MARMARA UNIVERSITY
INSTITUTE FOR GRADUATE STUDIES IN PURE AND APPLIED SCIENCES

MODELLING AND SIMULATION OF A CATALYTIC GASIFICATION INTEGRATED WITH SOLID OXIDE FUEL CELL SYSTEM

NUR ÇEKERYÜREKLİ

MASTER THESIS
Department of Chemical Engineering

Thesis Supervisor
Asst. Prof. Dr. Uğur ÖZVEREN

ISTANBUL, 2020

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TABLE OF CONTENT

ACKNOWLEDGMENT
ÖZET
ABSTRACT
SYMBOLS vi
ABBREVIATIONS vii
LIST OF FIGURES viii
LIST OF TABLES x
1. INTRODUCTION 1
1.1. Biomass 2
1.2. Coal 5
1.3. Gasification 7
1.3.1. Co-gasification 10
1.3.2. Catalytic Gasification 12
1.4. Fluidized Bed Gasifier 13
1.5. Solid Oxide Fuel Cell 14
2. METHODS 16
2.1. Fuel Characterization 16
2.1.1. Proximate Analyze 16
2.1.2. Ultimate Analyze 16
2.1.3. Thermal Gravimetry 17
2.2. ASPEN 18
2.2.1. Unit operation models 18
2.2.2. Gasifier Literature Experiments 20
2.2.3. Solid Oxide Fuel Cell 23
3. RESULTS 24
3.1. Preparation of Biomass and Coal Samples 24
3.2. Feedstock Characterization 24
3.2.1. Proximate Analysis 24
3.2.2. Ultimate Analysis 25
3.3. Aspen Plus Model 26

3.3.1. Co-Gasification Model Development 26
3.3.2. Solid Oxide Fuel Cell Model Development 28
3.4. Model Validation 29
3.4.1. Validation of Fluidized Bed Gasifier 29
3.4.2. Validation of SOFC 31
3.5. Parametric Study 32
3.5.1. Effect of Gasifier Temperature on Syngas Composition 32
3.5.2. Effect of Gasifier Pressure on Syngas Composition 34
3.5.3. Effect of Steam/Fuel Ratio on Syngas Composition 41
3.5.4. Effect of CaO Catalyst on Syngas Composition 43
3.5.5. Effect of CaO/Fuel Catalyst on Syngas Composition 46
3.5.6. Effect of Syngas Composition on SOFC Efficiency 48
4. CONCLUSION 50
REFERENCES 52

ÖZET

KATI OKSİT YAKIT HÜCRESİ SİSTEMİ İLE ENTEGRE KATALİTİK GAZLAŞTIRMA MODELLEMESİ VE BENZEŞİMİ

Enerji alanında çalışan araştırmacıların en büyük sorunu; sürdürülebilir bir ekonomi için çevreyi korurken yüksek verimli ve düşük maliyetli enerji üretimini de beraberinde sağlamaktır. Entegre gazlaştırıcı-yakıt hücre sistemleri; gazlaştırma (biyokütle ve/veya kömür) ve katı oksit yakıt hücrelerini (SOFC) birleştirerek çevresel ve yüksek verimli enerji üretimi için yeni fırsatlar sunmaktadır. Bu tez çalışmasının amacı, katalizör ve birlikte gazlaştırma işleminden oluşabilecek sinerjik özelliklerin sentez gazı bileşimini değiştirmesi ve entegre gazlaştırıcı-SOFC bazlı güç sistemlerinin performansı üzerindeki etkilerini araştırmaktır. Bu tez çalışması kapsamında aşağıdaki çalışmalar yapıldı:

- Yakıt özelliklerinin (Çan Kömür ve/veya Pirinç Samanı) ve çalışma koşulların, sentez gazı bileşimi üzerindeki etkilerini incelemek,
- Sentez gazı içerisindeki H_2'nin yüksek verim ile elde edilebilmesi için katalitik gazlaştırma prosesinin optimizasyonu ve geliştirilmesi,
- Yüksek verimli entegre Gazlaştırıcı - SFOC hibrit sistemin verimini incelemek.

Bu çalışmada; entegre gazlaştırıcı - katı oksit yakıt hücre sistemini modellemek ve elde edilen modelin verimliliğini incelemek için AspenTech firmasına ait Aspen PLUS yazılımı kullanıldı. Aspen PLUS yazılımına ait yerleşik reaktör modülleri ve entegre sistemin verimliliğini inceleyen termodinamik fonksiyonlar kullanılarak parametrik çalışma yapıldı. Elde edilen sonuçlar, katalitik gazlaştırmanın entegre güç sistemleri için uygulanabilir ve enerji üretimi için verimli olduğunu gösterdi.

Anahtar Kelimeler: Gazlaştırma, Akışkan Yatak, Yakıt Hücresi

ABSTRACT

MODELLING AND SIMULATION OF A CATALYTIC GASIFICATION INTEGRATED WITH SOLID OXIDE FUEL CELL SYSTEM

Researchers in energy society encounter great challenges: to deliver highly efficient and low-cost energy while protecting the environment that is essential to sustainable economy. Integrated gasification fuel cell systems that combine solid oxide fuel cells (SOFC) and gasification (biomass and/or coal) are promising unexploited opportunities for highly efficient and environmentally energy production. This research presents a multifaceted study of an integrated Fluidized Bed Gasifier-SOFC based power system utilization, with an emphasis on catalytic gasification, for high energy efficiency. The goal of this dissertation research is to investigate the effects of catalyst including synergetic properties of co-gasification on the syngas composition and performance of integrated Gasifier-SOFC based power systems through detailed thermodynamic analyses including the study of:

- Effects of fuel type (Çan Coal and/or Rice Straw) and operating conditions,
- The development and optimization of a catalytic gasification process aimed at the production of synthesis gas with a highly efficient H_2 formation.
- To investigate the efficiency of the integrated Gasifier-SOFC hybrid system.

To achieve the goals, Aspen Plus software from AspenTech has been conducted using built-in reactor modules and the sensitivity analysis of the proposed SOFC and Gasifier models has been conducted by using thermodynamic models able to investigate the efficiency of integrated systems. Results show that an integrated Gasifier-SOFC based power system including catalytic gasification is feasible and leads to energy production.

Keywords: Gasification, Fluidized Bed Gasifier, Solid Oxide Fuel Cell

SYMBOLS

A/m^2	: Ampere/square meter
GW	: Gigawatt
kcal	: Kilocalorie
kWe	: Kilowatt-electric
MJ	: Mega Joule
m^2	: Square meter
t	: Time
T	: Temperature (K)
V	: Voltage
Wt	: Weight
µm	: Micrometer

ABBREVIATIONS

AFT : Ash fusion temperature

ASTM : American Society for Testing and Materials

CHP : Combined Heat and Power

CFB : Circulating Fluidized Bed

CV : Calorific Value

FBG : Fluidized Bed Gasifier

FC : Fixed Carbon

IEA : International Energy Agency

LHV : Lower heating value

MTEP : Million tons of petrol equivalent

NIST : National Institute of Standard and Technology

S/B : Steam to biomass ratio

SOFC : Solid oxide fuel cell

TWh : Terawatt hour

TGA : Thermogravimetric Analysis

VM : Volatile matter

WGS : Water gas shift

LIST OF FIGURES

Figure 1.1 Biomass utilization potential 3

Figure 1.2 Sankey chart of mass flow distribution throughput biomass gasification 4

Figure 1.3 Gasification process steps 9

Figure 1.4 Process diagram of co-gasification of biomass and coal into fuel 11

Figure 1.5 The diagram of fluidized bed gasifier 13

Figure 1.6 The diagram of SOFC 15

Figure 3.1 Flowsheet of fluidized bed gasifier model 26

Figure 3.2 Flowsheet of SOFC model 28

Figure 3.3 Effect of gasifier temperature on syngas composition; (a) Rice Straw, (b) Çan Lignite, (c) Blend 34

Figure 3.4 Effect of gasifier pressure on syngas composition for rice straw; (a) H_2, (b) CO, (c) CO_2, (d) CH_4 36

Figure 3.5 Effect of gasifier pressure on syngas composition for Çan lignite; (a) H_2, (b) CO, (c) CO_2, (d) CH_4 38

Figure 3.6 Effect of gasifier pressure on syngas composition for blend; (a) H_2, (b) CO, (c) CO_2, (d) CH_4 40

Figure 3.7 Effect of steam/fuel ratio on syngas composition; (a) Rice Straw, (b) Coal, (c) Blend 42

Figure 3.8 Effect of CaO catalyst on syngas composition for rice straw; (a) without CaO, (b) with CaO 44

Figure 3.9 Effect of CaO catalyst on syngas composition for Çan lignite; 45

(a) without CaO, (b) with CaO

Figure 3.10 Effect of CaO catalyst on syngas composition for blend; 46

(a) without CaO, (b) with CaO

Figure 3.11 Effect of CaO/fuel ratio on syngas composition; (a) Rice Straw, 48

(b) Çan Lignite, (c) Blend

Figure 3.12 Effect of syngas composition on solid oxide fuel cell 49

LIST OF TABLES

Table 1.1 IEA Coal Statistics of Turkey 7

Table 1.2 List of gasification reactions present gasification model 9

Table 2.1 Reactor model description shows the usage and purpose 20

Table 3.1 Proximate analysis results of rice straw & Çan lignite 25

Table 3.2 Ultimate analysis results of rice straw & Çan lignite 25

Table 3.3 Input values of fluidized bed gasifier block elements developed for biomass & coal mixture 27

Table 3.4 Comparison of the literature and the model for coal 30

Table 3.5 Comparison of the literature and the model for biomass 30

Table 3.6 Comparison of the literature and the model for coal & biomass mixture 31

Table 3.7 SOFC model validation results 32

1. INTRODUCTION

Growing industrialization and population in the world have led to an increase in demand for fuels and chemicals [1]. Among fossil fuels, coal is one of the most abundant solid with high energy content and low cost. However, CO_2 emission profile causes an environmental issue leading global warming. One solution to mitigate the CO_2 release is an implementation of coal by an eco-friendly feedstock. Biomass, in this manner, is an important solution since it releases zero CO_2 into the atmosphere. Some drawbacks of using biomass are its high bulk volume and moisture with low caloric heat value. Utilization of coal and biomass blend considerably decreases harmful gas evolution. Some other technological techniques even change gas composition of combustion reaction.

Gasification is a thermolysis process which converts any carbon-based raw materials to a fuel gas including mainly CO and H_2. Co-gasification of coal and biomass blends is a promising alternative in terms of improved efficiency, economy and environmental benefits [2, 3]. The need for increased energy recovery, processes and the economic benefits have been demonstrated advantageously with studies on the co-gasification of coal and biomass [4-8]. The main idea behind co-gasification is to increase the desired syngas percentage composition obtained from the pyrolysis of coal in the gasification process with the catalyst effect in the content of biomass. The presence of inorganic matter in the biomass serves as a catalyst in the process of gasification of the coal [4]. Thanks to biomass is rich in alkali content, co-gasification of coal and biomass provides a desirable method for catalytic gasification of coal.

The use of catalysts has an undeniable prospect of increasing gas yield on the co-gasification [9]. According to the literature researches, the increase in gas yield by using catalysts is indicated by numerical data; hydrogen yield increased from 33.3 to 52.5 mol% and syngas ratio from 1.15/2.15 to 1.87/4.45 [10, 11].

Some undesirable components occur in gasification process. Particularly higher hydrocarbon content (tar) not only raise issues of operation and maintenance such as deposition, colloguing, and blockage but also decrease the yield of product gas [12]. Tar form depends

on numerous factors such as thermal conditions of gasifier, fuel used, operating conditions, and processing technique. In order to avoid the formation of tar which causes serious problems in cyclones, filters and heat exchangers, gas turbines and gas engines, pipelines, the use of an effective catalyst should be employed [13]. When selecting the catalysts to be used, certain properties should be taken into consideration in order to provide an advantage. For example, they are cost-effective, continue to be efficient under strong reaction conditions, and contribute to the desired syngas product yield. Moreover, they should have high tar reduction potentials and be capable of preventing and regaining sintering [14]. The development and progress in catalytic gasification technology is an indicator of a critical point in catalyst selection. The main criteria of catalyst selection are that it is easy and inexpensive to reproduce and increases product yield at the reduction tar level.

Extensive studies on co-gasification have been found in the literature. On the downside, the number of studies on catalytic co-gasification so far has been very limited [15]. As a result of this, catalytic co-gasification of biomass and coal has been received much attention in recent years [16-21].

Fuel cells show high energy efficiency and SOFC is one of the most attractive fuel cell technology, which allow the integration with catalytic co-gasification process achieving very high electric efficiency. However, gas quality from catalytic gasification and co-gasification is important to prevent degradation of the electrodes of the SOFC. Since the gasifier operating conditions drive the choice of the SOFC and combined system configuration [31].

The aim of this dissertation was to investigate the feasibility of a combined heat and power plant for the gasification and catalytic co-gasification, where a solid oxide fuel cell system has been combined with a circulating fluidized bed (CFB) gasifier.

1.1. Biomass

Biomass has been a dominant energy source long before the discovery of fossil fuels and has been used for a thousand years. In developed countries, while the goal is to produce clean energy, biomass stands out among the raw material sources. The use of biomass makes possible to obtain biofuels; ethanol and biodiesel and to obtain chemical raw materials;

pharmaceuticals and plastics. Lipid and protein rich agricultural crops like rapeseed and palm oil can be utilized to generate biofuels such as biodiesel. This is a versatile substitute/blender material for fossil diesel. Unlike other energy sources, biomass is advantageous with solid, liquid and gas fuel forms from which it can be converted. Production of chemicals, fuel for transportation and generation of heat or electrical energy are the three main product types in which biomass can be used as a resource [22]. As a result of the researches, as shown in Figure 1.1, biomass-used energy potential will be around 190 EJ by 2085. The use of biomass has increased its importance over time and has become a major resource in energy production.

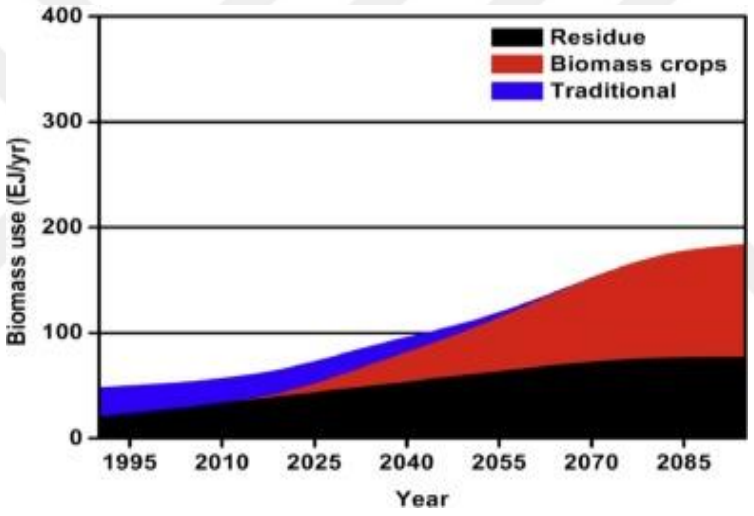


Figure 1.1 Biomass utilization potential [23]

There are different methods exist to convert biofuels to heat and power generation. Correspondingly, the power of biomass power plants to be established by 2030 is estimated to be around 70 GW [24]. Biomass plants based on small-scale steam cycle can be used in residential heating as well as lacking in terms of high investment costs and low electricity efficiency. Combined heat and power (CHP) biomass plants with gasification technology enables the development of commercial applications that implementation of gas engines, gas turbines or fuel cells, since they empower the use of small to large scale power generation devices [25]. It is inevitable that biomass raw material, which has the potential to be converted into hydrogen and carbon monoxide gas with high heating value, will emerge as a brilliant option in syngas production (Figure 1.2).

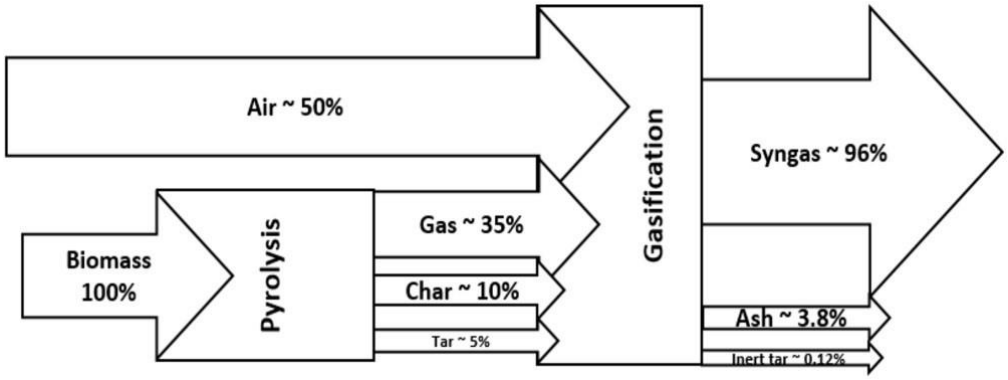


Figure 1.2 Sankey chart of mass flow distribution throughput biomass gasification [26]

The thermal conversion process in which biomass is converted to synthesis gas by gasification in the presence of a gasification agent containing steam and oxygen is called biomass gasification. Thanks to its high efficiency, it has become an application that has attracted the attention of energy producers in recent years. Great efforts have been made to ensure that gasification technology is functional but also competitive in the process of making it ready for use in the industry. The main factor in attracting such attention to biomass gasification process; is a versatile syngas composition. Gasification as an alternative to combustion holds some issues like tar formation and impurity content which cause problems in downdraft use [27].

There is a fairly constant atomic ratio of $C_{10}H_{14}O_6$ for most of the biomass samples. There is a direct link between the chemical composition of the biomass and the structure of the synthesis gas obtained as a result of gasification[28]. As the energy source, biomass can be burned together with other fuels ranging from 2-25 %, which has the effect of decreasing the carbon dioxide emission occurring in fossil-based energy sources. For example, coal in a coal-fired power plant with a rate of 33-37 % sulfur dioxide and nitrogen oxide emissions when burning with biomass has been seen that a 30 % reduction in emissions [29, 30].

1.2. Coal

Coal is a type of fossil fuel that occurs as a result of millions of years of chemical and physical reactions underground in the regions with rich vegetation. Due to its high reserve potential and widespread worldwide, coal is a solid fossil fuel in terms of energy markets. On the other hand, the fact that coal has negative consequences for the environment and climate has kept the use of this energy source at the center of intense criticism. In recent years, parallel to the technological advances in the field of clean energy, the losses caused by coal consumption can be reduced to minimum levels. Although coal has some negative consequences for the environment and human health, the high potential of reserves is an energy source that can be preferred due to the low cost of production costs and ease of use of other fossil fuels. The coal in ensuring energy security of a country with a high rate of dependence on foreign fossil fuels, such as in Turkey has a critical mission.

High carbon (energy) and low moisture content are important factors. In terms of carbon content, coal is classified as ”peat“ if carbon is 60 % or less, 70 %, as “lignite“ and between 80-90 % “charcoal” and over 90% ”anthracite“ [31]. Thermal values are 2600 kcal/kg, 5700 kcal/kg, 4500-7500 kcal/kg and 7300-8000 kcal/kg for peat, lignite, bituminous coal and anthracite, respectively.

Although all these thermal values are determined according to international standards, they may vary from region to region for different countries. The priorities of developing countries are sustainability and accessibility. Therefore, there is a very serious competition in global markets in terms of low cost and sustainable energy supply. In this competition, countries utilizing their own resources in energy production have a significant advantage. World Coal Association has reported that coal is frequently used in electricity production and 37 % of global electricity is generated from coal. Table 1.2 reveals coal statistics by “International Energy Agency for Turkey in 2015”.

Turkey's geographical location makes it a natural bridge between the energy-rich Middle East and Central Asian regions. As Tunc et al. [32] pointed out; Energy consumption is increasing much faster than production in Turkey. In order to reduce its dependence on imported sources

in Turkey's energy policy for the use of domestic resources has come to the fore. Electricity production in Turkey mainly coal, natural gas, geothermal energy, hydropower, and thermal power plants is provided through. With most potential energy source is lignite coal in the domestic context of Turkey's fossil resources list. For Turkey's total electricity production, the first energy source is the natural gas and the second one is coal. The 97.5 TWh of the electricity at 294.9 TWh produced in 2017 was provided by coal [33].

According to calculation of the total proven reserves of lignite / sub-bituminous coal reserves of 17 billion tons, anthracite and bituminous coal reserves once high is 1.5 billion tons for Turkey’s 2017 data [31]. By the end of 2017, Turkey's total coal production volume reached 100 million tons. In 2002, Turkey's total coal consumption of 19 MTEP, while this amount is evaluated to be around 45 MTEP by the end of 2017.

The low energy value of lignite coal utilized locally in Turkey and its inability realization of an efficient production process is ongoing trend towards imported coal. However, lignite usage has become widespread in parallel with the technological advances that increase the efficiency of the environment. If the lignite sources are burned according to clean gasification technologies and especially in the plants to be installed with fluidized bed technology, both the efficiency will increase and the harmfulness on the environment will decrease. Turkey has significant potential for coal in electricity production and this potential should be provided with suitable and clean gasification technology is activated.

The coal gasification process started in the 1800s and was developed in line with the researches carried out over 200 years. As a result, coal has become the potential source for obtaining synthesis gas and liquid fuel [34].

Table 1.1 IEA Coal Statistics of Turkey [35]

	Coking Coal	**Bituminous Coal**	**Sub-bituminous Coal**	**Lignite**	**Coal Tar**	**Blast Furnace Gas**
Unit	kt	kt	kt	kt	kt	TJ
Production	767	668	857	56122	157	56647
Imports	5931	28048	0	0	0	0
Exports	0	-151	0	0	-85	0
Stock Changes	-10	-435	177	539	-3	0
Domestic Supply	6688	28130	1034	56661	69	56647
Statistical Differences	0	-164	0	-57	0	0
Transformation	6688	16161	492	49940	0	29580
Electricity Plants	565	15132	492	48416	0	23569
CHP Plants	83	358	0	1524	0	6011
Heat Plants	0	0	0	0	0	0
Other Transformation	6040	671	0	0	0	0
Energy Industry Own Use	0	284	0	47	0	24158
Losses	0	0	0	0	0	0
Final Consumption	0	11521	542	6617	69	2909
Industry	0	4782	300	3723	69	2909
Transport	0	0	0	0	0	0
Residental	0	1516	242	2084	0	0
Commercial and Public Services	0	5223	0	810	0	0

* Gases are expressed in terajoules (TJ) on a gross calorific value (CV) basis.

Technologies that will be effective in reducing emissions and ensuring efficient energy production should be utilized. In this context, coal-gasification, fuel production, coal-enrichment activities are continuing [36].

1.3. Gasification

Gasification is a process that takes place in reactors which are called gasifiers, converting carbonaceous materials to combustible gases including CO, H_2, CO_2, and CH_4 by partial

oxidation and the product realized is called syngas [37]. For generating heat, electricity, or both; the syngas is a supreme raw material. The most striking feature of the gasification process is that it enables energy production from carbon-based fuels with minimum damage to the environment. Hence, the shift to the use of hydrogen-rich gases rather than the demand for consumption of fossil fuel helps to prevent both the tendency for depleted primary fossil resources and the landfill of waste generated [38]. Another striking feature of gasification is that it prevents the CO_2 pollutant caused by the fossil fuel to be released into the atmosphere.

The advantages of the gasification process have been discovered and referred for a long time. The used gas engines, gas turbines, and fuel cells are the variables that effective in increasing the efficiency of the energy systems that generate electricity using syngas [39]. The first syngas production was produced by the pyrolysis of coal during the iron retorting of the Scottish engineer Murdoch. In 1812, the first gas company was established in London, producing gas from coal and thanks to this, it generated lightning the Westminster Bridge. In 1816, the first gas production facility to produce gas from coal was established in the United States, and the streets of Baltimore were illuminated by the synthesis gas produced. In 1826, gas was produced in big cities such as New York and Boston and street lighting was achieved; the process was started to be implemented in major cities all over the world [40]. In the 1920s, Carl von Linde's commercialization of air into its components by the refrigeration cycle led to the production of syngas and hydrogen with the use of oxygen in air gasification. Winkler-Fluidized Bed Process in 1926, Lurgi-Pressure Gasifier Process in 1931, Koppers-Totzek Circulating Flow Gasification Process in 1940s were found and applied. In the 1980s, researchers and various industries became aware of the environmental advantages of the gasification process. Some governments and industry stakeholders have imposed stricter and restrictive environmental standards, particularly the reduction of emissions and greenhouse gases in power plants and industrial establishments. With the encouragement of this obligation, the commercialization of gasification processes gained momentum [40].

The process selection in the gasification is determined by taking into consideration the syngas properties to be obtained and the type and properties of the raw material used. Simply, in four

steps (Figure 1.3), drying, pyrolysis, combustion and reduction are defined as reactions occurring in the gasifier.

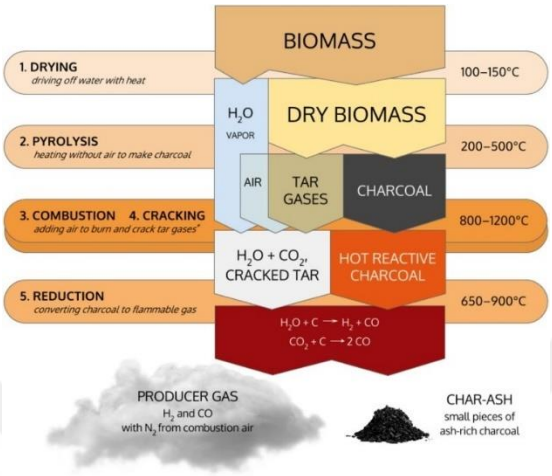


Figure 1.3 Gasification process steps [41]

Gasification reactions are various endothermic reactions favored by combustion. Combustible H_2, CO, and CH_4 gases are released as gasification products [42]. The reaction mechanisms that occur in the gasification process are presented in the Table 1.2 which describes the chemical reactions of gasification in air and/or steam.

Table 1.2 List of gasification reactions present gasification model [42]

Reaction Name	Heterogeneous Reactions
Water gas reaction	$C + H_2O \rightarrow CO + H_2$
Boudouard	$C + CO_2 \rightarrow 2CO$
Methane Formation	$C + 2H_2 \rightarrow CH_4$
Combustion	$C + 0.5O_2 \rightarrow CO$ $C + O_2 \rightarrow CO_2$
	Homogeneous Reactions
Shift	$CO + H_2O \leftrightarrow CO_2 + H_2$
Reforming	$CH_4 + H_2O \leftrightarrow CO + 3H_2$

1.3.1. Co-gasification

Co-gasification is a notable technology to obtain power, heat energy and gaseous biofuels through syngas [43]. Co-gasification of coal and biomass is a more useful method comparing to other methods. In addition, it provides more homogeneous fuel as it has significant advantages such as low moisture, and higher energy density [44].

Implementing of co-gasification include: firstly, substitution of coal and biomass with each other depending on availability. Secondly, the use of producer gas composition from biomass as a renewable energy source eliminates greenhouse gas emissions. Enabling the high and unstable moisture content to become the high calorific value and low cost provided by the syngas are the basis of co-gasification. In the selection of coal and biomass to be used in co-gasification, the ultimate aim should be to increase the H_2 / CO ratio in the product gas. In order to synthesize high quality products, this is considered crucial [45, 46]. Coal with cellular structure, moisture, and volatile matter content and inorganic structure has very complex chemical properties. Due to its complexity, coal is hard to degrade. On the contrary, biomass has the ability to disintegrate at lower thermic energy than coal. The structures of coal with the general molecular formula CHmOn [47], and biomass with CHxOyNzSs [48, 49] are helpful for chemical reactions they undergo.

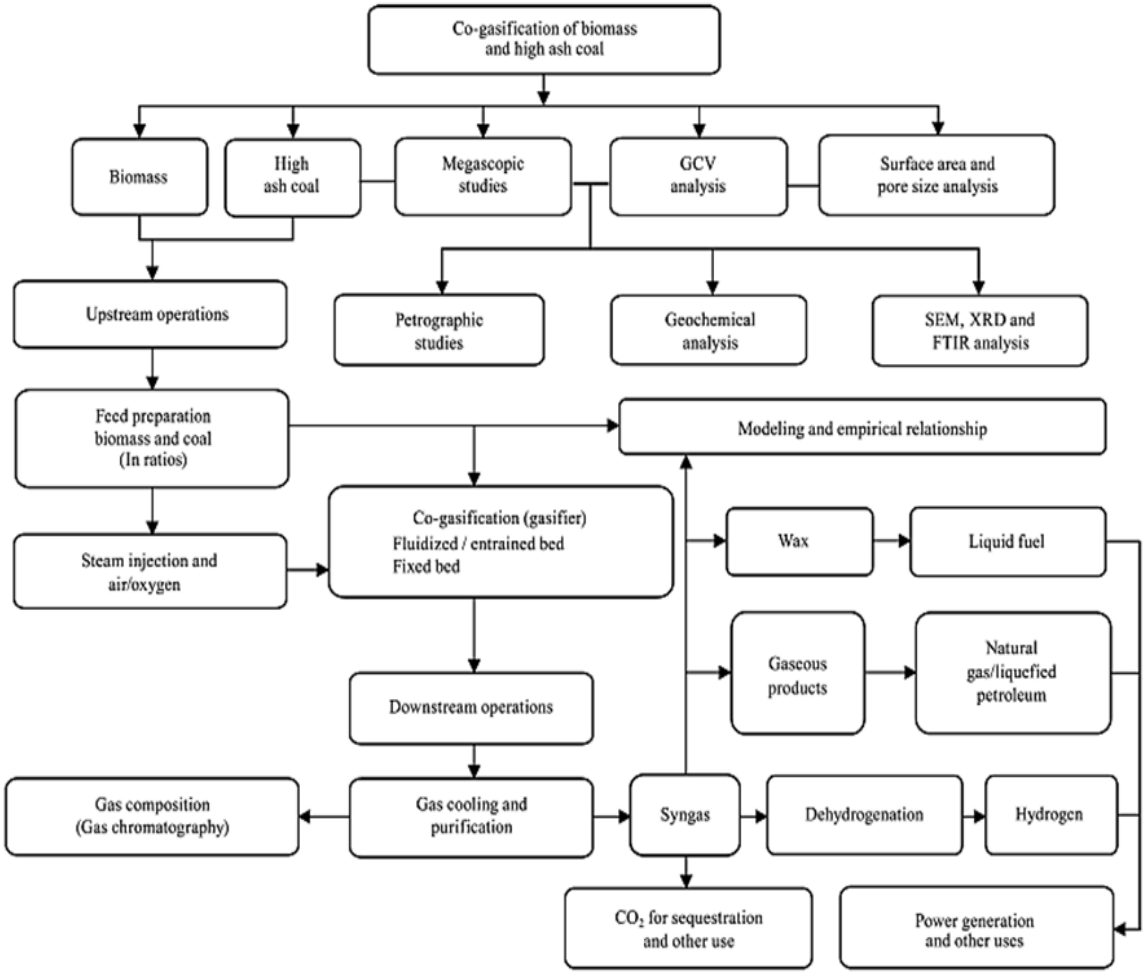


Figure 1.4 Process diagram of co-gasification of biomass and coal into fuel [50]

The co-gasification progress is as follows; at temperatures below 125 °C retroflex, coal and biomass lose water. The active pyrolysis process occurs at a temperature of 125-500 °C and as a result hemicellulose, cellulose and lignin structures are exposed to decompose. At the end of the passive pyrolysis lignin that occurs over 500 °C streams slowly and continuously in the form of disintegration [51, 52].

Co-gasification needs to an oxidizing agent to occurs at higher than 800 °C. The manner of procurance this temperature is heating the gasifier using oxidizing agents or compositions such as oxygen, nitrogen, carbon dioxide, air, steam. Considering that steam provides less tar

production and high product yield, it is more important to arrange the composition than other gasifier agents [50, 53].

1.3.2. Catalytic Gasification

The main priority in the catalytic gasification of coal and biomass; increase the H_2/CO ratio in the product composition obtained to synthesize fuel. The product gas varies with the selected catalyst.

The principal pollutants of fossil fuel are the following have carbon dioxide, the oxides of sulfur (represented as SOx); oxides of nitrogen (NOx). Nitrogen oxides react further with water and oxygen to form nitric acid. Pollution may result also from unburned hydrocarbons. These pollutants affect the air and the greenhouse effect leads to global warming [20]. CO_2 gas in the synthesis gas obtained as a result of gasification can be absorbed using the appropriate absorbents and thus the concentration of H_2 gas in the synthesis gas can be increased. For example, as an absorbent Calcium Oxide (CaO) is defined as an economical and effective material. The use of CaO in the gasification process stands out with its tar reform feature as well as its CO_2 absorption. Ultimately, it contributes to obtaining more hydrogen. Its function is not only to reduce the tar amount in the product gas but also heighten hydrogen yields. Essentially, as a gasification product CO_2 would be seized by CaO through a carbonation reaction then form into $CaCO_3$. The $CaCO_3$ composition needs to be treated at a temperature as high as 900 ˚C degrees to calcitize to the CaO composition. The expectation that the tar amount in the synthesis gas is reduced is met by using calcitized CaO as a CO_2 absorber. The use of CaO has gained lots of heed due to its cost and abundance [54].

When the advantageous aspects of alkali catalysts are examined, besides being low in price, it is more reactive than transition metal catalysts. They are seen to be more advantageous compared to other options due to the high contact capacity it provides with the carbon surface [55].

1.4. Fluidized Bed Gasifier

According to the result of investigation on gasification, fluidized bed gasifier (FBG) is appropriately used through its extensive adaptability, large-scale, scale-up, high efficiency of heat and mass transfer. Using steam as a gasifying agent in a FBG, CV of the produce gas is moderate [56]. The diagram of FBG is showed in Figure 1.5.

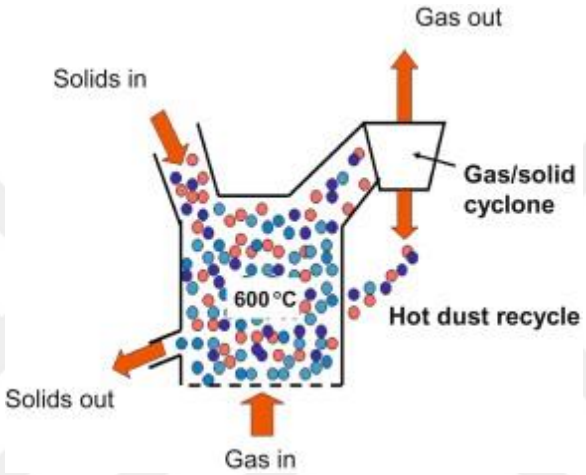


Figure 1.5 The diagram of fluidized bed gasifier [57].

The FBG is applicable for use in a multifarious of fuel particle sizes that are sensitive to co-gasification residues. Owing to demonstrating a flexible and robust technology, it is noted versatile [7, 58-60]. In view of all these advantages of use, the FBG is recognized as the most suitable gasifier for co-gasification of coal and biomass compared to other types. The systems of choice for fluidized bed gasification can be named bubbling and circulating beds. Fluidizing velocity and gas path disengage these gasifier types. In the bubbling beds, the gas flow rate is relatively slow, and the circulating bed speed is considered to be close to the pneumatic flow. Solids passing through the circulating bed are recycled after passing through a cyclone. On the other hand, the amount of solid carried in the bubbling beds is quite little.

The FBG processes are characterized as having high yield. These reactor models are complex systems because of the turbulent flow they use. FBG also improves heat storage and volumetric capacity as well as its ability to control temperature. The application of new

models which will help to predict the operating principle of these gasifiers has a considerable precaution because it allows the realization of the process modelled and at the same time precisely predicts the composition of the syngas [61].

For the FBG, the feed must be supplied to the system with well-mannered pulverized and mixed. Wherein the purpose of regular milling and mixing is to reduce the expectation of high energy volume by reducing the high bulk density. Studies showed that the results obtained from the type of gasifier used considering the appropriate parameters showed how important the choice of a suitable gasifier. In a typical FBG, the stock is fed into the system at the bottom through the gasifying agents such as steam. The gas obtained from the gasifier unit passes through cyclone to be separated from solid particles. When the important factors affecting gasification performance are taken into consideration, the effects of gasification operating parameters are remarkable. Ash fusion, critical viscosity, and temperatures in the cooling processes are the steps to be examined in the gasification process. There are important criteria to be considered when determining the operating temperature of the gasifier. One of these criteria is the regulation of temperature to be applied considering the maximum carbon conversion, that temperature is always lower than the ash fusion temperature (AFT), which results in dry ash [62].

The management and running of gasification process will be feasible in case physical and chemical reactions occurring in gasification. It is quite expensive to perform experiments directly in reactors and is impossible to do under the same conditions. Since simulation programs for gasification processes become noteworthy in science and the industry in general to obtain syngas with suitable properties such as chemical composition and heat value [63].

1.5. Solid Oxide Fuel Cell

Solid oxide fuel cells convert the chemical energy of a H_2 and/or Carbon-based fuel into electrical energy. It comprises of two interconnects, cathode, anode, and electrolyte. The working principle of the cathode is to reduce the oxygen atoms to the oxide ions. Oxide ions react with fuel atoms and are transported to the porous anode with releasing electrons along the electrolyte. The principal of SOFC is schemed in Figure 1.6.

The electrolyte in the ceramic structure provides structural stability and the inability to be affected by the CO and allowing CO to be viable SOFC fuel along with H_2. The preheating of the incoming air and fuel, steam production and hot air, combining with the gas turbine for integrated heat and power cycle are met by the high temperature exhaust stack of the fuel cell. The most advanced T-SOFC was developed by Siemens Westinghouse Power Corporation [64], which is modelled in this thesis.

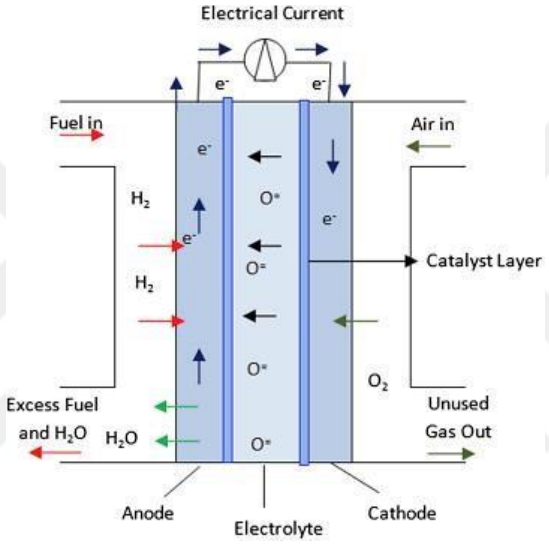


Figure 1.6 The diagram of SOFC

SOFCs has low emission and high efficiency as well as large energy conversion appliances. Regulating in accordance with the SOFC is the process of breaking up high hydrocarbons into a syngas mixture of H_2 and CO by the addition of a controlled amount of steam and / or oxygen at elevated temperatures.

2. METHODS

In this section, gasification process modeling approach, involving process assumptions, specification of different blocks and diagrams used in Aspen Plus is submitted. The proximate and ultimate analysis are the evaluation method in the examination of the form of carbonaceous material.

2.1. Fuel Characterization

2.1.1. Proximate Analyze

The major distinction in terms of fuel composition is the ash, the volatile matter, and the fixed carbon [65, 66]. These compositions provide an unrefined approximation of the fuel behavior when it is burned, and also can ensure specific traditional emission constituents such as ash and sulfur. These arguments are imperative but not adequate to determine the properties of the fuel and the fuel mixture. The comparison of coal and biomass wastes in some respects is as follows. Coals' fixed carbon content is significantly higher than the biomass fuels. On the contrary, volatile matter compactness for biomass fuels is much greater. Nitrogen and sulfur concentrations for biomass fuels also incline to be much lower. Considering all these differences, cofiring biomass with coal, inherently decrease SOx emissions [67]. Proximate analysis of rice straw and Çan coal used in experimental test were determined according to American Society for Testing and Materials (ASTM) D1762-84 standard testing methods.

2.1.2. Ultimate Analyze

The method of analysis in which the composition of a hydrocarbon-based fuel is expressed in terms of its basic elements, excluding moisture and inorganic components, is called elemental analysis. The volatiles of coal and biomass consist of carbon, hydrogen, oxygen, and nitrogen based on the ultimate analysis. Ultimate analysis reflects weight percentages of C, H, O, N and S elements of the fuel, respectively. Not all solid fuels contain all these elements. Majority of biomass fuels do not contain any sulfur. The carbon composition in the

elemental analysis content is divided into organic carbon and mineral carbon in solid fuel. The total amount of carbon in these two structures gives the percentage composition of carbon that constitutes the elemental analysis content. While determining the sulfur value in elemental analysis, organic sulfur and inorganic sulfur quantities should be included. The nitrogen content of the fuel is an important source of NOx pollutants. The amount of nitrogen is calculated from the degradation of the organic structure content in biomass and coal. Oxygen is calculated by subtracting the calculated content from 100. The carbon content increases the heating value. Some of the carbon is present in the volatile material, while the other fractions form the majority of coal. Hydrogen contributes to the heating value of the fuel, and during pyrolysis, most of the hydrogen is contained in the volatile material. The oxygen content reduces the heating value. Both the structures of coal and biomass are very intricate and random and have insufficient hydrogen and oxygen content. The carbon content specifies the grades of coal. For instance, lignite is a low carbon containing coal type compared to anthracite or bituminous coal. On the other hand, it has the highest oxygen content.

2.1.3. Thermal Gravimetry

Thermogravimetric analysis (TGA), as a function of time and temperature; is an analysis method that examines the change in weight. The worldwide energy supply system is mainly based on solid fuels including coal and biomass. The knowledge of the kinetic parameters of any solid fuel is vital for designing and optimizing the thermal process. The activation energy can be theoretically evaluated through enriching the information of the decomposition mechanism via thermogravimetric analysis (TGA) instrument. Thermal gravimetry device consists of scales, conveyor system and furnace. Weighing accuracy of thermal gravimetry device is one millionth of a gram. The scales of thermogravimetry devices consist of a very sensitive equipment.

Thermolysis applications are specified in 4 main topics; combustion, pyrolysis, liquefaction and gasification. As a hydrogen production process, combustion is not appropriate for sustainable development. Liquefaction is not favorable because of the low level of hydrogen

production and strain in achieving the operation conditions [68]. Pyrolysis is not preferred in terms of high temperature, high heating rate and long volatile phase residence time requirements [69].

Unlike pyrolysis, gasification, in situations requiring higher heating, is designed for maximizing the gas product, typical of expedient residence time, and the efficient tar and char reduction. Gasification reactions are mostly endothermic and appropriate for operation of a reactor [70, 71].

2.2. ASPEN

Aspen Plus is a process simulation software, which is an integrated solution to chemical process industries [72] and it is composed of interconnecting streams, feed streams and product streams, and several unit operations such as reactors, compressors, heat exchangers, separators, splitters, etc. that represent the actual processes coming about chemical industries. Aspen Plus also use FORTRAN program lines in the flow sheet for specific programming [72].

2.2.1. Unit operation models

The main modules are; splitter, mixer, compressor, heater, heat exchanger, separator, reactor.

2.2.1.1. Compressor

The compressor block works as a pressure changer for mixing streams.

2.2.1.2. Mixer

A Mixer block purpose is to combine streams into one stream. Its usage mode is combining tees; stream mixing; adding heat streams.

2.2.1.3. Splitter

Splitter streams flows; dividing inlet streams into component sub streams.

2.2.1.4. Heater

Heater block determines thermal and phase conditions. Its typical utilization is heaters, coolers, valves.

2.2.1.5. Reactor

Reactor block comprises 3 main models in this study; RStoic, RYield, RGibbs.

RSTOIC model, is used to specify outlet conditions and whether the reactions occur simultaneously or in series. For a two-phase or three-phase flash calculation, at least two of the features should be defined: temperature, heat duty, pressure, or vapor fraction. RStoic accepts any combination except vapor fraction and heat duty. For a one-phase calculation, either temperature - pressure, or pressure - heat duty couples must be defined. RStoic becomes useful when the stoichiometry is known. RStoic is used in conditions where the reaction temperature is to be calculated as well as the calculation by specifying the fractional conversion of key components through an In-Line Fortran calculator. It is also preferred with its product selectivity feature.

The ASPEN PLUS yield reactor RYIELD is used to simulate feed separation. At this stage, solid fuel is converted to its elemental analysis components; carbon, hydrogen, oxygen, sulfur, nitrogen, and ash by specifying the yield distribution. RYield reactor is used in situations where outlet conditions are specified. For a two-phase or three-phase flash calculation, at least two of the features should be specified: temperature, heat duty, pressure, or vapor fraction. RYield accepts any combination except vapor fraction and heat duty. For a one-phase calculation, either temperature - pressure, or pressure - heat duty couples must be specified. RYield is used to model coal decomposition by specifying the yield distribution vector through an In-Line Fortran calculator according to the coal ultimate analysis.

The ASPEN PLUS Gibbs reactor, RGIBBS, is used for volatile material and coal gasification reactions, for the analogy of reactions following the assumption that it follows Gibbs balance. Solid fuel mainly consists of C, H, N, O, S, Cl, ash and moisture. For RGibbs, specified outlet

conditions of the reactor and parameters are used that control the calculations. Either temperature - pressure, or pressure - heat duty couples must be defined. By default, vapor phase chemical equilibrium is considered. The Gibbs reactors are easy use modules don't require detailed reaction kinetics and stoichiometry.

Table 2.1 Reactor model descriptions

MODEL	DESCRIPTION	PLAN	USE
RSTOIC	Stoichiometric reactor	To specify outlet conditions	RStoic is used to calculate by specifying the fractional conversion components.
RYIELD	Yield reactor	Reactor with certain yield calculation	"Unconventional" stream is converted into a "conventional" feed stream using a certain yield calculation.
RGIBBS	Gibbs reactor	Chemical and phase equilibrium by Gibbs energy minimization	Unburned carbon and ash run in a combustion reaction, while the solid particles are retained, and the gas is separated.

2.2.1.6. Separator

Separator as a unit operation module can split up a feed stream into two or more streams.

2.2.1.7. Heat Exchanger

Heat exchangers, which can be utilized to set the thermodynamic condition of any stream, are used for simulating the phase and thermal conditions.

2.2.2. Gasifier Literature Experiments

There are several studies on co–gasification of coal/biomass blends in many countries around the world. An experimental study in this area was conducted by Velez et al. [60]. In this study, gasification of mixtures of various biomasses such as rice shells, coffee husks and sawdust with Colombian coal using a fluidized bed gasifier was investigated experimentally. The gasification process was carried out in an atmospheric environment by preheating the

mixture of air-water vapor to 350 °C. The variables used in the experiments were steam/fuel ratio between 0.1 - 0.8 kg / kg, air/fuel ratio between 2-3 kg / kg. The resulting change in the synthesis gas composition was examined. Using a gas chromatography device, the resulting syngas composition was examined. However, since this analyzer was not effective in measuring methane, the amount of methane in the recovered gas could not be measured. At the end of all these experimental studies, it is seen that the biomass added to the gasification of coal affects the amount of H_2 in the gas mixture. However, the observed decrease in yield is negligible. Ultimately adding biomass appears to help reduce CO_2 emissions. One of the most important problems during the experimental study states that ash melts in bed and disrupts the fluidization regime in the bed. The melting temperature of ash can be lower than the specified value according to ASTM standards. For this reason, it is recommended not to analyze above 1000 ºC.

Kumabae et al. [46] studied the increase of biomass fraction of raw materials in the change of H_2 in the product gas. The effect in change of H_2 content was noticed from 37.5 % to 47.9 % by volume and the effect in CO_2 from 33.7% to 26.1%. A noticeable difference in carbon conversion was obtained with increasing biomass fraction. The value increased from 59% to 89%. However, the char and tar fraction, which had a significant effect, decreased from 36% to 1% and from 7% to 1%, respectively. The fractions of CO, CH_4 and C_2H_4 gases were relatively independent of the biomass fraction in the feed stream.

Andre et al. studies [72] showed that the amount of biomass (up to 40 wt %) into feedstock plays important role at increasing of hydrocarbon ability to produce in the product gas.

Czaplicki et al. [73] reported that temperature of gasification during co-gasification have significant influence on creating a highly productive process and using of feedstock actively, and also the amount of increasing biomass (75–100 wt %) in feedstock enables fuel to participate in the reaction at maximum level and lower char yield in product gas.

Kern et al. [17] reported that in coal/biomass blends, increasing coal fraction accompanies with dropping of tars liberating in the product gas. The drop in liberated tar depends on

catalytic action of ash in lignite coal which has several chemical components such as Ca, Mg, Fe, and Na. Vreugdenhil et al. [74] and Sjostrom et al. [4] claim the same idea.

Vreugdenhil et al. [74] examined co–gasification of lignite and wood in a fluidized bed gasifier. They resulted in increasing impulse power of char and lesser amount of tar production. These studies come out that the co-gasification is an instrumental in decreasing both in quantity of coal used and the catalyst price.

Since experimental studies bring time loss and cost, there are studies in which gasification process is realized with models created based on experimental data. In this field, package programs, such as Aspen PLUS, are widely used in the design of gasification processes. This program uses two different approaches in modeling of gasification systems. Some models consider the final gas composition in chemical equilibrium, while some models take complex mechanism into account throughout the gasifier. Generally, the modeling can be classified as kinetic models, chemical equilibrium models, artificial neural networks and computational fluid dynamics models [75].

In their work, Mahinpey and Nikoo [76] studied the gasification of biomass in a fluidized bed system operating at atmospheric pressure using the Aspen Plus program. In this model, the approximation that is valid for the bed hydrodynamics and kinetics in the fluidized bed system is written in Fortran code and calculated as nested together with Aspen Plus. In the Aspen Plus model, biomass was defined in the system according to elemental analysis data. Different reactor types were used for gasification reactions in different phases. The Gibbs reactor was used for the reaction of the volatiles, while the continuously stirred tank reactor (RCSTR) was used for the char using the gasification kinetics data written in Fortran. In the model, the effect of bed temperature, air/fuel ratio, particle size change and steam addition on carbon conversion and gas composition were investigated. Increasing bed temperatures showed an increase in carbon conversion and hydrogen production but a decrease in CH_4 and CO formation. It was concluded that the change in particle size had no significant effect on the gas composition. In order to validate the model, experimental data using Scotch shavings in laboratory scale gasifier was used.

2.2.3. Solid Oxide Fuel Cell

SOFC offers potential for high conversion efficiency, high energy utilization, low emissions. The focus of this study is to advance a SOFC model by using Aspen Pluss' current functions and unit operation models. This approach uses the facilities provided by the process simulator. In addition, it supplies an advantageous procedure owing to performing detailed thermodynamic and parametric analysis of SOFC based power generation cycles [45]. This model calculates the Nernst voltage, the current density, the necessary cell surface as well as other dependent values on the choice of fuel inlet, operating voltage and fuel utilization.

Briefly stated, the working principle of SOFC in this dissertation is as follows. The compressor compresses the fuel and the heater block increases the temperature of syngas for fuel cell operating conditions. Mixer block combines the fresh fuel and recirculate anode gas. Splitter manipulates the amount of exhaust gas that leaves the anode block for recirculation. Reformer is a Gibbs reactor which are based on Gibbs free energy minimization. Anode is also a Gibbs reactor that simulates the electrochemical reaction and this reaction occurs between H_2 and O_2. Cathode is an Aspen Plus separator block that separates O_2 from air needed by the electrochemical reaction. Unburned H_2 and CO are burned in postcombuster reactor to release energy. Heat exchanger block supplies heat to the air feeding cathode block.

3. RESULTS

3.1.Preparation of Biomass and Coal Samples

The samples used in this study were provided from local producers and Turkish Coal Enterprises Institution. Rice straw was chosen as a biomass feedstock from local producers in Çanakkale. All samples were grinded, and particles sieved under 250 μm. The shredder "IKA M20 Universal Mill" was used to reduce the particle size of biomass and "Mortar Grinder Retsch RM 200" for coal samples to grind.

3.2. Feedstock Characterization

HCOALGEN models are used to calculate the enthalpy and DCOALIGT are for the density of non-conventional components. The HCOALGEN model requires proximate analysis, ultimate analysis, and sulfur analysis results for non-conventional components. Aspen Plus representations are PROXANAL, ULTANAL, SULFANAL, respectively. The proximate analysis defines in terms of moisture and ash content, fixed carbon, volatile matter, while the ultimate analysis tells the composition of coal ash, carbon, hydrogen, nitrogen, chlorine, sulfur, and oxygen. The sulfur analysis gives the weight fractions of sulfur divided into pyritic, sulfate, and organic sulfur. The DCOALIGT model requires the determination of ULTANAL and SULFANAL component properties.

3.2.1. Proximate Analysis

The proximate analysis values were obtained from experiments that were carried out in Thermal Analysis Laboratory, Marmara University Faculty of Engineering. Experiments were performed according to ASTM Standard D5142-04 standards via "Netzsch 409 PC" thermogravimetric analysis device. Proximate analysis of the feedstock is given in the Table 3.1.

Table 3.1 Proximate analysis values of Rice straw and Çan lignite

Rice Straw (% wt)		**Çan Lignite (% wt)**	
Moisture	3.11	Moisture	3.04
Volatile Matter	68.50	Volatile Matter	28.83
Fixed Carbon	14.59	Fixed Carbon	26.30
Ash	13.80	Ash	41.83

3.2.2. Ultimate Analysis

Ultimate analysis experiments were performed according to ASTM Standard D5373-2 standards in Advanced Technologies Application and Research Center, Hacettepe University. Elemental analyses of biomass and coal samples were carried out with LECO brand Truspec micro elemental analyzer. Table 3.2 shows the elemental analysis results of biomass and coal used in this study.

Table 3.2 Ultimate analysis results of Rice straw and Çan lignite

Rice Straw (%wt)		**Çan Lignite (%wt)**	
C	38.362	C	30.144
H	5.125	H	2.849
O	53.667	O	60.254
N	0.788	N	0.689
S	2.057	S	6.062

3.3. Aspen Plus Model

In this study, gasification models were made in Aspen Plus program which is a universal simulation, design and optimization software for complex chemical processes. The gasification process is based on minimizing Gibbs free energy. When the Gibbs free energy is minimized; the process is considered to reach chemical equilibrium in terms of thermodynamics. The assumptions for the gasification process are as follows:

- Feedstock devolatilization products mainly include H_2, CO, CO_2, CH_4 and H_2O.
- Tar and other heavy hydrocarbons are neglected.
- Gasification process is isothermal and steady state.
- All reactions occur rapidly and reach the chemical equilibrium.
- Ash component in solid fuel is not involved in reactions.
- Char includes only ash and carbon.

3.3.1. Co-Gasification Model Development

The design with the blocks of the co-gasification process for the biomass/coal mixture in Aspen Plus is given in Figure 3.1.

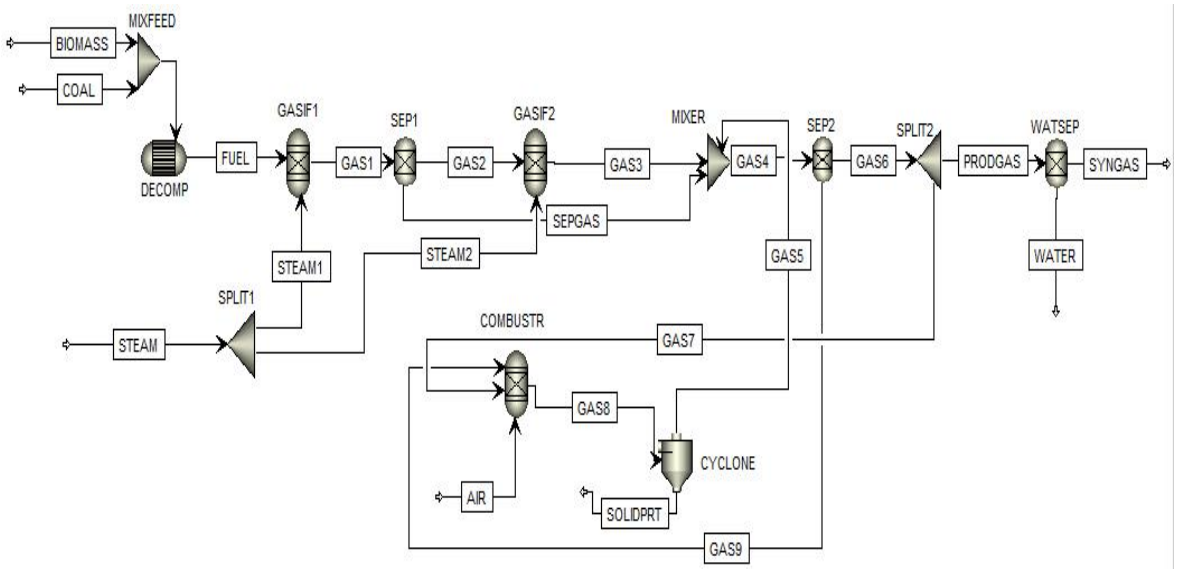


Figure 3.1 Flowsheet of co-gasification process model

The explanations of these blocks are given in Table 3.3. The “COAL” and “BIOMASS” streams define the “unconventional solid” biomass and coal feed. Proximate analysis and ultimate analysis of fuels are used as input in feed streams. These two streams are combined into the mixer to form a single “non-conventional” stream. The feed stream flows into “DECOMP” block named “RYield” reactor; where the “unconventional” stream is converted into a “conventional” feed stream using a certain yield calculation.

Table 3.3 Input values of fluidized bed gasifier block elements developed for biomass/coal mixture

Block Name	**Aspen Plus ID**	**Function**
SPLIT1	FSplit	STEAM1 : % 95 H_2O STEAM2 : % 5 H_2O
SEP1	Sep	SEPGAS : % 100 H_2O % 100 CO_2 % 100 CH_4
SEP2	Sep	SEPGAS2 : % 100 C % 100 ASH
WATSEP	Sep	WATER : % 100 H_2O

The fuel reacts with the gasification agent that comes from the stream separator “SPLIT1” in the “RGibbs” reactors “GASIF1” and “GASIF2“. In the “COMBUSTR” reactor which is a “RGibbs”, unburned carbon and ash run in a combustion reaction, while the solid particles are removed from the gas in the cyclone. In the separator named “SEP1”, products of the first reactor are separated at a certain rate and prevented from entering the second reactor. In the “SEP2” separator, unconverted carbon and ash are separated and sent to the reactor for combustion. In the “WATSEP” separator, the water and/or nitrogen in the “PRODGAS” is purged to give a dry and/or inert free syngas.

3.3.2. Solid Oxide Fuel Cell Model Development

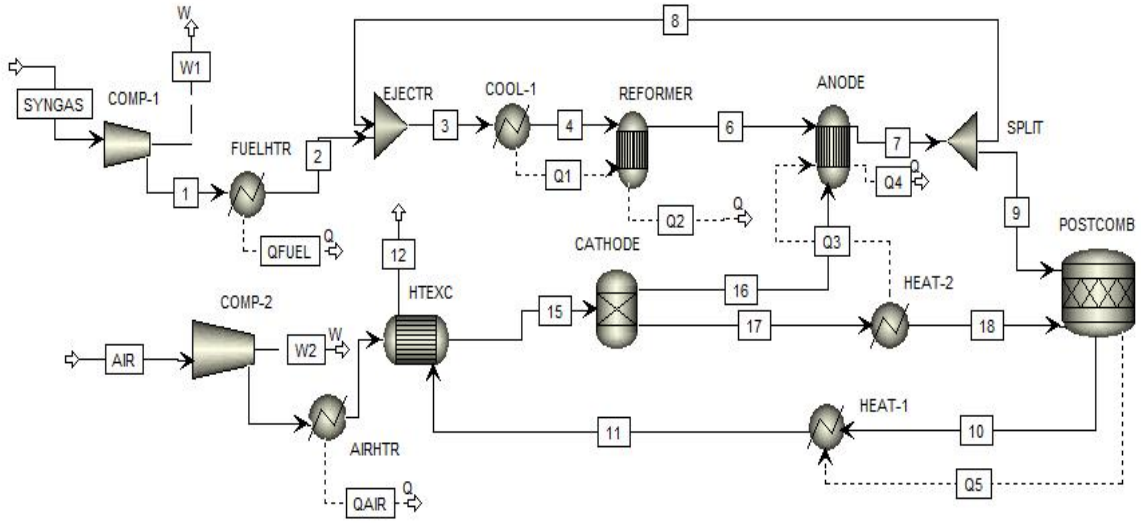


Figure 3.2 Flowsheet of solid oxide fuel cell model

The flow diagram of the solid oxide fuel cell is given in Figure 3.2. The stream "SYNGAS" represents the product of fluidized bed gasifier and used as fresh fuel for SOFC. Fuel is compressed in “COMP-1” block and pressure ratio is 3.0 [77]. “FUELHTR” which is an Aspen Plus heater block increases the temperature of syngas for fuel cell operating conditions. This pressure ratio is important because fresh syngas stream leads the recirculated anode exhaust stream that includes the heat and steam essential for autothermal reforming. “EJECTR” is a mixer block and standing to combine the fresh fuel and recirculated anode gas. “SPLIT” manipulates the amount of exhaust gas that leaves the “ANODE” for recirculation.

The autothermal reforming of syngas is simulated in “REFORMER” which is a Gibbs reactor. Gibbs reactor blocks are based on Gibbs free energy minimization. Normally, some other hydrocarbons occur in reformer, but it is assumed that at high operating temperature in SOFC hydrocarbons are reformed to H_2 and CO. Hydrogen is assumed more oxidizable and only fuel electrochemically consumed. This assumption simplifies the electrochemical behavior of the SOFC [78].

“ANODE” is also a Gibbs reactor that simulates the electrochemical reaction and this reaction occurs between H_2 and O_2. The “AIR” stream is compressed little higher than atmospheric pressure in “COMP-2” and heated up in “AIRHTR” block. Subsequently, pre-heated air is more heated in so-called “HTEXC” heat exchanger by the hot exhaust gas coming from the “POSTCOMB” reactor.

Heated and compressed air stream which is “15” enters the “CATHODE”. “CATHODE” is an Aspen Plus separator block that separates O_2 from air needed by the electrochemical reaction. This block, as a result, simulates the solid oxide fuel cell cathode. The temperature of stream “17”, which is evacuated air, is heated up in heater block “HEAT-2”.

The stream “7” which comes from “ANODE” block majorly includes steam with some unburned CO and H_2. While a portion of the discharged air is returned to the "EJECTR" block by the recirculating stream, the continuing stream is sent to the "POSTCOMB" reactor. Unburned H_2 and CO are burnt in this reactor. Streams "9" and "18" are burnt in the "POSTCOMB" reactor to release energy, and this energy heats up the stream "11". This part of the process is simulated with RStoic reactor and heater block named "HEAT-1". The high temperature "11" stream flows to the heat exchanger "HTEXC" to supply heat to the air feeding "CATHODE" block.

3.4. Model Validation

3.4.1. Validation of Fluidized Bed Gasifier

In order to validate the accuracy of the model, information such as syngas compositions, input variables and operating conditions was obtained from various experimental studies. In Table 3.4 and 3.5, there are experimental studies for gasification of coal and biomass, Table 3.6 shows experimental data for co-gasification.

Table 3.4 Comparison of the literature and the model for coal

1	Sample	Comp. (%vol.)	Literature **[79]**	The Developed Model
	Coal Coke	CH_4	1.0	1.8
		H_2	46.0	46.5
		CO	44.0	43.1
		CO_2	4.0	4.1
	Temperature (°C)		800	800
	Pressure (bar)		1.013	1.013
	Fuel Rate (kg/h)		1	1
	Steam Rate (kg/h)		1	1
	Steam Temperature (°C)		152	152
2	Sample	(%dry vol.)	Literature [80]	Model
	Xuzhou Bituminous Coal	CH_4	2.3	2.4
		H_2	10.6	10.0
		CO	10.5	10.7
		CO_2	15.3	14.2
	Temperature (°C)		940	940
	Pressure (MPa)		0.5	0.5
	Steam Rate (kg/h)		3.04	3.04
	Fuel Rate (kg/h)		8	8
	Steam Temperature (°C)		300	300
	Air Rate (kg/h)		25.67	25.67
	Air Temperature (°C)		300	300

Table 3.5 Comparison of the literature and the model for biomass

1	Sample	Comp.(%dry vol.)	Literature **[81]**	The Developed Model
	Hazelnut Shell	CH_4	9.5	9.1
		H_2	28.9	28.9
		CO	21.7	28.4
		CO_2	31.8	32.5
	Temperature (°C)		850	850
	Pressure (bar)		1.013	1.013
	Fuel Rate (kg/h)		122	122
	Steam Rate (kg/h)		48.8	48.8
	Steam Temperature (°C)		-	152
	Oxygen Rate (kg/h)		44	44
2	Sample	Comp. (%dry vol.)	Literature [82]	Model
	Woody Biomass	CH_4	6.0	9.4
		H_2	49.0	49.2
		CO	20.0	19.9
		CO_2	23.0	21.0
	Temperature (°C)		800	800
	Pressure (bar)		1.013	1.013
	Steam Rate (kg/s)		0.45	0.45
	Fuel Rate (kg/s)		1	1
	Steam Temperature (°C)		180	180
	Air Rate (kg/s)		1.84	1.84
	Air Temperature (°C)		280	280

Table 3.6 Comparison of the literature and the model for coal & biomass mixture

1	Sample	Comp. (% vol.)	Literature **[83]**	The Developed Model
	Pine Wood & German Brown Coal	CH_4	5.0	9.0
		H_2	35.0	35.0
		CO	9.0	10.0
		CO_2	18.0	18.0
	Temperature (°C)		800	800
	Pressure (bar)		1.013	1.013
	Steam / Biomass		0.92	0.92
	Biomass : Coal		7 : 3	7 : 3
2	Sample	Comp. (%dry vol.)	Literature [84]	Model
	Tabas Coal & Wood Waste	CH_4	8.4	13.1
		H_2	41.2	40.4
		CO	31.5	31.4
		CO_2	18.8	16.4
	Temperature (°C)		850	850
	Pressure (atm)		20	20
	Steam Rate (kg/h)		6.0	6.0
	Fuel Rate (kg/h)		7.5	7.5
	Coal / Feed		0.5	0.5

As seen in the tables, the results of the newly developed fluidized bed model in Aspen Plus successfully show similarity with experimental studies from literature. CH_4 gas may be different in some experiments because methane formation reactions do not have enough time to reach equilibrium in experimental studies. However, the simulation acknowledges that the reactions reach to chemical equilibrium quickly. The newly developed gasifier model provides acceptable results for the parametric study in the combined fuel cell- gasifier cycle.

3.4.2. Validation of SOFC

Validation was performed on the model to test the reliability of SOFC simulation. Validation of the model was made by using (Campanari, 2001, Zhang et al. 2005)'s paper [77]. Fuel specifications and operating conditions in the literature used as input variables. Validation results can be seen in Table 3.7.

Table 3.7 SOFC model validation results

	Literature **[77]**	Model Results
Voltage (V)	0.7	0.8
Current Density (A/m^2)	1780	1494
Anode Exhaust Gas Composition (vol %)	H_2: 11.6	H_2: 10.6
	CO: 7.4	CO: 6.6
	H_2O: 50.9	H_2O: 53.6
	CO_2: 24.9	CO_2: 25.9
	N_2: 5.1	N_2: 3.1
Cathode Exhaust Gas Composition (vol %)	O_2: 17.7	O_2: 16.1
	N_2: 82.3	N_2: 83.9
Combustion Products Temperature (°C)	1012.35	910.00
Stack Exhaust Gas Composition (vol %)	H_2O: 4.5	H_2O: 6.4
	CO_2: 2.3	CO_2: 3.2
	O_2: 15.9	O_2: 13.8
	N_2: 77.3	N_2: 76.5

According to Table 3.7 the model results have good agreement with the literature results. Especially exhaust gas compositions have quite agreement with published paper. However, there are some slight differences in voltage, current density and combustion products temperature.

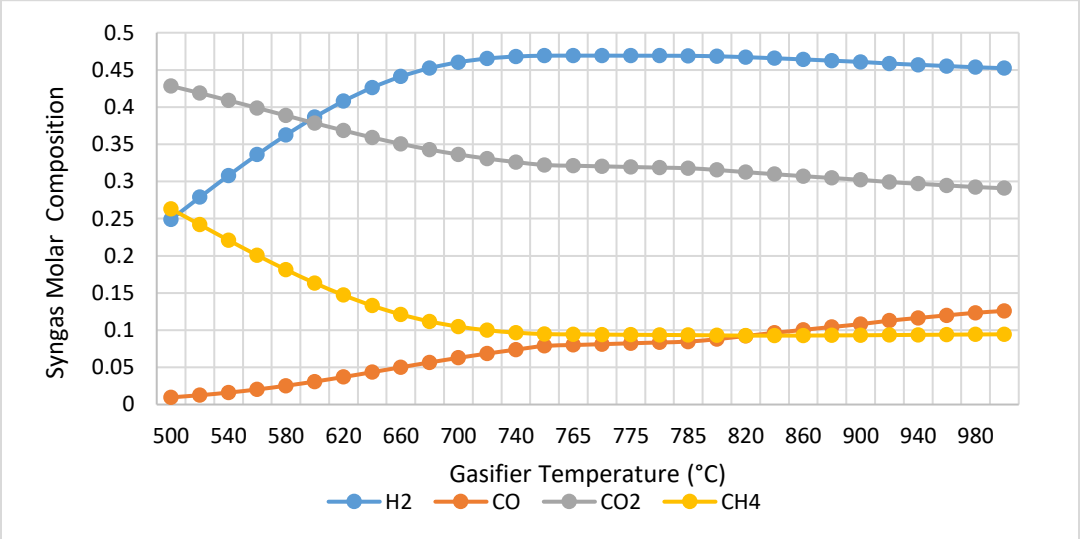
3.5. Parametric Study

In order to observe the gasification characteristics of rice straw and Çan lignite in the fluidized bed, the effect of gasifier temperature and pressure on the synthesis gas composition as well as the effect of steam / fuel ratio on the syngas composition were investigated by parametric studies. Rice straw and Çan lignite were fed separately to the gasifier and optimum conditions were determined for each. Subsequently, the fuels for co-gasification were fed simultaneously and finally the same studies were repeated with CaO catalysis. At the end of parametric study, the effect of catalyst in fluidized bed gasifier on the SOFC stack efficiency was presented.

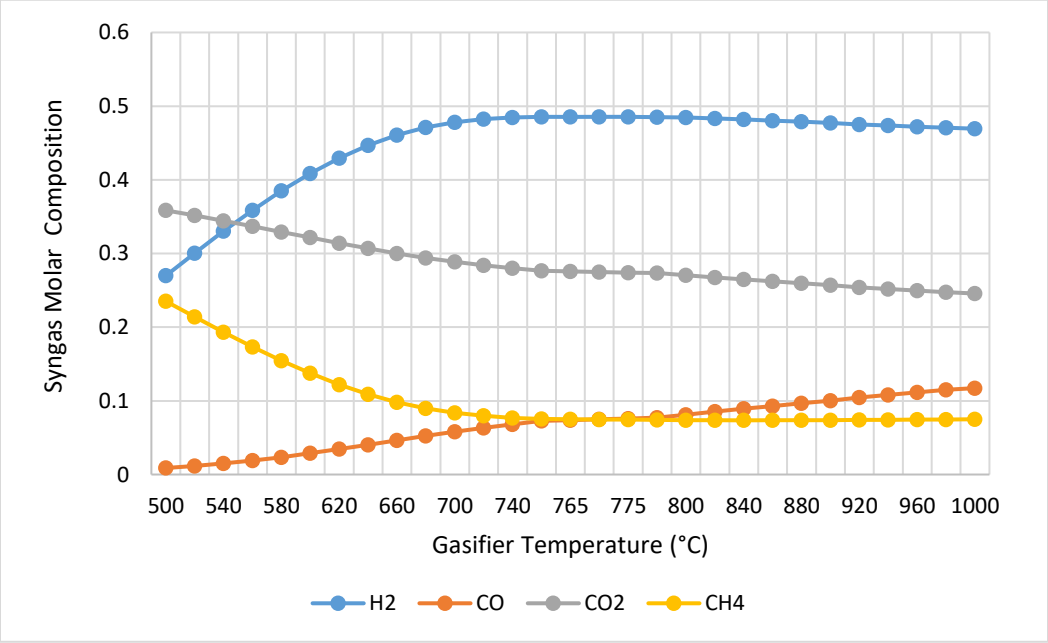
3.5.1. Effect of Gasifier Temperature on Syngas Composition

The effect of gasifier temperature on the synthesis gas composition for rice straw, Çan lignite and their blend is given in Figure 3.3. The gasifier temperature ranges from 500 °C to 1000

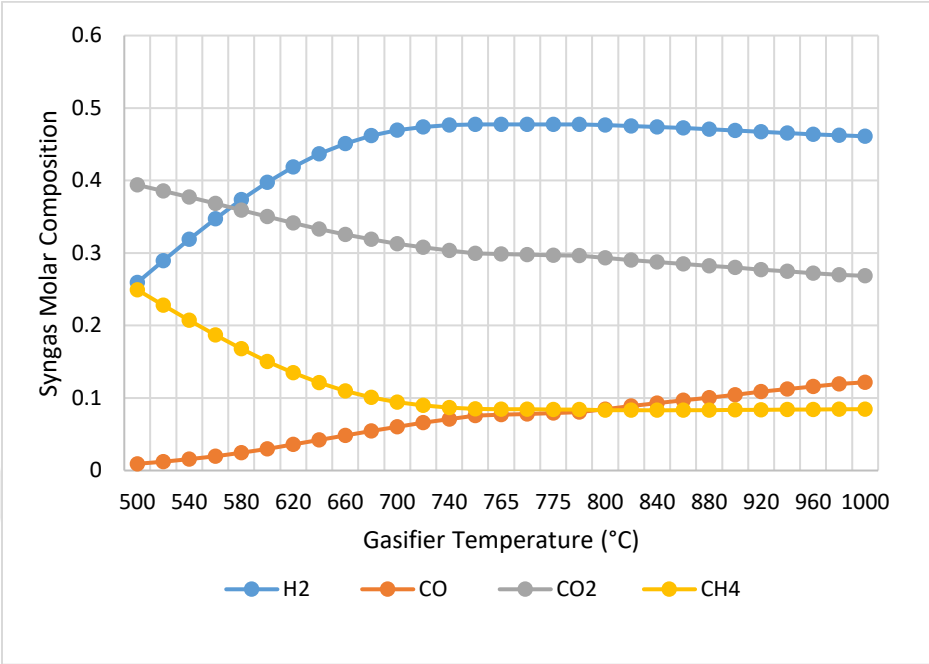
°C, the gasifier pressure is 10 bar and the steam / fuel ratio is 1.4 for biomass, 1.6 for coal and 1.5 for their blend.



(a)



(b)



(c)

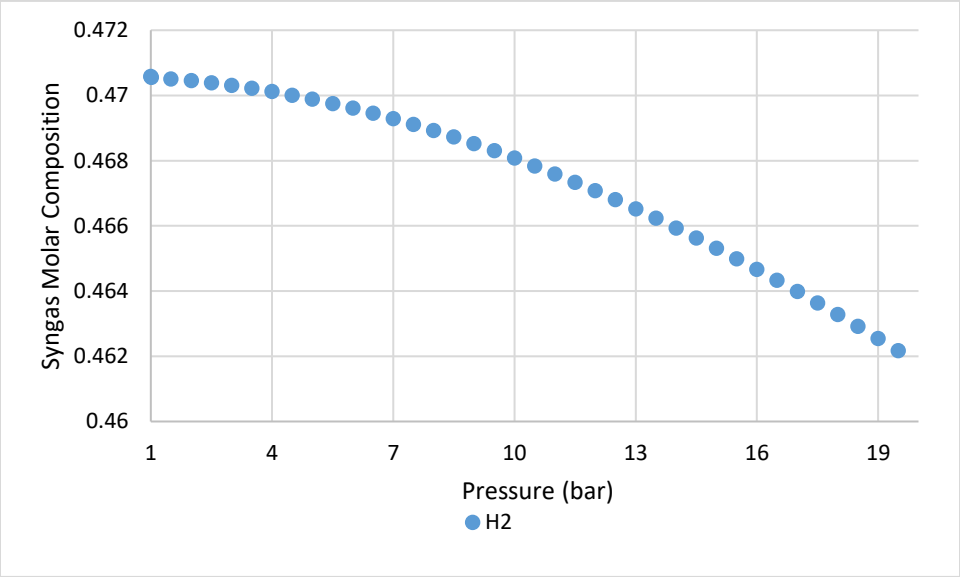
Figure 3.3 Effect of gasifier temperature on syngas composition; (a) Rice Straw, (b) Çan Lignite, (c) Blend

As seen in Figure 3.3, as gasifier temperature increases, H_2 gas molar composition increases; and after a certain peak occurred, H_2 composition decreases. The hydrogen composition reaches to a maximum value at 770 °C for rice straw and at 765 °C for Çan lignite and their blend. As the gasifier temperature increases, the CO concentration increases as well, and the CO_2 concentration decreases. This can be explained by shifting to right side of the Boudouard reaction. CH_4 concentration decreases as the temperature increases, that can be explained by the predominance of the exothermic Water-Gas Shift reaction.

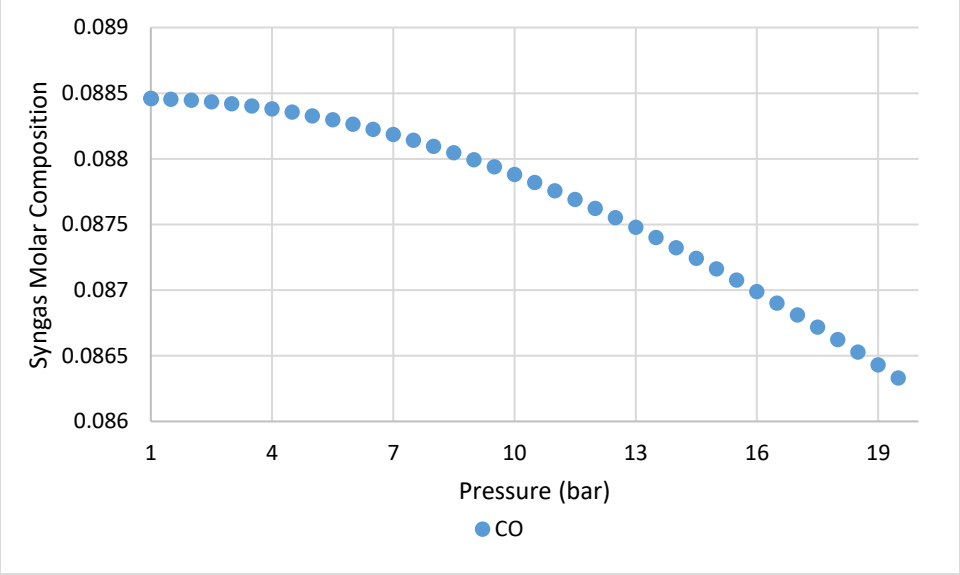
3.5.2. Effect of Gasifier Pressure on Syngas Composition

The gasifier pressure has a significant effect on the change of the synthesis gas composition. The pressure was varied between 1 bar and 20 bar to examine the effect of the gasifier

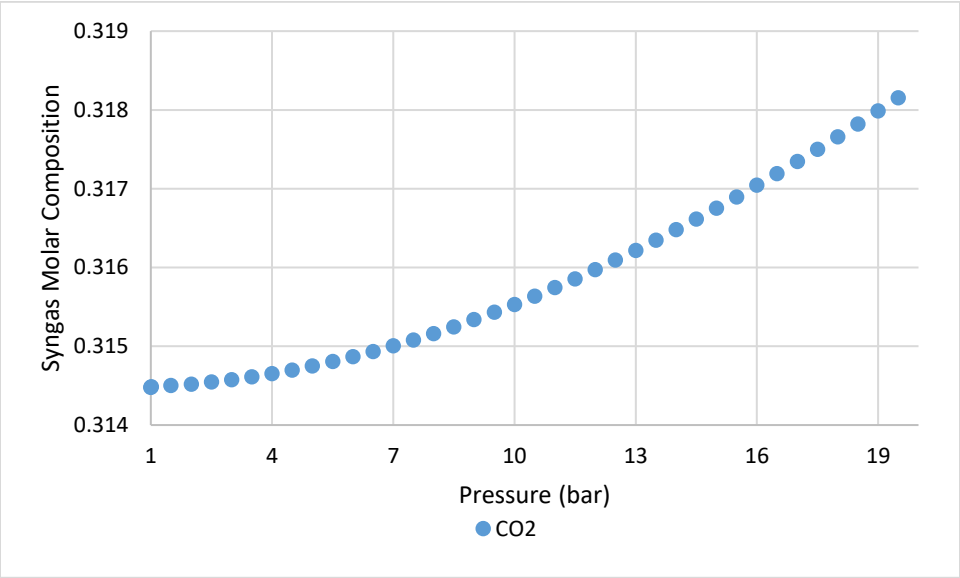
pressure on the synthesis gas composition. The gasifier temperature is constant at 770 °C for biomass and at 765 °C for coal and the blend. The effect of gasifier pressure on the synthesis gas composition is shown in Figure 3.4 for rice straw, in Figure 3.5 for Çan lignite and in Figure 3.6 for the blend.



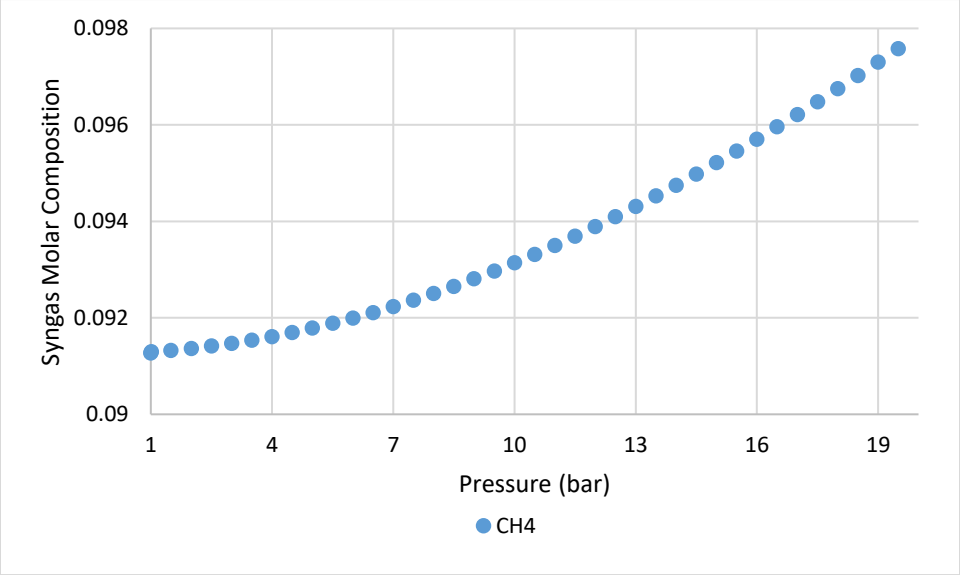
(a)



(b)

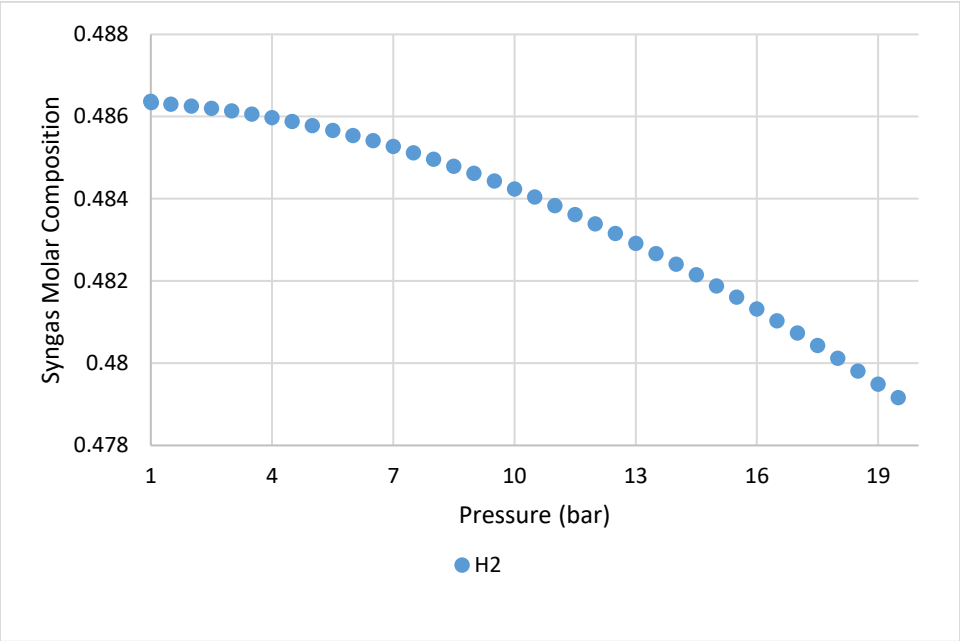


(c)

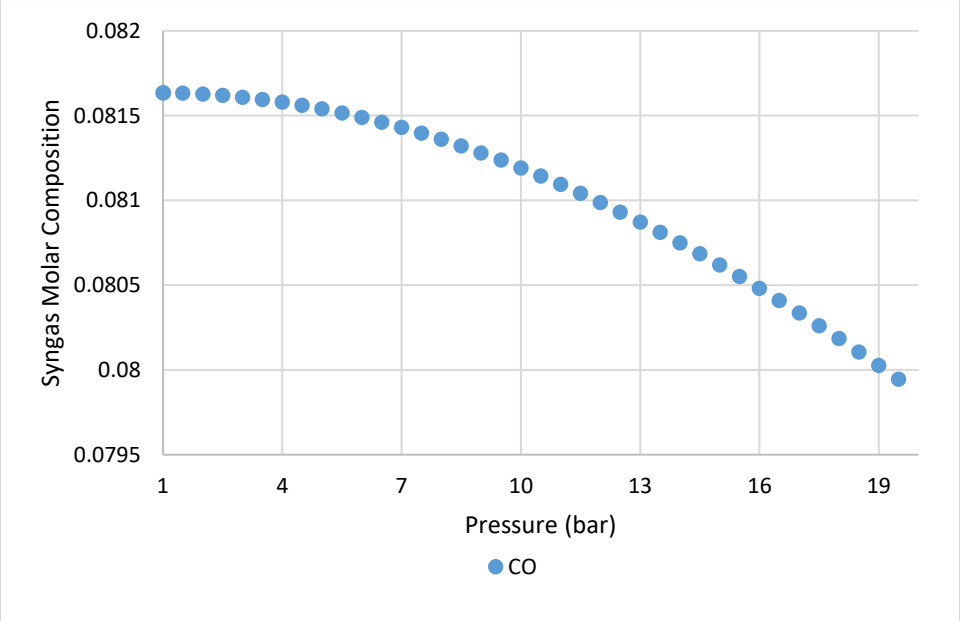


(d)

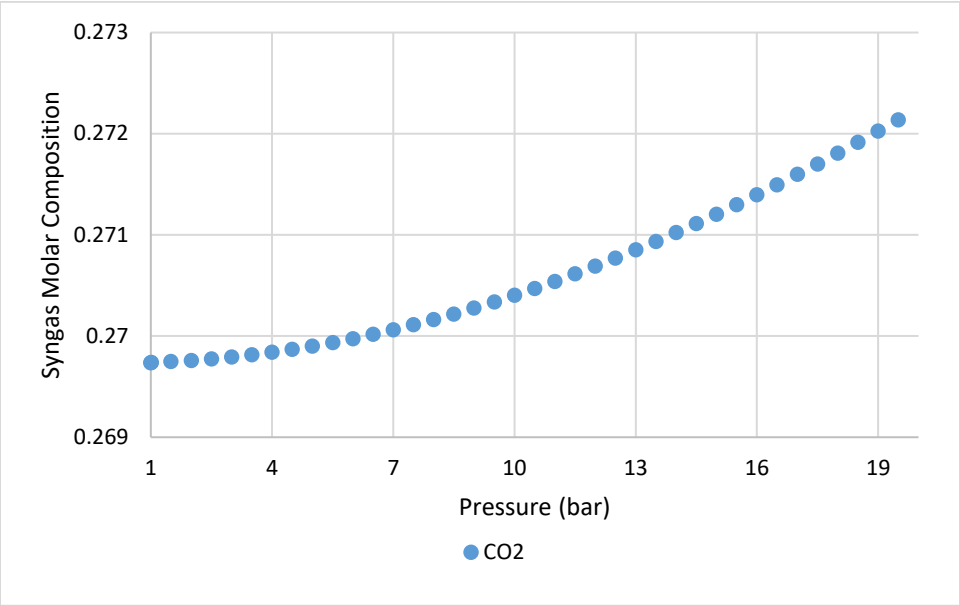
Figure 3.4 Effect of gasifier pressure on syngas composition for rice straw; (a) H_2, (b) CO, (c) CO_2, (d) CH_4


0.488
0.486
0.484
0.482
0.48
0.478
Syngas Molar Composition
1
4
7
10
13
16
19
Pressure (bar)
H2

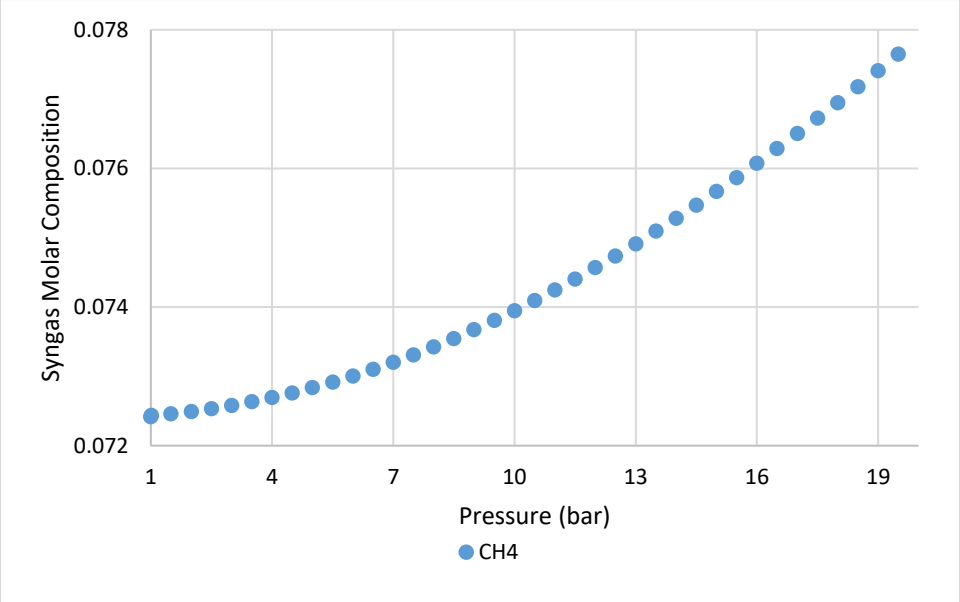
(a)


0.082
0.0815
0.081
0.0805
0.08
0.0795
Syngas Molar Composition
1
4
7
10
13
16
19
Pressure (bar)
CO

(b)

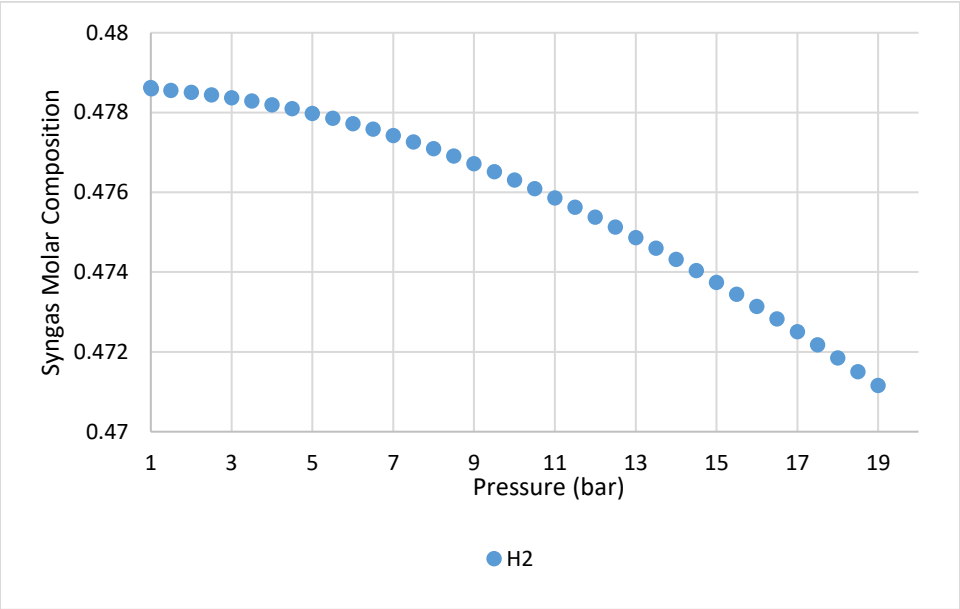


(c)

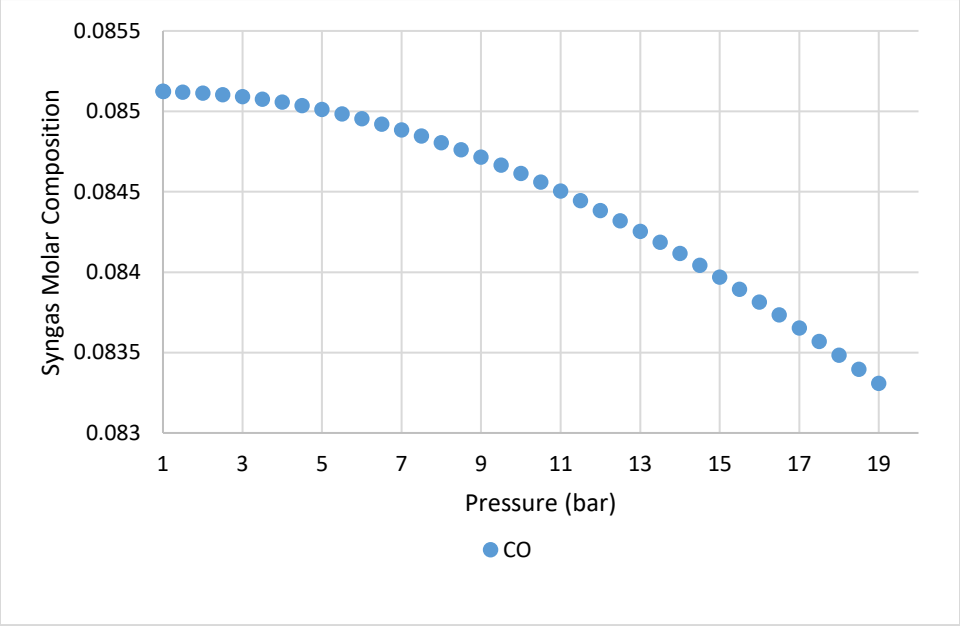


(d)

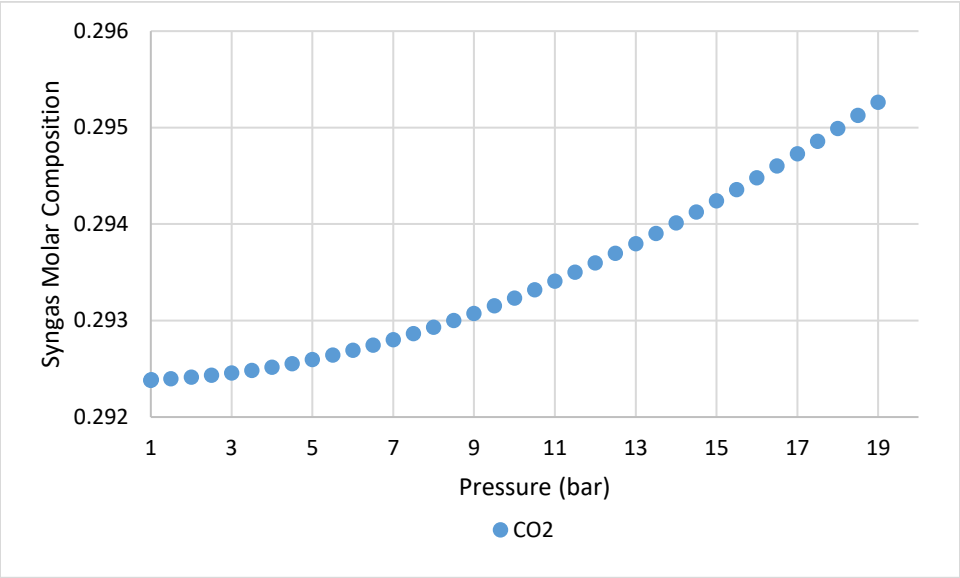
Figure 3.5 Effect of gasifier pressure on syngas composition for Çan lignite; (a) H_2, (b) CO, (c) CO_2, (d) CH_4


0.48
0.478
0.476
0.474
0.472
0.47
Syngas Molar Composition
1
3
5
7
9
11
13
15
17
19
Pressure (bar)
H2

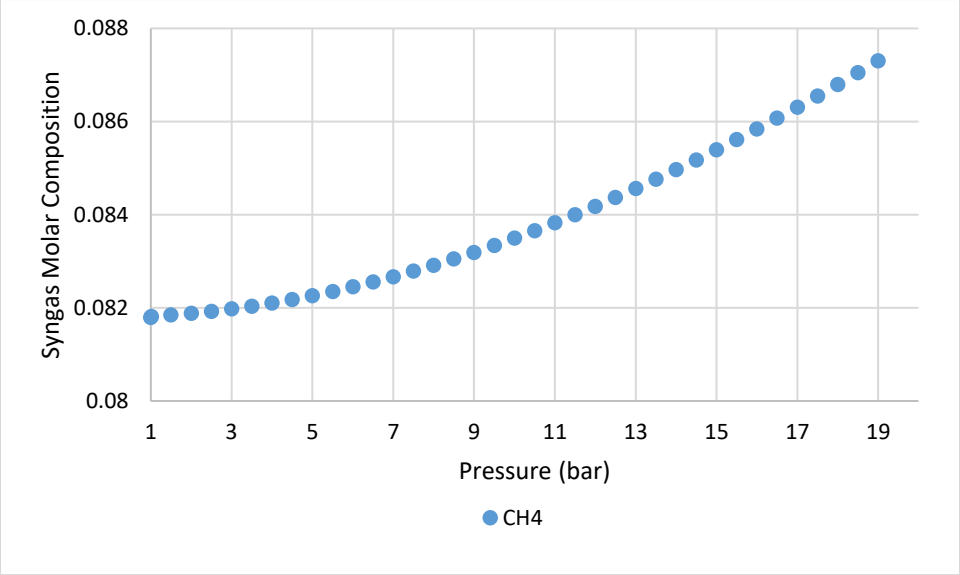
(a)


0.0855
0.085
0.0845
0.084
0.0835
0.083
Syngas Molar Composition
1
3
5
7
9
11
13
15
17
19
Pressure (bar)
CO

(b)



(c)



(d)

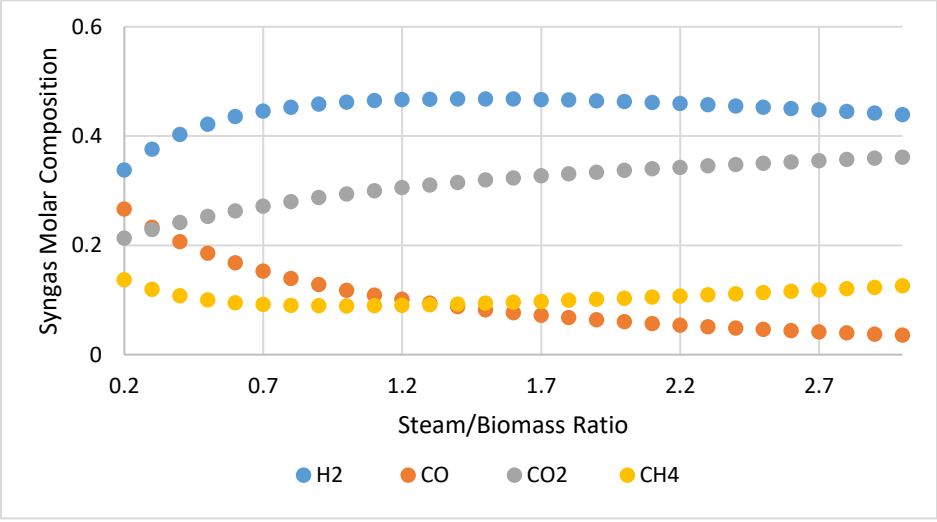
Figure 3.6 Effect of gasifier pressure on syngas composition for blend; (a) H_2, (b) CO, (c) CO_2, (d) CH_4

According to the Le Chatelier principle, when a dynamic equilibrium is changed by a disturbing factor, the system moves in a direction to minimize this effect. Since gasification

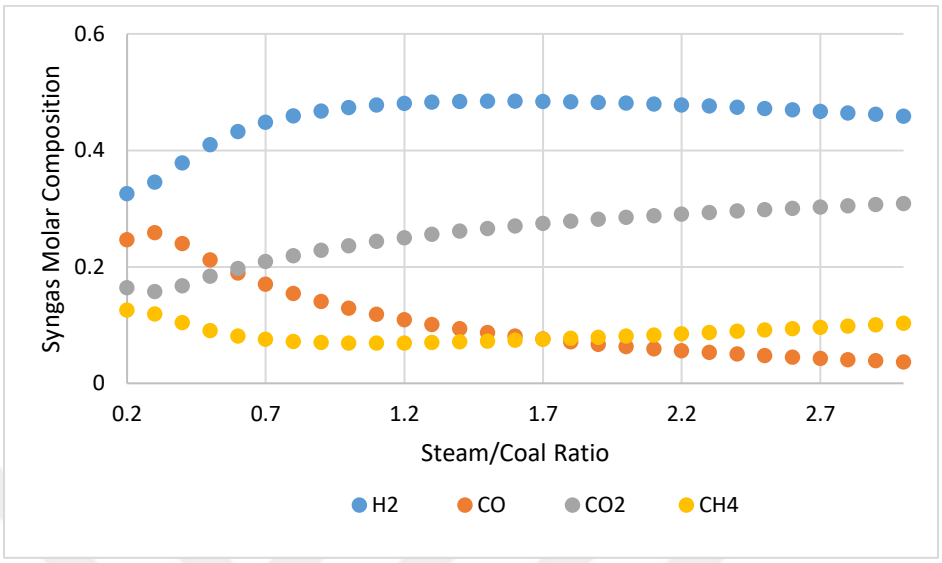
reactions are also equilibrium reactions, the gasifier pressure changes the direction of the reactions and shapes the synthesis gas composition. As the gasifier pressure increases, the concentrations of H_2 and CO gases decrease and the concentrations of CO_2 and CH_4 gases increase. The decrease in CO gas concentration and increase in CO_2 gas concentration can be explained by Boudouard reaction; The decrease in H_2 gas concentration and the increase in CH_4 gas concentration can be explained by the methane-reform reaction. CH_4 gas is the only gas whose concentration increases in precious chemicals at high pressure, so the pressure of the system should be adjusted with this factor in mind.

3.5.3. Effect of Steam/Fuel Ratio on Syngas Composition

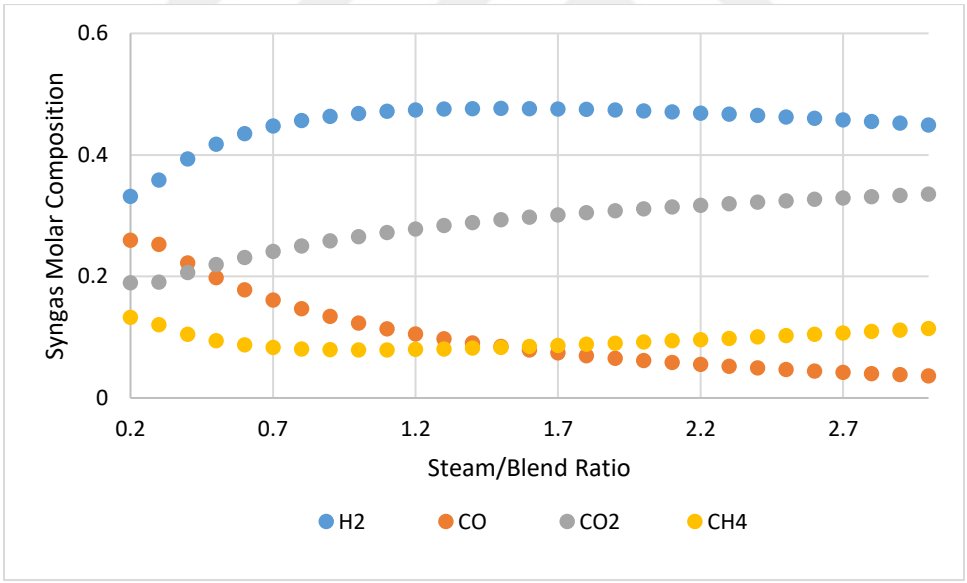
It is important to determine the steam/fuel ratio in order to obtain H_2 gas efficiently at the end of the gasification process. The effect of steam/fuel ratio on synthesis gas composition is shown in Figure 3.7. The steam/fuel ratio ranges from 0.2 to 3 and while the gasifier pressure is kept constant at 10 bar. The gasifier temperature is constant at 770 °C for biomass and 765 °C for coal and blend.



(a)



(b)



(c)

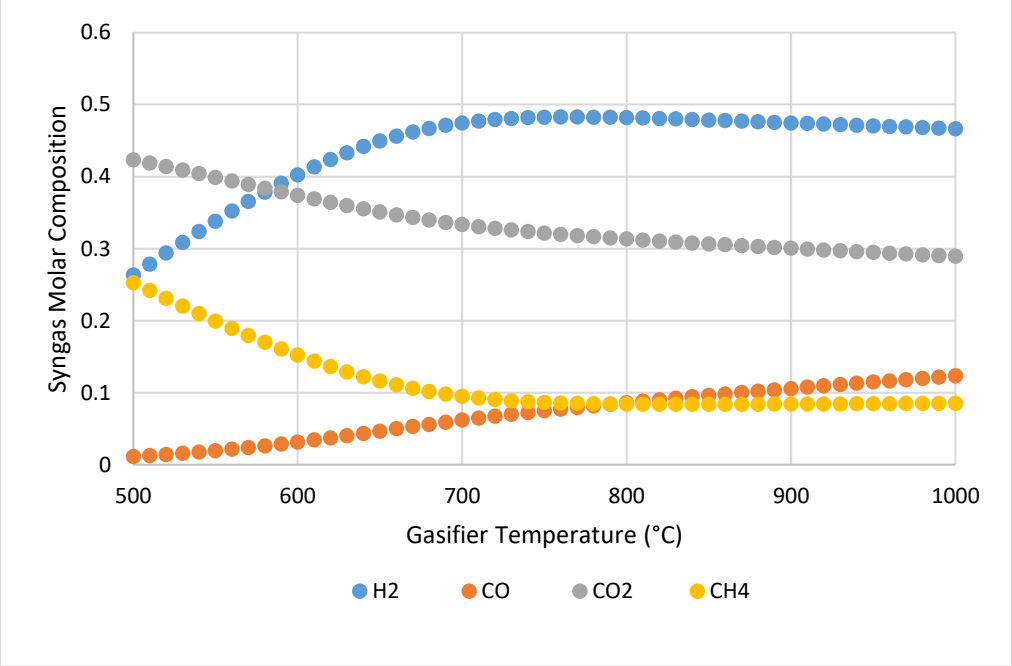
Figure 3.7 Effect of steam/fuel ratio on syngas composition; (a) Rice Straw, (b) Çan Lignite, (c) Blend

As the steam/fuel ratio increases, the H_2 gas fraction increases, but after a certain value, the increase starts slow down or decreases. The steam/fuel ratio with a maximum hydrogen fraction is 1.4 for rice straw, 1.6 for Çan lignite and 1.5 for the blend. Excessive steam flow

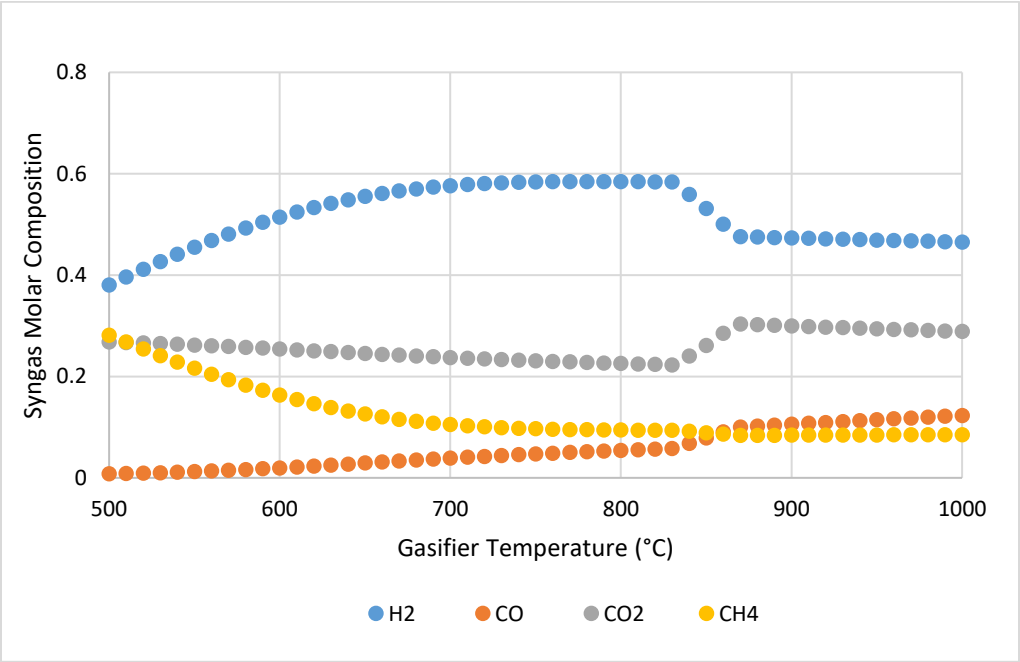
reduces the gasifier efficiency and disrupts the dynamic equilibrium states of complex reactions in the gasifier. As the steam flow increases, CO_2 gas concentration increases as well and CO gas concentration decreases, this phenomenon can be explained by the Water-Gas Shift reaction.

3.5.4. Effect of CaO Catalyst on Syngas Composition

The effect of the catalyst on the synthesis gas composition is shown in Figure 3.8, 3.9 and 3.10. The CaO/fuel ratio is 0.5, the steam/fuel ratio is 1.5, the gasifier pressure is constant at 10 bar, and the gasifier temperature ranges from 500 °C to 1000 °C.

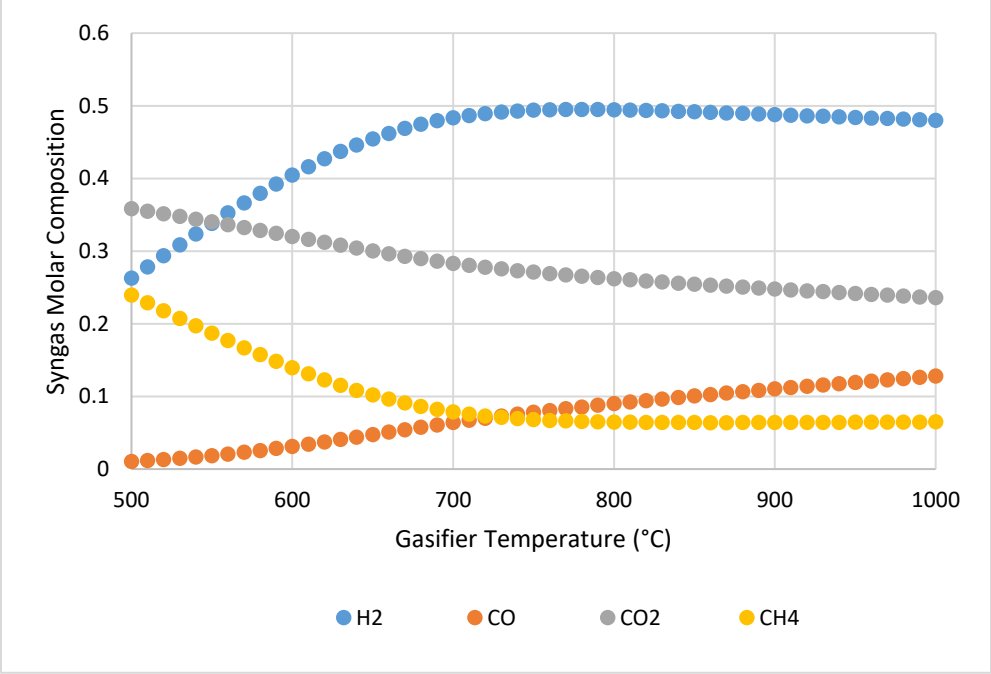


(a)

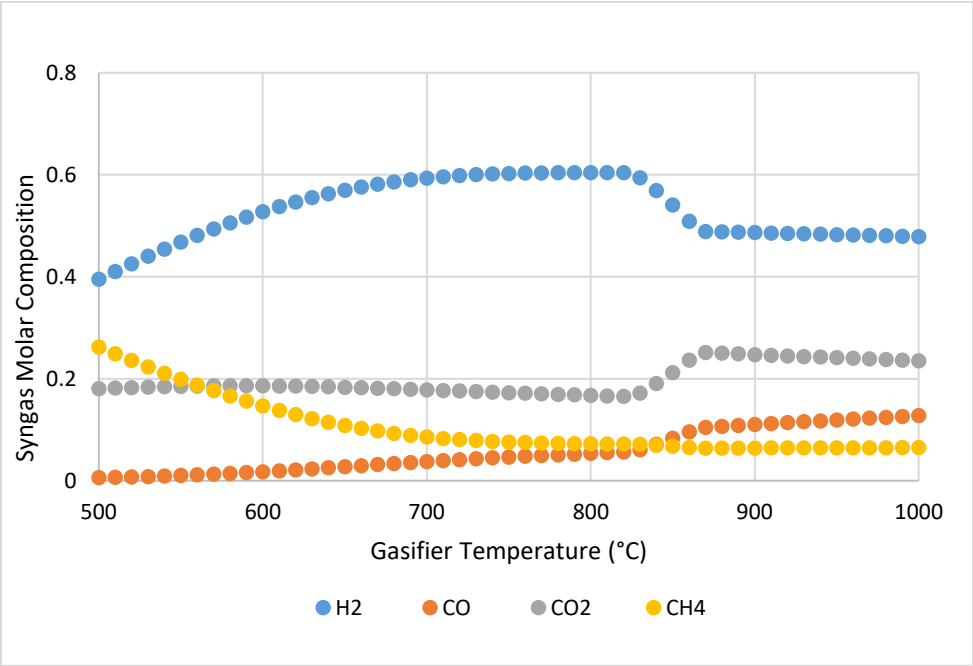


(b)

Figure 3.8 Effect of CaO catalyst on syngas composition for rice straw; (a) without CaO, (b) with CaO

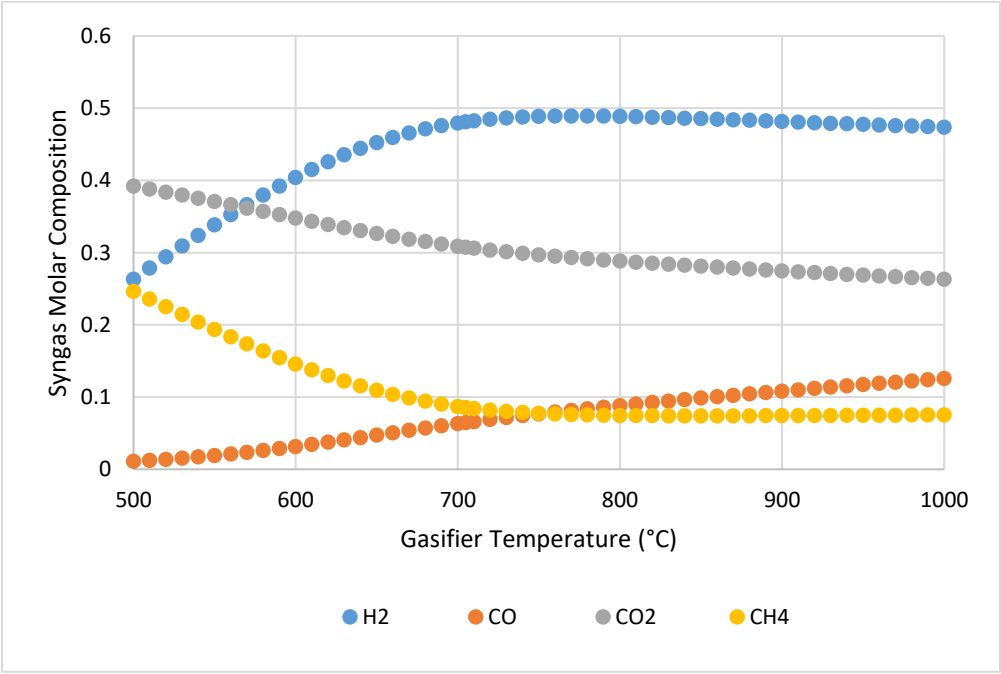


(a)

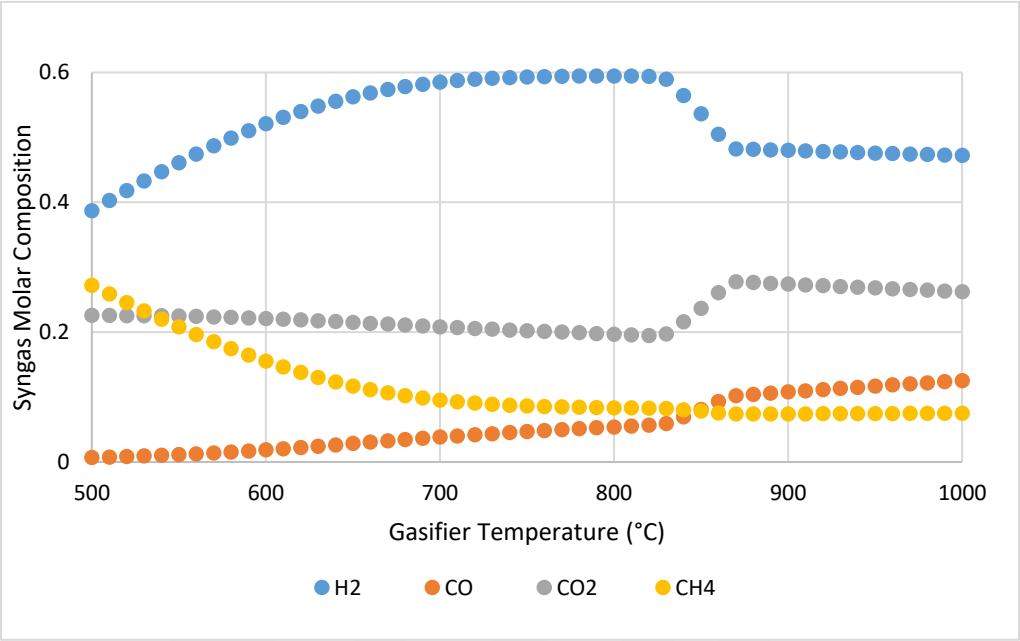


(b)

Figure 3.9 Effect of CaO catalyst on syngas composition for Çan lignite; (a) without CaO, (b) with CaO



(a)



(b)

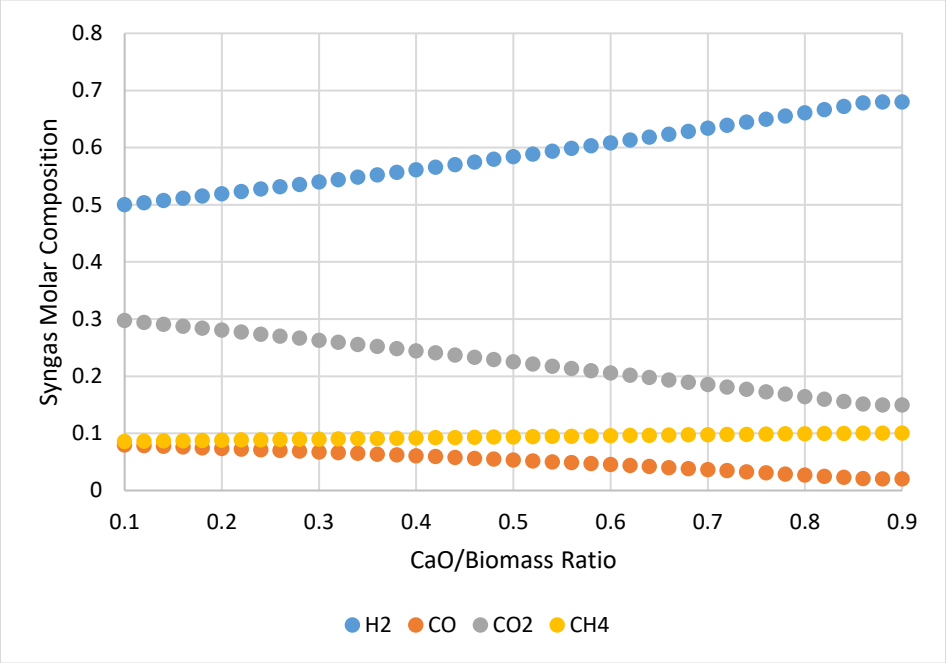
Figure 3.10 Effect of CaO catalyst on syngas composition for blend; (a) without CaO, (b) with CaO

As seen in the results, H_2 gas concentration is higher between 500 °C - 835 °C when catalyst is fed into the gasifier. H_2 gas production at gasification temperatures lower than 750 °C indicates a large increase in the use of CaO catalyst. Due to the adsorption characteristics of the CaO catalyst on the CO_2 gas, the reactions take place in order to increase the concentration of H_2 gas. However, as the temperature increases, especially after 830 °C, the H_2 gas concentration shows a significant decrease, since CaO, which adsorbs the CO_2 gas and transforms into $CaCO_3$, breaks down at high temperature and releases CO_2 gas back into the gasifier. CaO catalyst has no effect at high temperatures. The rapid rise experienced by CO and CO_2 gases can be explained by the lost catalytic effect and the series of complex reactions in the gasifier.

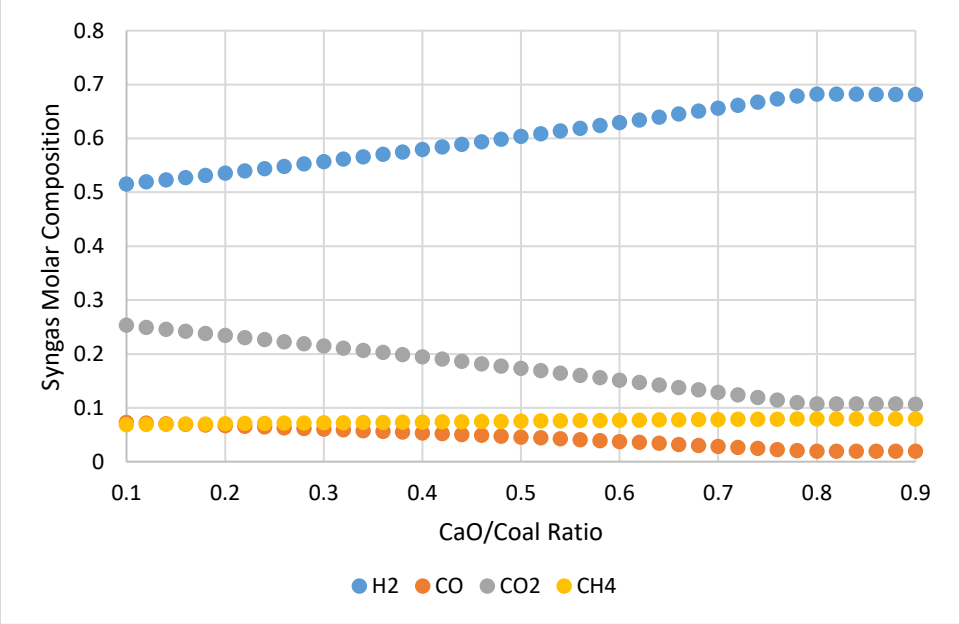
3.5.5. Effect of CaO/Fuel Catalyst on Syngas Composition

The amount of CaO fed to the gasifier affects both the thermodynamic and cost aspects of the gasification process. Parametric study was performed to find the optimum CaO/fuel ratio.

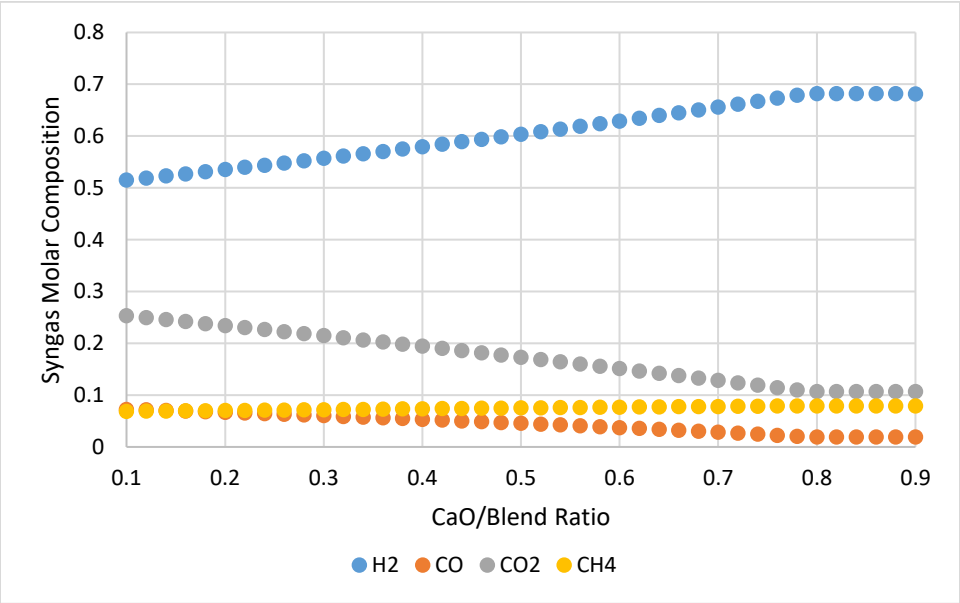
Gasifier pressure is constant at 10 bar and steam/fuel ratio is 1.5 for all fuels; temperature is 770 °C for biomass and 765 °C for coal and blend.



(a)



(b)



(c)

Figure 3.11 Effect of CaO/fuel ratio on syngas composition; (a) Rice Straw, (b) Çan Lignite, (c) Blend

As a result of the parametric studies, it was concluded that increasing the CaO/fuel ratio from 0.1 to 0.8 increased the H_2 gas concentration in the synthesis gas. No significant increase in H_2 gas concentration was observed after CaO/fuel ratio exceeded 0.8. In literature, the most appropriate CaO/fuel ratio is denoted to be around 1.0, but this value varies depending on the characteristics of the fuel and operating conditions.

3.5.6. Effect of Syngas Composition on SOFC Efficiency

To examine SOFC efficiency dependency on syngas composition, different parametric studies were conducted. The fluidized bed gasifier was fed with rice straw, Çan lignite and their blend (50 % biomass – 50 % coal) and optimum operating conditions were determined for each fuel type. Gasifier temperature was 770 °C, 765 °C and 765 °C, steam/biomass ratio was 1.4, 1.6 and 1.5 and CaO/fuel ratio was 0.88, 0.80 and 0.80 for biomass, coal and their blend respectively. These operating conditions relate to the moisture content, fixed carbon, volatile matter and ash content of the fuel. Fuels with a higher fixed carbon content, such as

coal, produce more H_2 gas through complex gasification reactions, but require higher amount of steam.

SOFC stack efficiency was calculated with FORTRAN code in Aspen Plus design spec module. The ratio of lower heating value (LHV) over produced power represents the stack efficiency. Stack efficiencies were determined as 60.402 %, 59.645 % and 60.029 % for biomass, coal and blend respectively.

This phenomenon is related to the content of favorable gases in the synthesis gas. When CaO catalyst is fed into the gasifier stack efficiencies are 61.382 %, 60.877 % and 61.141 % for biomass, coal and blend respectively. This can be explained the adsorption CO_2 leads the increment of H_2 which is important fuel source for fuel cells.

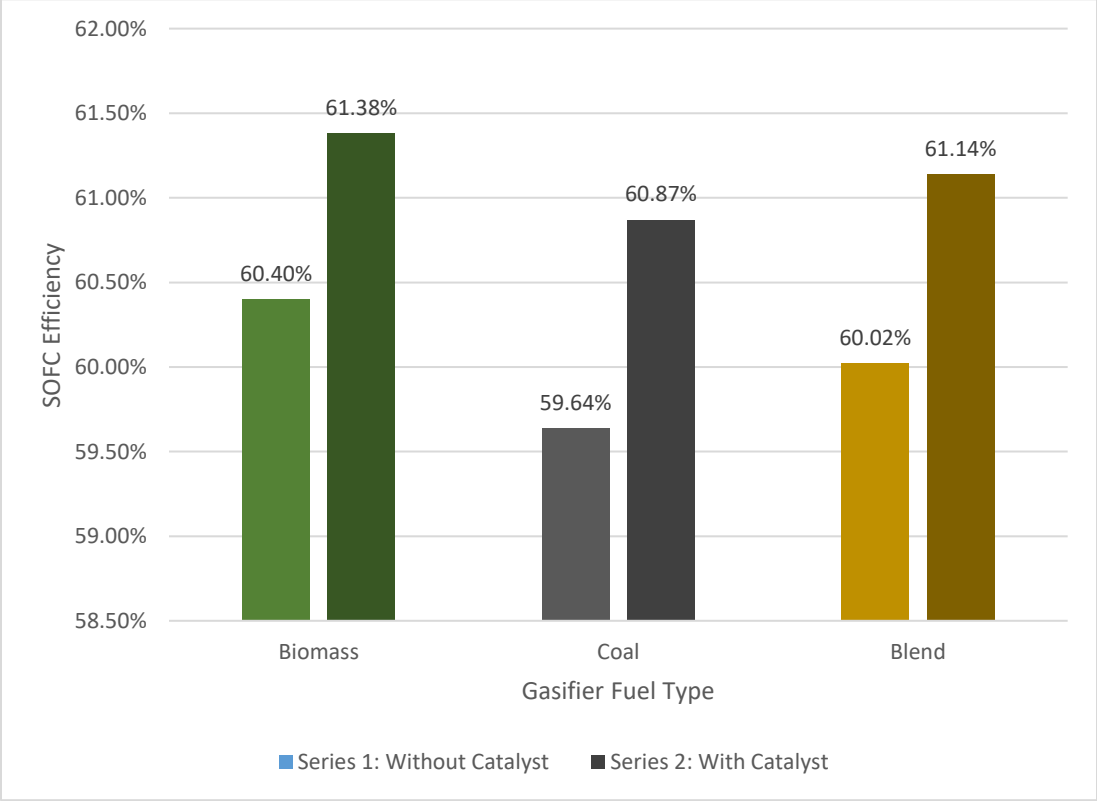


Figure 3.12 Effect of syngas composition on solid oxide fuel cell

4. CONCLUSION

This work deals with the design and assessment of the integrated SOFC/catalytic gasification (Çan coal and/or Rice straw with CaO) operates at higher temperature. The syngas composition from the developed gasifier model was used as the feed stream of the solid oxide fuel cell modelled in Aspen Plus. The effect of operating conditions on gas composition was examined. According to the data obtained:

- Modeling based methods provide alternative and cost-effective accession as compared with experimental studies to the designing and optimization of complicated systems. The Aspen plus is a useful program to design and optimize system parameters for power systems, which includes gasifiers and fuel cells.
- Aspen Plus models in this study for fluidized bed gasifier and SOFC are considered to reach chemical equilibrium in terms of thermodynamics.
- CH_4 gas composition in syngas from the developed fluidized bed gasifier may be different in some experiments because methane formation reactions do not have enough time to reach equilibrium in experimental studies however, the simulation acknowledges that the reactions reach quickly chemical equilibrium.
- As the steam/fuel ratio increases, the H_2 gas fraction increases, but after a certain value, the increase starts slow down or decreases.
- The most appropriate CaO / fuel ratio is denoted to be around 1.0, but this value varies depending on the characteristics of the fuel and operating conditions of gasifiers. In this study, it was concluded that increasing the CaO / fuel ratio from 0.1 to 0.8 increased the H_2 gas concentration in the synthesis gas. No significant increase in H_2 gas concentration was observed after the CaO / fuel ratio exceeded about 0.8.
- The SOFC model results have good agreement with the literature. Especially exhaust gas compositions have quite agreement with published paper. However, there are some slight differences for voltage, current density and combustion products temperature.
- When CaO catalyst is fed into the gasifier model, the stack efficiencies for SOFC model are 61.382 %, 60.877 % and 61.141 % for biomass, coal and blend,

respectively. Results showed that CaO as a catalyst in fluidized bed gasifier increased the stack efficiency.

- The gasifier temperature ranges from 500 °C to 1000 °C. The hydrogen composition reaches a maximum value of 770 °C for rice straw and 765 °C for Çan lignite and blend. After the appropriate temperature, a certain H_2 formation peak occurred and then decreased. While the evolved CO increases, the CO_2 and CH_4 formation decreases.
- In this study, the pressure was varied between 1 bar and 20 bar. As the gasifier pressure increases, the concentrations of H_2 and CO gases decrease and the concentrations of CO_2 and CH_4 gases increase. Consequently, it was observed that working at lower pressures was more appropriate.
- In the presence of catalysts, the hydrogen concentration in the systems reaches the highest level between 500 °C to 850 °C. H_2 gas production at gasification temperatures lower than 750 °C indicates a large increase in the use of CaO catalyst as the temperature increases, especially after 830 °C, the H_2 gas concentration shows a significant decrease, since CaO, which adsorbs the CO_2 gas and transforms into $CaCO_3$, breaks down at high temperature and releases CO_2 gas back into the gasifier. CaO catalyst has no effect at high temperatures.

REFERENCES

1. Chen, G., et al. (2004) Biomass gasification integrated with pyrolysis in a circulating fluidised bed. Solar Energy, 76(1-3), 345-349.
2. Howaniec, N. and A. Smolinski. (2013) Steam co-gasification of coal and biomass - Synergy in reactivity of fuel blends chars. International Journal of Hydrogen Energy, 38(36), 16152-16160.
3. Yan, L.B. and B.S. He. (2017) On a clean power generation system with the co-gasification of biomass and coal in a quadruple fluidized bed gasifier. Bioresource Technology, 235, 113-121.
4. Sjöström, K., et al. (1999) Promoted reactivity of char in co-gasification of biomass and coal: synergies in the thermochemical process. Fuel, 78(10), 1189-1194.
5. Cao, C., et al. (2017) Co-gasification of Alkaline Black Liquor and Coal in Supercritical Water at High Temperatures (600–750° C). Energy & Fuels, 31(12), 13585-13592.
6. Madhiyanon, T., P. Sathitruangsak, and S. Soponronnarit. (2009) Co-combustion of rice husk with coal in a cyclonic fluidized-bed combustor (ψ-FBC). Fuel, 88(1), 132-138.
7. Lapuerta, M., et al. (2008) Gasification and co-gasification of biomass wastes: effect of the biomass origin and the gasifier operating conditions. Fuel processing technology, 89(9), 828-837.
8. Pan, Y., et al. (2000) Fluidized-bed co-gasification of residual biomass/poor coal blends for fuel gas production. Fuel, 79(11), 1317-1326.
9. Rapagna, S. and A. Latif. (1997) Steam gasification of almond shells in a fluidised bed reactor: the influence of temperature and particle size on product yield and distribution. Biomass and Bioenergy, 12(4), 281-288.
10. Gebhard, S.C., et al. (1994) Catalytic conditioning of synthesis gas produced by biomass gasification. Biomass and Bioenergy, 7(1-6), 307-313.
11. Balat, M. (2008) Hydrogen-rich gas production from biomass via pyrolysis and gasification processes and effects of catalyst on hydrogen yield. Energy Sources, Part A, 30(6), 552-564.
12. Huber, G.W., S. Iborra, and A. Corma. (2006) Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering. Chemical reviews, 106(9), 4044-4098.
13. Wan Ab Karim Ghani, W., et al. (2009) Air gasification of agricultural waste in a fluidized bed gasifier: hydrogen production performance. Energies, 2(2), 258-268.
14. Wei, L., et al. (2007) Steam gasification of biomass for hydrogen-rich gas in a free-fall reactor. International Journal of Hydrogen Energy, 32(1), 24-31.
15. Xiaoqin Yang, X.L., Rui Lib, Chuang Liu, Tao Qing, Xiaoming Yue. (2018) Co-gasification of thermally pretreated wheat straw with Shengli lignite for hydrogen production. Renewable Energy, 117, 501-508.
16. Saw, W.L. and S.S. Pang. (2013) Co-gasification of blended lignite and wood pellets in a 100 kW dual fluidised bed steam gasifier: The influence of lignite ratio on producer gas composition and tar content. Fuel, 112, 117-124.

17. Kern, S., C. Pfeifer, and H. Hofbauer. (2013) Co-Gasification of Wood and Lignite in a Dual Fluidized Bed Gasifier. Energy & Fuels, 27(2), 919-931.
18. Miccio, F., et al. (2012) Combined gasification of coal and biomass in internal circulating fluidized bed. Fuel Processing Technology, 95, 45-54.
19. Brown, R.C., Q. Liu, and G. Norton. (2000) Catalytic effects observed during the co-gasification of coal and switchgrass. Biomass & Bioenergy, 18(6), 499-506.
20. Mallick, D., P. Mahanta, and V.S. Moholkar. (2017) Co-gasification of coal and biomass blends: Chemistry and engineering. Fuel, 204, 106-128.
21. Hofmann, P., et al. (2008) Integrating biomass gasification with solid oxide fuel cells: Effect of real product gas tars, fluctuations and particulates on Ni-GDC anode. International Journal of Hydrogen Energy, 33(11), 2834-2844.
22. REN21, J. (2009) *Renewables Global Status Report*.(2009) http://www.unep.fr/shared/docs/publications/RE_GSR_2009_Update.pdf (2009).
23. Speight, J.G., (2011). The biofuels handbook, Royal Society of Chemistry.
24. Staff, I., (2004). Energy Policies of IEA Countries: 2004 Review-Special, Simon and Schuster.
25. Beheshti, S., H. Ghassemi, and R. Shahsavan-Markadeh. (2015) Process simulation of biomass gasification in a bubbling fluidized bed reactor. Energy Conversion and Management, 94, 345-352.
26. Antonopoulos, I.S., et al. (2012) Modelling of a downdraft gasifier fed by agricultural residues. Waste Management, 32(4), 710-718.
27. Neubauer, Y., *Biomass gasification*, in *Biomass Combustion Science, Technology and Engineering*. 2013, Elsevier. p. 106-129.
28. Kaiho, M. and O. Yamada. (2012) Stoichiometric Approach to the Analysis of Coal Gasification Process. Stoichiometry and Materials Science - When Numbers Matter, 415-436.
29. Valero, A. and S. Usón. (2006) Oxy-co-gasification of coal and biomass in an integrated gasification combined cycle (IGCC) power plant. Energy, 31(10-11), 1643-1655.
30. Türkeş, M. (2002):İklim Değişikliği ve Sürdürülebilir Kalkınma Ulusal Değerlendirme Raporu. T.T.G.V. (TTGV), TR.
31. Bakanlığı, E.v.T.K. (2017):Kömür. TR.
32. Tunc, M., U. Camdali, and C. Parmaksizoglu. (2006) Comparison of Turkey's electrical energy consumption and production with some European countries and optimization of future electrical power supply investments in Turkey. Energy Policy, 34(1), 50-59.
33. Koç, E. and M.C. Şenel. (2013) Dünyada ve Türkiye'de enerji durumu-genel değerlendirme. Mühendis ve Makina, 54(639), 32-44.
34. Chmielniak, T. and M. Sciazko. (2003) Co-gasification of biomass and coal for methanol synthesis. Applied energy, 74(3-4), 393-403.
35. IEA. (2015) *International Energy Agency Statistics Search Report on Coal for Turkey*.(2015) https://www.iea.org/classicstats/statisticssearch/report/?year=2015&country=TURKEY&product=Coal

36. Enerji, T. and T.K. Bakanlığı. (2018) TC Enerji ve Tabii Kaynaklar Bakanlığının yazısı.
37. Kivisaari, T., et al. (2004) The feasibility of a coal gasifier combined with a high-temperature fuel cell. Chemical Engineering Journal, 100(1-3), 167-180.
38. Chang, A.C., et al. (2011) Biomass gasification for hydrogen production. International Journal of Hydrogen Energy, 36(21), 14252-14260.
39. Couto, N.D., et al. (2015) Assessment of municipal solid wastes gasification in a semi-industrial gasifier using syngas quality indices. Energy, 93, 864-873.
40. Rezaiyan, J. and N.P. Cheremisinoff, (2005). Gasification technologies: a primer for engineers and scientists, CRC press.
41. LABS, A.P. (2019) *How Gasification Works Process Flows of gasifier Gasification as incomplete combustion*.(2019) http://www.allpowerlabs.com/gasification-explained
42. Basu, P., (2006). Combustion and gasification in fluidized beds, CRC/Taylor & Francis, Boca Raton. 473 p.
43. Manzanares-Papayanopoulos, E., et al. (2014) The co-gasification of coal-biomass mixtures for power generation: a comparative study for solid fuels available in Mexico. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 36(1), 104-111.
44. Chew, J. and V. Doshi. (2011) Recent advances in biomass pretreatment–Torrefaction fundamentals and technology. Renewable and sustainable energy reviews, 15(8), 4212-4222.
45. Özveren, U. (2013) Theoretical and experimental investigation of biomass and coal gasification.
46. Kumabe, K., et al. (2007) Co-gasification of woody biomass and coal with air and steam. Fuel, 86(5-6), 684-689.
47. Kaiho, M. and O. Yamada, *Stoichiometric approach to the analysis of coal gasification process*, in *Stoichiometry and Materials Science-When Numbers Matter*. 2012, InTech.
48. Kumar, A., D.D. Jones, and M.A. Hanna. (2009) Thermochemical biomass gasification: a review of the current status of the technology. Energies, 2(3), 556-581.
49. Ramachandriya, K.D. (2009) Effect of biomass generated producer gas, methane and physical parameters on producer gas fermentations by Clostridium strain p11.Oklahoma State University
50. Kamble, A.D., et al. (2019) Co-gasification of coal and biomass an emerging clean energy technology: status and prospects of development in Indian context. International Journal of Mining Science and Technology, 29(2), 171-186.
51. Biagini, E., F. Barontini, and L. Tognotti. (2006) Devolatilization of Biomass fuels and Biomass components studied by TG/FTIR technique. Industrial & Engineering Chemistry Research, 45(13), 4486-4493.
52. Brar, J., et al. (2012) Cogasification of coal and biomass: a review. International Journal of Forestry Research, 2012.

53. Hosseini, M., I. Dincer, and M.A. Rosen. (2012) Steam and air fed biomass gasification: comparisons based on energy and exergy. International journal of hydrogen energy, 37(21), 16446-16452.
54. Lan, W.J., et al. (2018) Biomass gasification-gas turbine combustion for power generation system model based on ASPEN PLUS. Science of the Total Environment, 628-629, 1278-1286.
55. Peng, W.X., et al. (2017) Syngas production by catalytic co-gasification of coal-biomass blends in a circulating fluidized bed gasifier. Journal of Cleaner Production, 168, 1513-1517.
56. Puig-Arnavat, M., J.C. Bruno, and A. Coronas. (2010) Review and analysis of biomass gasification models. Renewable and sustainable energy reviews, 14(9), 2841-2851.
57. Winter, K.M., J. Kalucki, and D. Koshel. (2015) Process technologies for thermochemical surface engineering. Thermochemical Surface Engineering of Steels, (62), 141-206.
58. Natarajan, E., A. Nordin, and A. Rao. (1998) Overview of combustion and gasification of rice husk in fluidized bed reactors. Biomass and bioenergy, 14(5-6), 533-546.
59. Makwana, J., et al. (2015) Air gasification of rice husk in bubbling fluidized bed reactor with bed heating by conventional charcoal. Bioresource technology, 178, 45-52.
60. Vélez, J.F., et al. (2009) Co-gasification of Colombian coal and biomass in fluidized bed: An experimental study. Fuel, 88(3), 424-430.
61. Nikrityuk, P.A. and B. Meyer, (2014). Gasification processes: modeling and simulation, John Wiley & Sons.
62. Massoudi, M. and P. Wang. (2011):A brief review of viscosity models for slag in coal gasification.
63. Wachowicz, J., T. Janoszek, and S. Iwaszenko. (2010) Model Tests of the Coal Gasification Process. Archives of Mining Sciences, 55(2), 249-262.
64. Singhal, S.C. and K. Kendall, (2003). High-temperature solid oxide fuel cells: fundamentals, design and applications, Elsevier.
65. Habibi, R., et al. (2012) Co-gasification of biomass and non-biomass feedstocks: synergistic and inhibition effects of switchgrass mixed with sub-bituminous coal and fluid coke during CO2 gasification. Energy & Fuels, 27(1), 494-500.
66. Masnadi, M.S., et al. (2015) From coal towards renewables: Catalytic/synergistic effects during steam co-gasification of switchgrass and coal in a pilot-scale bubbling fluidized bed. Renewable Energy, 83, 918-930.
67. Mukhopadhyay, P. and P. Hatcher. (1993) In Hydrocarbons from Coal; Law, BE; Rice, DD, Eds. American Association of Petroleum Geologists: Tulsa, OK, 38, 79-118.
68. Ni, M., et al. (2006) An overview of hydrogen production from biomass. Fuel processing technology, 87(5), 461-472.

69. Demirbaş, A. (2002) Gaseous products from biomass by pyrolysis and gasification: effects of catalyst on hydrogen yield. Energy conversion and management, 43(7), 897-909.
70. Franco, C., et al. (2003) The study of reactions influencing the biomass steam gasification process☆. Fuel, 82(7), 835-842.
71. Shen, L., Y. Gao, and J. Xiao. (2008) Simulation of hydrogen production from biomass gasification in interconnected fluidized beds. Biomass and Bioenergy, 32(2), 120-127.
72. Andre, R.N., et al. (2005) Fluidised bed co-gasification of coal and olive oil industry wastes. Fuel, 84(12-13), 1635-1644.
73. Czaplicki, A. and M. Sciazko. (2011) Coal and biomass Co-gasification in a circulating fluidized bed reactor.
74. Vreugdenhil, B., A. Van der Drift, and C. Van der Meijden. Co Gasification of biomass and lignite in the indirect gasifier Milena. International Pittsburgh coal conference, Pittsburgh, USA; 20e23 September, 2009.
75. Puig-Arnavat, M., J.C. Bruno, and A. Coronas. (2010) Review and analysis of biomass gasification models. Renewable & Sustainable Energy Reviews, 14(9), 2841-2851.
76. Nikoo, M.B. and N. Mahinpey. (2008) Simulation of biomass gasification in fluidized bed reactor using ASPEN PLUS. Biomass & Bioenergy, 32(12), 1245-1254.
77. Zhang, W., et al. (2005) Simulation of a tubular solid oxide fuel cell stack using AspenPlusTM unit operation models. Energy Conversion and Management, 46(2), 181-196.
78. Tanim, T.R. (2012) Modeling of a 5 kWe Solid Oxide Fuel Cell Based Auxiliary Power Unit Operating on JP-8 Fuel.Ohio University
79. Gokon, N., T. Izawa, and T. Kodama. (2015) Steam gasification of coal cokes by internally circulating fluidized-bed reactor by concentrated Xe-light radiation for solar syngas production. Energy, 79, 264-272.
80. Xiao, R., et al. (2007) Partial gasification of coal in a fluidized bed reactor: Comparison of a laboratory and pilot scale reactors. Korean Journal of Chemical Engineering, 24(1), 175-180.
81. Marcantonio, V., et al. (2019) Process analysis of hydrogen production from biomass gasification in fluidized bed reactor with different separation systems. International Journal of Hydrogen Energy, 44(21), 10350-10360.
82. Myöhänen, K., J. Palonen, and T. Hyppänen. (2018) Modelling of indirect steam gasification in circulating fluidized bed reactors. Fuel Processing Technology, 171, 10-19.
83. Chen, J., et al. (2017) Modelling of coal/biomass co-gasification in internal circulating fluidized bed using kinetic theory of granular mixture. Energy Conversion and Management, 148, 506-516.
84. Peng, W.-X., et al. (2017) Syngas production by catalytic co-gasification of coal-biomass blends in a circulating fluidized bed gasifier. Journal of cleaner production, 168, 1513-1517.

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