63%, 16.59%, 3.68%, 23.74% for CO, CO₂, CH₄ and H₂, respectively. For the pine cone particle gasification, H₂ content in syngas increased from 16.11% to 21.39%, and CO showed no positive change in the direction of increase, while CH₄ and CO₂ decreased in the time interval between 19th-33rd minutes. Because of methane cracking, hydrogen content of the syngas increased in the given interval. Carbon monoxide was 24.31% at 19th minutes and then slightly decreased to 23.52% at 33rd minutes. Moreover, CO₂ decrease from 12.43% to 11.92%. Due to large increase in hydrogen content, the percentage of CO and CO₂ decreased even if it increases in intensity. The increase in temperature promotes endothermic reactions (R5-R7, R9 and R11), thereby increasing the amount of H₂. As the increase rate of H₂ was greater than CO, H₂/CO increased gradually. Since carbon gasification and methane steam reforming are endothermic reactions, the content of CH₄ decreased [123, 131]. In cases where the temperature is relatively low, the tendency is to produce CO₂ because the reactions such as R8 and R10 are exothermic.

When we look at the results of gasification of wood pellets, the produced syngas composition was in the range of 19.73-33.83% CO, 5.80-14.42% CO₂, 0.30-4.02% CH₄, and 10.00-26.56% H₂. The pinecones experiment was carried out for 54 minutes, while the wood pellet experiment took about 95 minutes. The starting point of the wood pellet experiment was accepted as 54th minutes to give place to the two graphs in the same graph.

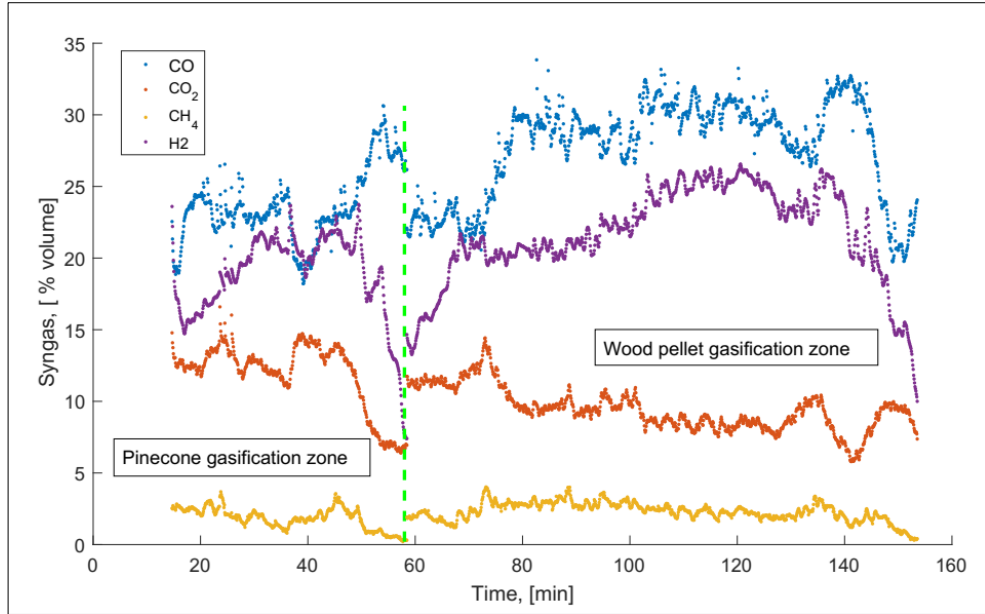


Figure 5.2: Composition of syngas produced from pine cone and wood pellet gasification.

For the wood pellet gasification, H₂ content in syngas increased from 15.71% to 25.15%, and CO increased from 22.11% to 29.69%, while both of CH₄ and CO₂ decreased in the time interval between 62nd-123rd minutes. Due to drying of fresh wood pellets, a large amount of steam develops and steam methane reforming reaction promotes in the given interval. Moreover, temperature values also decreased in the time interval between 62nd-123rd minutes because of endothermic nature of the methane reforming reaction.

The average values of the syngas compositions of the experiments are as follows: For pine cone, 23.62% CO, 11.87% CO₂, 1.83% CH₄, 18.76% H₂ and for wood pellet, 27.74% CO, 9.43% CO₂, 2.30% CH₄, 21.62% H₂, respectively and in all measurements the rest was nitrogen. In the gasification process of the wood pellet, syngas that has higher calorific value is obtained compared to gasification of the pine cone, because methane and hydrogen content in the syngas are produced more and carbon monoxide is produced less. As described by [124], this difference arises from the physical and chemical composition differences of the gasification feedstocks given in Table 5.2 and the higher heating value of the pelletized sources.

Table 5.2: Physical and chemical characterization of the pine cone and wood pellet.

Physical analysis (mm)	Pine cone	Wood pellet
Width	8	7
Length	12	20
Proximate analysis (wt%)		
Moisture	9.6	12
Volatile matter	77.8	79.17
Fixed carbon	11.7	7.83
Ash	0.9	1
Ultimate analysis (wt% db)		
Carbon	42.62	50.67
Hydrogen	5.56	6.18
Oxygen	51.01	40.97
Nitrogen	0.76	2.0
Sulphur	0.05	0.18
Calorimetric analysis (MJ/kg db)		
Lower heating value	16.25	18.69

Figure 5.3 shows the molar ratios of H_2/CO and CO/CO_2 in the syngas. For the production of the value-added chemicals such as methanol, iso-butanol and naphtha require the H_2/CO ratio of syngas to be varied between 1 and 2 [132-135]. The CO/CO_2 ratio expected to drop slowly while the H_2/CO ratio expected to increase with the increase of the reaction temperature.

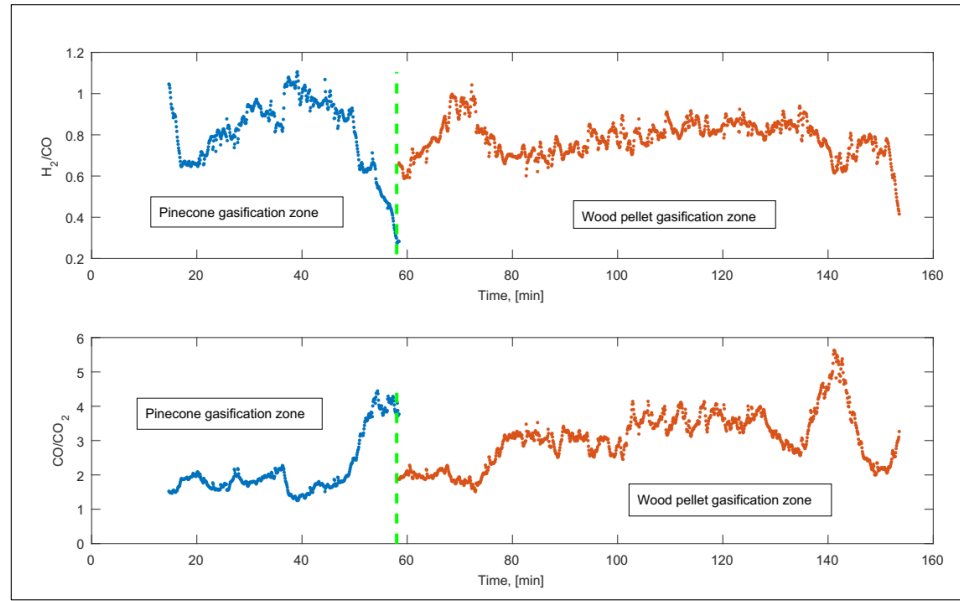


Figure 5.3: H_2/CO and CO/CO_2 molar ratio variation during the experiments.

In this study, for the pine cone gasification, the molar ratio of H_2/CO is between 0.6 and 1.1. Hydrogen may occur various ways such as fast pyrolysis of biomass, endothermal reactions, and cracking reactions of heavy hydrocarbons such as tar during gasification processes. The gasification process cannot be control properly, because it consists of many complex reactions and the composition of the produced syngas depends on many parameters such as gasification temperature, pressure and residence time. As can be seen from Figure 5.1, the temperature distribution in the gasifier varies throughout along the gasifier. However, when examining the effect of temperature on gasification, it may be more accurate to analyse with more than one temperature data instead of a single temperature. In the Figure 5.1, T_0 , T_1 and T_2 temperatures are 809, 861 and 842 °C at the 19th minutes, respectively and at this time point, H_2/CO ratio is 0.66 and CO/CO_2 is 1.95. As the experiment proceeded, the in-reactor temperature increased from top to bottom, resulting in an increase in ratio of H_2/CO . In parallel with increasing temperature, H_2/CO ratio increased and this ratio was 1.09 and CO/CO_2 was 1.25. The temperature of T_0 - T_2 at 39th minutes were 814, 899, and 895 °C, respectively. In particular, the increase in T_1 and T_2 was more effective in increasing H_2/CO than T_0 . In the wood pellet gasification, the highest H_2/CO ratio was 0.98 and at this point, the T_1 and T_2 temperatures were above 900 °C at 62nd minutes and also CO/CO_2 value was 1.745. H_2/CO ratio declined with the decrease of temperature values from 62nd minutes up to the 80th minutes, and the value at 78th minute was 0.68. CO/CO_2 value become almost double and increased to 3.07.

5.2.3. Gasification Performance

Cold gas efficiency expressed as the ratio of the amount of energy produced from each kg of gaseous products to the heating value of biomass material (Eq.5.4) it is a measure of gasification performance and depends on both calorific value and the amount of syngas released at constant LHV of biomass.

$$CGE = \frac{LHV_{gas} \cdot V_{gas}}{LHV_{fuel} \cdot \dot{m}_{fuel}} \times 100(\%) \quad (5.4)$$

In Eq. (5.4), V_{gas} implies the normal volume flow of gas (m^3_n/s), $\dot{m}_{fuel}$ implies the solid fuel flow (kg/s). The CGE depends on several parameters, such as the gasifier design, the feedstock, its moisture content (due to syngas composition) and syngas flow rate. However, the CGE increases with ER due to increase in gas yield and LHV at higher ER. The variation of pine cones and wood pellets gasification cold gas efficiency with equivalence ratio presented in Figure 5.4.

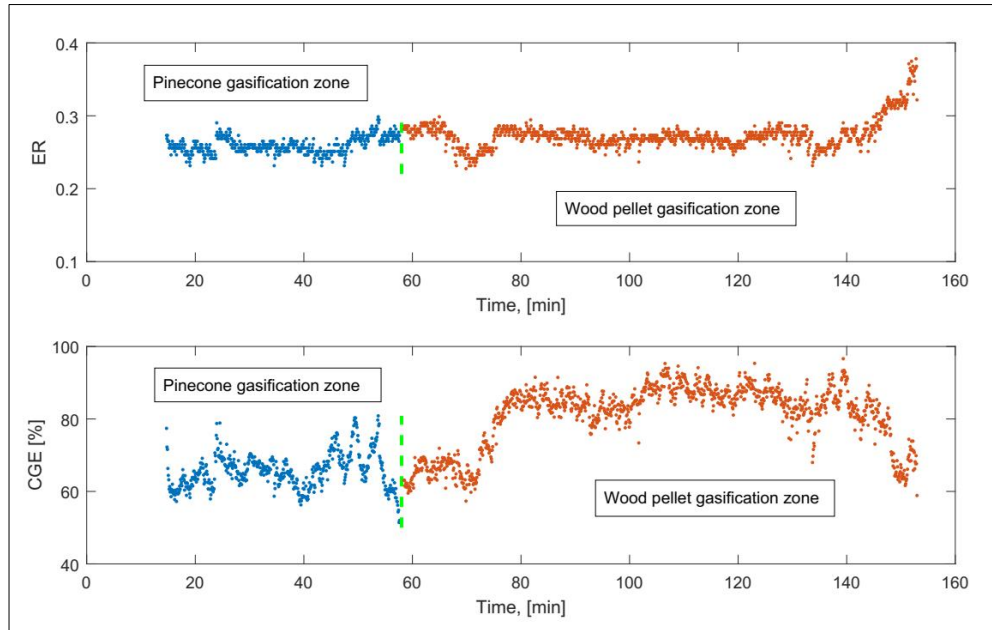


Figure 5.4: Effect of equivalence ratio on cold gas efficiency.

In case of the pine cones gasification, between 20th and 40th minutes when equivalence ratio value is most stable, the cold gas efficiency showed behavior parallel to ER value. During the pine cones gasification process, the cold gas efficiency

calculated as 58% for ER value of 0.23 at 19th minutes. The CGE value gradually increased to 65% as ER value approaches to 0.26 at 20th minutes. When the value of ER (0.28) was increased further, the CGE values were calculated as 78% and 68% for 24th and 49th minutes, respectively. A slightly change in the value of ER (0.28 to 0.2945) increased the value of CGE from 78% to 79% at the 53rd minutes. When all gasification experiments compared, the CGE value was always higher in the wood pellet gasification than in the pine cones gasification. In the beginning of the wood pellet experiment, at the 62nd minutes, the CGE value calculated as 67% when the value of ER was 0.29. The decrease in the ER (0.24) value at the 70th minute led to a decrease in the CGE (65%). When the value of ER increased to 0.27, the CGE reached a 90% efficiency value at the 105th minute. A dramatic increase in ER value towards the end of the wood pellet gasification experiments resulted in a decrease in the CGE value. The equivalence ratio at ER = 0.378, the cold gas efficiency calculated as 69% at the 152nd minutes. In the literature, the CGEs were found higher for ER 0.376 (79.46%) and 0.386 (80.03%) for gasification of lignite and sawdust briquette (70:30, %wt.) by Upadhyay et al. [136]. Zheng et al. [137] obtained the maximum CGE of 75% at a ER value of 0.3. Khosasaeng and Suntivarakorn [138] found the highest CGE at 73.04% at ER = 0.35 because the heating value of syngas produced from gasification RDF was highest at 5.87 MJ/Nm³.

6. CONCLUSIONS

A stoichiometric equilibrium model, SEM1, was developed and validated with published experimental data $C_{F, \text{methane}}$ and $C_{F, \text{water-gas shift}}$ were introduced which were derived using experimental results for various wood based fuels while gasified with air in downdraft gasifiers, thus modified SEM1 model showed best accuracy in the prediction of the concentration for all gaseous species in the syngas. The overall RMSE value of SEM1 model which is the criterion of the agreement between experimental data and model, reduced from 4.34 to 1.46 and total RMSE value reduced from 138.793 to 46.997 for 32 cases. For SEM2 model, the total RMSE value reduced from 130.048 to 53.637. It was seen that ER have a large influence on downdraft gasification as well as gasification temperature.

Since tar is generally a non-equilibrium and undesired product, tar yield estimation via a thermodynamic equilibrium model is a difficult task. The model including gas species and only yield of tar, called SEM3 also was modified and showed better results than modified SEM1 in the determination of all the gaseous species and the yield of tar. Later, SEM3 was modified again using the correlations presented in Eqs. (3.22-3.23). After modification, the average RMSE value reduced from 6.30 to 2.02 for the 9 sets of experiments. The results of SEM3 model show that as ER value increases, the yield of tar decreases. Optimal conditions for downdraft gasification in terms of tar conversion and heating value of syngas can be determined with using modified SEM3 model.

Finally, HHV correlations were used to develop a sensitivity analysis of the model and Dulong-Berthelot's correlation showed best accuracy among the other correlations. Overall RMSE value reduced from 4.34 to 3.85 and total RMSE value reduced from 138.793 to 123.336. It has shown that, the modified models are reliable for predicting the syngas composition, yields of char and tar, by varying the gasification temperature, equivalence ratio and moisture content.

Distinct from all other models in the literature, this work validated through the comparison with 32 cases from 8 different sets of experimental data. Also woody biomasses with different chemical compositions were tested in this study. To enhance accuracy of equilibrium models, equilibrium correction coefficients and the carbon conversion factor should be adjusted on the basis of experimental data. Furthermore,

the heat loss through the wall of the equilibrium zone should be measured to increase accuracy. Therefore, SEM models could be used in the design, evaluation and optimization of downdraft gasifiers. A stoichiometric equilibrium model has been developed and validated with published experimental data in order to investigate the relationship between the hydrogen-rich syngas production and the gasification parameters. In this work, the gasification of biomass to produce hydrogen-rich syngas was studied by considering the thermodynamic equilibrium limit in fixed bed downward gasifier using air, oxygen and air-steam mixture as the gasification medium. The influence of various air-to-biomass, oxygen-to-biomass and steam-to-biomass ratios to hydrogen-rich syngas production investigated. For validation, the results obtained from the mathematical model were compared with the experimental data obtained from the gasifier that uses air as gasification medium. The theoretical results clearly indicate that maximum hydrogen production is %30.09, %43.05 and %42.59 for air, oxygen and air-steam gasifying medium, respectively. Comparing the results that obtained from the stoichiometric model showed that biomass oxygen/air-steam gasification is more effective than biomass air gasification technique for producing hydrogen-rich syngas. As a final conclusion, this study clearly shows that gasification technology can be utilized to produce hydrogen as an alternative way. The gasification of pinecones particles and wood pellets in a pilot scale 10kW_{th} downdraft fixed bed gasifier using air as oxidizing agent investigated experimentally. The following results were found after analyzing the gasification temperature, equivalence ratio on the syngas composition, H_2/CO ratio and gasification performance. The average values of the syngas compositions for pine cone gasification were 23.62% CO, 11.87% CO_2 , 1.83% CH_4 , 18.76% H_2 and for wood pellet gasification were 27.74% CO, 9.43 CO_2 , 2.30% CH_4 , 21.62% H_2 . Higher hydrogen and methane were produced in the wood pellet gasification because of its high hydrogen content. In addition, the total carbon content in the syngas obtained from the wood pellet gasification is greater than the total carbon content in the syngas obtained from the pinecones gasification. According to the elemental analysis of feedstock, pinecone has 10% higher oxygen content than wood pellets. Thus, produced CO_2 from pinecone gasification is more than wood pellet gasification. Hydrogen and carbon monoxide production increased with increasing gasification temperature as expected. For the pine cone gasification, optimal gasification temperature interval is 900-950 °C to obtain high calorific syngas. In this region, H_2 molar ratio ranged between 17.28-21.39% while CO molar ratio was around

23%. For the wood pellet gasification, optimal gasification temperature interval found to be 850-900 °C. H₂ content of syngas ranged between 20.39 and 25.15 while CO molar ratio was 29.69%. In the pinecone gasification experiment, mean H₂/CO ratio was 0.80 and for the wood pellet gasification, mean H₂/CO ratio was 0.78. The cold gas efficiency for pine cone gasification was found be %78 at ER value of 0.28 and for wood pellet gasification, CGE value calculated %90 at ER 0.27.

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BIOGRAPHY

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APPENDICES

Appendix A: Published articles and book chapter from thesis

Aydin E. S., Yucel O., Sadikoglu H., (2017), “Development of a semi-empirical equilibrium model for downdraft gasification systems”, *Energy*, 130, 86-98.

Aydin E. S., Yucel O., Sadikoglu H., (2018), “Numerical and experimental investigation of hydrogen-rich syngas production via biomass gasification”, *International Journal of Hydrogen Energy*, 43(2), 1105-1115.

Aydin E. S., Yucel O., Sadikoglu H., (2018), “Numerical Investigation of Fixed-Bed Downdraft Woody Biomass Gasification”, In: Dincer, İ., Colpan, O, Kizilkan, O., Editors, “Exergetic, Energetic and Environmental Dimensions”, Academic Press.

Aydin E. S., Yucel O., Sadikoglu H., (2019), “Experimental study on hydrogen-rich syngas production via gasification of pine cone particles and wood pellets in a fixed bed downdraft gasifier”, *International Journal of Hydrogen Energy*, 44(32), 17389-17396.

Appendix B: Comparison of SEM2 and SEM3 model results with experimental data

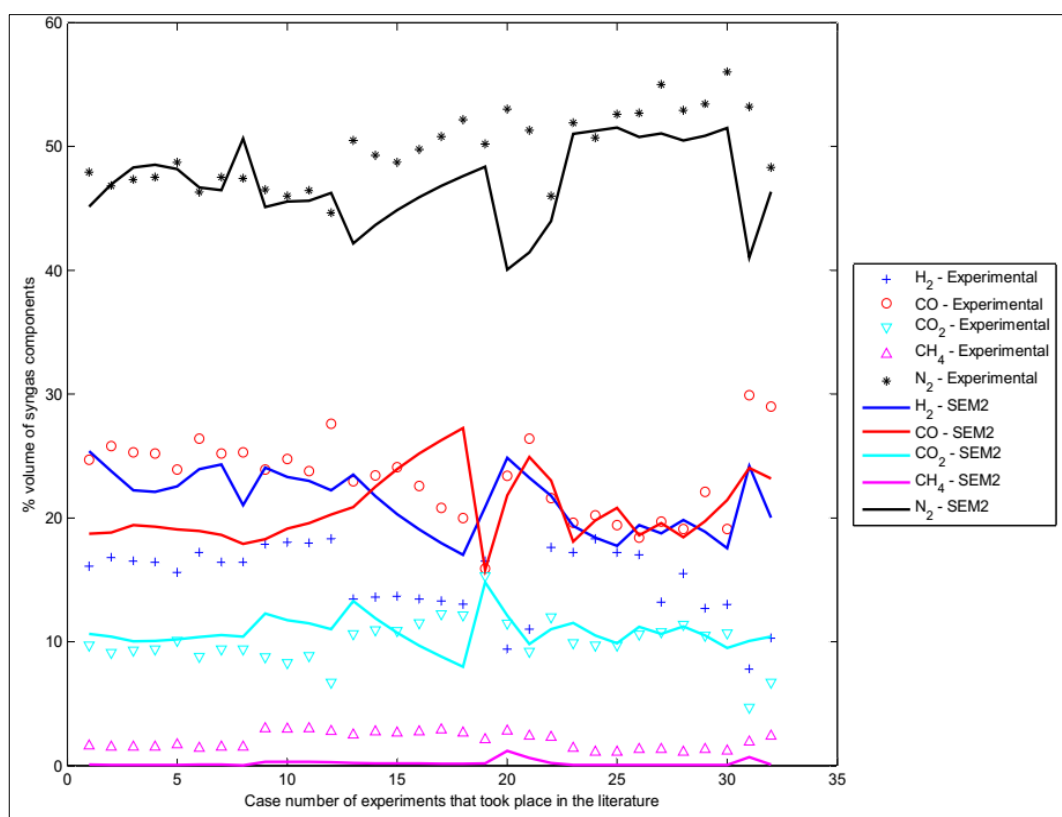


Figure B1.1: Comparison of SEM2 model with experimental data.

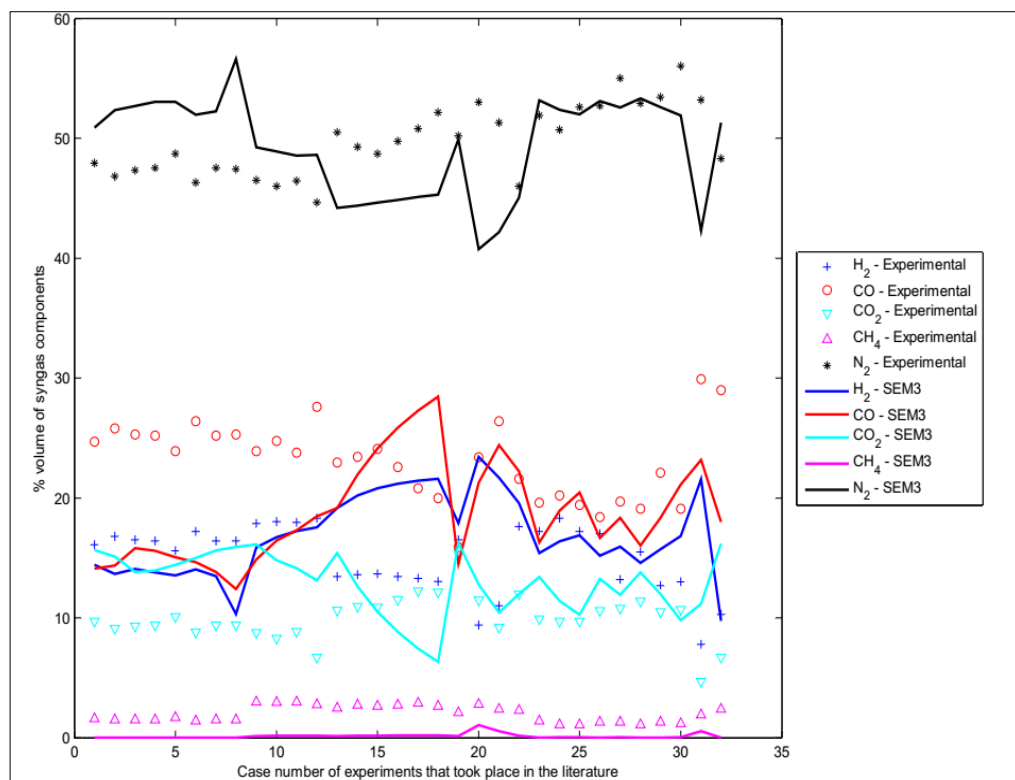


Figure B1.2: Comparison of SEM3 model with experimental data.