

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**THERMODYNAMIC EQUILIBRIUM ANALYSIS OF OXIDATIVE STEAM
REFORMING OF ETHYLENE GLYCOL AND SORBITOL**



M.Sc. THESIS

Alper CESUR

Department of Chemical Engineering

Chemical Engineering Programme

AUGUST 2019

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**ETİLEN GLİKOL VE SORBİTOLÜN OKSİDATİF SU BUHARI REFORMLAMA
PROSESİNİN TERMODİNAMİK DENGİ ANALİZİ**

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To my own youth,



FOREWORD

First of all, I would like to express my deep appreciation and thanks to my thesis advisor, Prof. Dr. Filiz KARAOSMANOĞLU, for her support during writing this thesis.

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ABBREVIATIONS

K	: Kelvin
kcal	: KiloCalorie
KJ	: KiloJoule
s	: Second
cP	: CentiPoise
pH	: Power of Hydrogen
wt %	: Percentage by Weight
PR	: Peng-Robinson Equation of State
SRK	: Soave-Redlich-Kwong Equation of State
NRTL	: Non-Random Two Liquid Model
WGS	: Water-Gas Shift Reaction
EG	: Ethylene Glycol



SYMBOLS

ΔH_{rxn}^0	: Standard Enthalpy of Reaction
ΔG^0	: Standard Gibbs Energy
i	: Component definer
N	: The total number of moles of components in reaction
n_i	: The number of moles of component i
μ_i	: Chemical Potential of Component i
^{0}	: Standard
P	: The total number of pressure of the system
R	: Molar gas constant
T	: Temperature
G_t	: Total Gibbs free energy
f_i	: Fugacity of component i
f_i^0	: Standard fugacity of component i
ΔG_{fi}^0	: Standard Gibbs free energy for the formation of component I
^0C	: Centigrade Celcius
T_c	: Critical temperature
T_p	: Critical pressure



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THERMODYNAMIC EQUILIBRUM ANALYSIS OF OXIDATIVE STEAM REFORMING OF ETHYLENE GLYCOL AND SORBITOL

SUMMARY

Energy is one of the most significant resources for humanity and developments of country's economics. Moreover, energy is irreplaceable part of social and economic life. Consumption of energy increases in direct proportion to population growth, industry development and enhance the life quality. Usage of fossil sources brings with many problems like as global warming, climate changing and greenhouse gas emission problems. Environmental problems can be prevented as taking measure such as changing production and consumption mechanism of energy.

One of the most important centers producing renewable energy is biorefineries. A biorefinery can be defined as a plant where combines biomass process and process equipment which to use for producing fuels, power and precious chemicals from biomass. Biomass is converted to solid, liquid, gas products and energy by using thermochemical processes such as combustion, pyrolysis, gasification. When gasification is applied to biomass, tar and methane gas observed in the product composition. In the case of application of pyrolysis, biomass is heated to about 773 K in the gas phase and oxygen-free environment and converted to solid, liquid and gas components.

The bio-oils are produced by pyrolysis from woody biomass contain complex compounds and the bio-oils are named according to these compounds. Ethylene glycol and sorbitol, which are the selected bio-oil model components, are models with a high weight ratio in the bio-oil.

Chemical equilibrium in a reaction gas mixture is a dynamic process. A spontaneous approach toward equilibrium is observed when the initial partial pressures of the reactants are high and collisions between reactant molecules cause product molecules to form.

The purpose of this thesis is to find the most suitable process and process conditions for obtaining syngas and hydrogen gas from the model components ethylene glycol and sorbitol. Steam reforming, oxidation steam reforming and sorption enhanced reforming processes of ethylene glycol and sorbitol, the basic model components of bio-oil, have been investigated to effect of product yield etc. H_2 , CO, CH_4 , coke, H_2/CO ratio and input conversion etc. $C_2H_6O_2$, $C_6H_{14}O_6$, H_2O , O_2 by changing temperature, pressure and feed composition. Analysis are simulated by Gibbs free energy minimization method in RGibbs reactor by using Aspen Plus V8.8. CaO is used as CO_2 adsorbent in sorption enhanced processes. Optimum process is selected for maximum H_2 and CO yield, minimum coke, CO_2 and CH_4 yield as side reaction products.

The properties of reactants and products were described as the first step into Aspen Plus simulation program at the specified temperature and pressure while executing simulation sets. After then, the second step is minimization were run to obtain compositions of reactants and products at the equilibrium state. 5 sets of both ethylene glycol and sorbitol were performed using RGibbs reactor at the simulation. Then, 2 more sets were studied to see effect of ethylene glycol and sorbitol mixture.

It is seen that the while H_2O addition is increased, the H_2 yield is decreased in steam reforming of both ethylene glycol and sorbitol. In the meantime, it is seen that the usage of O_2 in steam reforming, the coke yield is decreases.



ETİLEN GLİKOL VE SORBİTOLÜN OKSİDATİF SU BUHARI REFORMLAMA PROSESİNİN TERMODİNAMİK DENGİ ANALİZİ

ÖZET

Enerji, insanlık ve ülke ekonomisinin gelişmesi için en önemli kaynaklardan biridir. Dahası, enerji sosyal ve ekonomik yaşamın vazgeçilmez bir parçasıdır. Enerji tüketimi, nüfus artışı, endüstri gelişimi ve yaşam kalitesini arttırmakla doğru orantılı olarak artar. Fosil kaynakların kullanımı, küresel ısınma, iklim değişikliği ve sera gazı emisyonu sorunları gibi birçok sorunu beraberinde getirmektedir. Değişen üretim ve enerji tüketim mekanizmaları gibi önlemler alarak çevre sorunları önlenabilir.

Yenilenebilir enerji üreten en önemli merkezlerden biri biyorafinerilerdir. Bir biyorafineri, biyokütle işleminden elde edilen ve biyo-kütleden yakıt, güç ve değerli kimyasallar üretmek için kullanılan işlem ekipmanlarını birleştiren bir tesis olarak tanımlanabilir. Biyokütle, yanma, piroliz, gazlaştırma gibi termokimyasal işlemler kullanılarak katı, sıvı, gaz ürünlerine ve enerjiye dönüştürülür. Biyokütleye gazlaştırma uygulandığında, ürün bileşiminde katran ve metan gazı gözlenir. Piroliz uygulaması durumunda, biyokütle gaz fazında ve oksijensiz ortamda yaklaşık 773 K'ye ısıtılır ve katı, sıvı ve gaz bileşenlerine dönüştürülür.

Biyo-y yağlar odunsu biyokütleden pirolizle üretilir ve içinde kompleks bileşikler bulunur ve bu yağlar bu bileşiklere göre adlandırılır. Seçilen biyo-y yağ modeli bileşenleri olan etilen glikol ve sorbitol, biyo-y ağda yüksek ağırlık oranına sahip modellerdir.

Sıvı ürünü maksimum verimle elde etmek piroliz prosesinin temel amacıdır. Sıvı ürün; biyoyağlar ve sulu faz olmak üzere iki kategoriye ayrılır. Biyoyağlar, hidrokarbonlardan oluşan karmaşık yapılu kimyasal bileşenlerdir. Bu değerli kimyasal bileşenler su buharı reformlama prosesi, oksidatif su buharı reformlama prosesi ve adsorpsiyon destekli reformlama prosesleri ile yüksek hidrojen içeren gaz karışımına dönüştürülmektedir. Elde edilen yüksek hidrojen içeren gaz karışımı, hidrojene ek olarak karbonmonoksit, karbondioksit, metan gazlarını da içermektedir. Kullanılan termokimyasal dönüşüm yöntemleriyle kok kömürü katı ürünü de reaksiyon ortam şartlarına bağlı olarak elde edilmektedir.

Bir reaksiyon gazı karışımındaki kimyasal denge, dinamik bir işlemdir. Reaktantların başlangıçtaki kısmi basınçları yüksek olduğunda ve reaktif moleküller arasındaki çarpışmalar ürün moleküllerinin oluşmasına neden olduğunda dengeye doğru kendiliğinden bir yaklaşım gözlenir. Gibbs serbest enerji minimizasyonu, bir sistemin belirlenen çalışma parametrelerine göre faz ve bileşen dağılımlarının belirlenmesini sağlayan termodinamik bir analiz yöntemidir. Denge sıcaklık, basınç ve bileşen konsantrasyonunun fonksiyonu olan toplam Gibbs serbest enerjisinin. Bu yöntemin en önemli avantajı, reaksiyon mekanizmasına ihtiyaç duyulmamasıdır. Bu nedenle, bu teknik spesifik olmayan sistemlerin termodinamik analizinde kullanılır. Termodinamik denge hesaplamalarında Aspen Plus v.8.8 kullanılarak Gibbs serbest

enerji minimizasyonu metodu kullanılmıştır. Simülasyon programında RGibbs reaktörü kullanılmıştır. Reaksiyon sistemindeki bileşiklerin bileşimi, RGibbs reaktörü ile Gibbs serbest enerjisini azaltma yöntemi ile hesaplandı. RGibbs Reaktörü, reaksiyon sistemindeki tüm bileşenlerin Gibbs serbest enerjisini, kullanılan enerji minimizasyonu prensibi ile reaksiyon mekanizmasına göre hesaplar.

Bu tezin amacı, model bileşenleri etilen glikol ve sorbitolden sentez gazı ve hidrojen gazı elde etmek için en uygun işlem ve işlem koşullarını bulmaktır. Biyo-yagın temel model bileşenleri olan etilen glikol ve sorbitolün su buharı reformingi, oksidatif su buharı reforming ve adsorpsiyon destekli su buharı reforminginin termodinamik analizleri sıcaklık, basınç ve besleme kompozisyonu değiştirilerek ve Aspen Plus V8.8 kullanılarak RGibbs reaktöründe Gibbs serbest enerji azaltma yöntemi ile simüle edilmiştir.

CaO, adsorpsiyon destekli su buharı reforminginde CO₂ adsorbanı olarak kullanılmıştır. Optimum proses yüksek H₂ ve CO verimi, düşük kok, metan ve karbondioksit gibi yan ürünlerin olduğu durum için seçilir.

Reaktanların ve ürünlerin özellikleri, simülasyon setleri yürütülürken, belirtilen sıcaklık ve basınçta Aspen Plus simülasyon programına ilk adım olarak tanımlandı. Bundan sonra, ikinci aşama enerjiyi en aza indirmeye, denge durumunda reaktanların ve ürünlerin bileşimlerinin elde edilmesi için gerçekleştirildi. Simülasyonda RGibbs reaktörü kullanılarak beşer set hem etilen glikol hem de sorbitol için yapıldı. Daha sonra, etilen glikol ve sorbitol karışımının etkisini görmek için 2 set daha çalışıldı. Simülasyon, 200-1000 °C sıcaklık aralığında ($\Delta T = 50$ °C) ve basınç 1, 10, 20 bar altında gerçekleştirildi. Her çalışma koşulunda etilen glikol, sorbitol ve oksijen tükenmiştir.

Reaksiyona giren su buharı dönüşümü ve reaksiyonlar sonucunda üretilen hidrojen, karbonmonoksit, karbondioksit, metan ve kok oluşumu tablo ve grafikler ile belirtilmiştir. Sıcaklık, basınç ve besleme akımındaki bileşen kompozisyonunun; hidrojen verimine etkisi incelenmiştir. Reaksiyonlar etilen glikol ve sorbitol için ayrı ayrı ve etilen glikol-sorbitol karışımı olarak farklı besleme kompozisyonlarında gerçekleştirilmiştir. Besleme akımındaki H₂O artışı; H₂, CO, CH₄, kok verimlerini ve H₂O dönüşümünü olumsuz, CO₂ verimini ise olumlu yönde etkilemiştir. Besleme akımındaki O₂ artışı H₂O artışıyla aynı etkiyi oluşturmuştur. Yüksek sıcaklıklarda ve besleme akımında su buharı veya oksijen içeriğinin fazla olması kok oluşumunun azalmasına sebep olmuştur. CaO adsorpsiyon destekli reformlama prosesinde 700 °C'nin üzerindeki sıcaklıklarda adsorpsiyonun ürün verimine bir etkisi olmadığı gözlemlenmiştir. Bu etki karbonlama reaksiyonun egzotermik yapısına dayandırılarak açıklanmıştır. Besleme akımındaki CaO artışı sıcaklıkla birlikte H₂ ve CO verimine olumlu etki yaparken, kok oluşumunu azaltmıştır. Reformlama prosesleri sonucunda elde edilen gaz karışımının içerdiği karbondioksit miktarını, eklenen CaO ile azaltmak amaçlanmıştır.

Su buharı reformlama prosesinde, literatürdeki istenen H₂/CO oranı ve en düşük yan ürün verimi 1000 °C ve 1 bar altında C₂H₆O₂/H₂O=1/2 iken gerçekleşmiştir. Bu prosesin veriminin artırılması amacıyla daha sonra simülasyona oksijen eklemesi yapılarak oksidatif su buharı reforming prosesi gerçekleştirilmiştir. Oksijen ve su buharının toplam mol sayısı 2 olacak şekilde oksijen ve su mol sayıları ayrı ayrı değiştirilerek oksidatif su buharı prosesi için optimum H₂O/O₂ oranı bulunulmaya çalışılmıştır.

Simule edilen ve grafiklerle anlatılan su buharı reforming ve oksidatif su buharı reforming proseslerine CO_2 adsorbanı olarak CaO katılmış ve CaCO_3 oluşması sağlanarak; ortamdan CO_2 ayrılmasıyla proses veriminde olan değişiklikler incelenmiştir. Bunun için iki ayrı su buharı reforming prosesine de ayrı ayrı 1 ve 3 mol CaO giriş akımında tanımlanmıştır.

Bu çalışmada su buharı reforming proseslerine basınç etkisi de incelenmiş ve $\text{C}_2\text{H}_6\text{O}_2/\text{H}_2\text{O}=1/2$ durumu ve $\text{C}_6\text{H}_{14}\text{O}_6/\text{H}_2\text{O}=1/6$ durumu için basınçlar 1 bardan 10 bar ve 20 bar olacak şekilde tekrar simule edilmiştir. Yüksek basınçların düşük sıcaklıklarda kok oluşumunu ve CH_4 verimini arttırdığı, H_2 verimini düşürdüğü gözlemlenmiş olup; grafiklerle açıklanmıştır.





1. INTRODUCTION

Energy is one of the most significant resources for humanity and developments of country's economics. Moreover, energy is irreplaceable part of social and economic life. Consumption of energy increases in direct proportion to population growth, industry development and enhance the life quality. Energy resources can be divided as two main groups: non-renewable and renewable sources. The basic sources which meet the demands of energy can be ranked respectively such as coal, petroleum, nature gas. The sources which are given previously are based on the fossil resources. However, the importance of renewable energy sources can be positive impacted on the energy demand of fossil fuels. The fact that fossil fuels are non-renewable energy sources increases the demand of renewable energy resources [1].

Usage of fossil sources brings with many problems like as global warming, climate changing and greenhouse gas emission problems. Environmental problems can be prevented as taking measure such as changing production and consumption mechanism of energy. The environmental damage caused by non-renewable energy sources and the reduction of resource reserves lead to alternative energy sources [1].

One of the most important centers producing renewable energy is biorefineries. A biorefinery can be defined as a plant where combines biomass process and process equipment which to use for producing fuels, power and precious chemicals from biomass. Biomass, a renewable energy source, is a carbon-containing source that can be obtained from organic raw materials such as plant and animal microorganisms. Biomass is produced by woody biomasses, which are forest wastes, agricultural wastes, energy plant wastes, domestic wastes [2].

Biomass is converted to solid, liquid, gas products and energy by using thermochemical processes such as combustion, pyrolysis, gasification. The combustion process is converted biomass into heat and energy and is not converted it into chemicals. In gasification, biomass is converted various forms containing H_2 and CO at high temperatures with gases such as air, steam and oxygen. When gasification

is applied to biomass, tar and methane gas observed in the product composition. In the case of application of pyrolysis, biomass is heated to about 773 K in the gas phase and oxygen-free environment and converted to solid, liquid and gas components. The distribution of products varies depending on temperature, steam retention time and biomass used. Liquid products are divided into two categories, which are bio-oil and aqueous phase. Bio-oils consist of different amounts of hydrocarbons such as phenol, furfural, acid and aldehydes [3]. Bio-oil can be used as fuel to produce heat and power, and can be used to produce hydrogen rich gas mixture as a consequence of steam reforming, partial oxidation reforming and sorption enhanced reforming processes. Hydrogen rich gas mixture is also contained carbon monoxide, carbon dioxide and methane gas in addition to hydrogen. With the thermochemical conversion methods are used, the char has been obtained as a solid product depending on the reaction conditions.

The bio-oils are produced by pyrolysis from woody biomass contain complex compounds and the bio-oils are named according to these compounds. Ethylene glycol and sorbitol, which are the selected bio-oil model components, are models with a high weight ratio in the bio-oil. Since ethylene glycol is an efficient bio-oil for the production of hydrogen and is completely converted in the reactions, it has been chosen as a model. As the percentage of sugars in bio-oil is one of the most common components and due to the wide literature studies, sorbitol is selected as another bio-oil model.

Chemical equilibrium in a reaction gas mixture is a dynamic process. A spontaneous approach toward equilibrium is observed when the initial partial pressures of the reactants are high and collisions between reactant molecules cause product molecules to form. Once the partial pressures of the products have increased sufficiently, the reverse reaction (forming “reactants” from “products”) begins to occur. As the equilibrium state is approached, the forward and backward rates of reaction become equal and there is no further net change in reactant and product partial pressures. The total Gibbs free energy function governs the forward and backward directions of chemical reactions. The composition at thermochemical equilibrium can be calculated by minimizing the Gibbs free energy, and so such equilibrium calculations.

The purpose of this thesis is to find the most suitable process and process conditions for obtaining syngas and hydrogen gas from the model components ethylene glycol

and sorbitol. Steam reforming, oxidation steam reforming and sorption enhanced reforming processes of ethylene glycol and sorbitol, the basic model components of bio-oil, have been investigated to effect of product yield etc. H_2 , CO, CH_4 , coke, H_2/CO ratio and input conversion etc. $C_2H_6O_2$, $C_6H_{14}O_6$, H_2O , O_2 by changing temperature, pressure and feed composition. Analysis are simulated by Gibbs free energy minimization method in RGibbs reactor by using Aspen Plus V8.8. CaO is used as CO_2 adsorbent in sorption enhanced processes. Optimum process is selected for maximum H_2 and CO yield, minimum coke, CO_2 and CH_4 yield as side reaction products.





2. THEORETICAL STUDY

2.1 Biorefineries

A biorefinery can be defined as a plant combining biomass process and process equipments used for producing fuels, power and precious chemicals from biomass. In the last decade, a biorefinery concept has been more popular compared to traditional refineries manufacturing various products and fuels from petroleum. Conversion of biomass feedstock into precious chemicals with maximum energy production explains the biorefinery term.

With a more specific definition used, “The biorefinery term is a sequence of biomass conversion processes involving the production of a wide variety of chemical substances such as fuel, energy, heat and added value where biomass is used as the raw material.” [4-5].

Significant improvements due to advance technology is in progress in today’s world. These improvements make biomass industry more efficient in regard of sustainability. Therefore, more sustainable economy is achieved compared the fossil fuel based industry [5].

In biorefineries, there are several ways of producing bioproducts from biomass via different conversion technologies including biochemical, thermochemical or combination of biochemical and thermochemical methods [6].

Biorefineries can be classified in different groups including platforms, products, feedstocks and processes. Platforms are based on intermediates from feedstocks converting the final biorefinery products, for example, lignin, sugar, plant-based, or algae oil platform. Intermediates may be biogas, syngas, sugar, lignin, and pyrolysis oil. These intermediates are the building blocks for synthesizing the final products [6].

Process classification includes thermochemical and biochemical conversion processes. Biorefineries can be classified in two different categories according to the type of

feedstock, such as woody or non-woody feedstocks. Non-woody feedstocks include wet feedstocks such as grass and algae.

The biorefinery term is a sequence of biomass conversion processes involving the production of a wide variety of chemical substances such as fuel, energy, heat and added value where biomass is used as the feedstock. Biomaterials, biochemicals and biofuels are three main groups of biorefinery products.

Biomaterials are materials formed by the passage of biomass through various processes. They are generally used for commercial purposes. It is most commonly used in the health sector to correct the loss of function caused by the tissues and losses in the human body. Contact lenses, hip prostheses, artificial heart vessels, polymeric skin cover and artificial cornea are other examples of use in the healthcare sector. The main biomaterials produced for industrial purposes can be listed as follows;

- Inks
- Paints and coatings
- Solvents and cleaners
- Adhesives
- Polymers
- Construction materials
- Composite materials
- Fibers, paper and packaging

Biochemicals are synthesized from biomass for use in the chemical and pharmaceutical industries as enzymes and hormones. Biomass is a good source of raw material for producing biochemicals as it is produced from a living mass. Biochemicals have many environment-friendly applications. Main biochemicals are intermediate chemicals, lubricants and functional fluids.

One of the biggest environmental problems of our era is the greenhouse gas that causes the global warming problem by causing destruction in the ozone layer. This gas is most often produced by the use of fossil fuels. To cope with this problem, the world has begun to reduce its use of fossil fuels and generate energy from renewable sources. Renewable energy sources are geothermal, wind, solar energy, hydraulic energy and biofuels.

Biofuel is the general name for gas, liquid and solid products obtained through the biochemical or thermochemical conversion processes of living organism output.

Modern biofuels are produced by converting various biomass such as agricultural products, wood, animal, plant and municipality residues into fuel using variety conversion methods. Gas biofuels are biohydrogen, biogas, synthetic gas called syngas; solid biofuels are wood charcoal, biochar, biopellet, bio briquette and liquid biofuels may be named as bioethanol, biodiesel, bioethanol, bio-dimethyl ether, bio-ethyl tertiary butyl ether and vegetable oils. Biofuels are used in the transport sector for vehicle fuel, in the service sector for heat and electricity production.

Biorefineries aim to produce biochemicals, biomaterials and biofuels by collecting biomass (agricultural resources, forest resources and urban-industrial resources etc.) through physical processes such as downscaling, grinding, drying, filtration, extraction, briquetting and conversion processes such as biochemical and thermochemical processes [7].

The basic operations performed in a biorefinery are sequentially listed below,

- Finding biomass source
- Procurement of biomass
- Classification of the biomass as a raw material according to the product
- Application of physical processes to raw material
- Application of conversion technology to raw materials
- Obtaining products [8].

The first step is to find the biomass source with the most efficient thermal value for the production of the target products. The raw materials are classified according to their specifications after they have been subjected to physical pre-treatments such as collection, storage, transportation, separation and compaction in the supply phase.

Secondly, biomass conversion technology methods are applied on raw materials; biochemical processes such as biophotolysis, anaerobic digestion and fermentation and thermochemical conversion processes such as direct combustion, pyrolysis, hydrolysis, gasification, esterification and carbonization (Table 2.1).

Biomass is used in order to produce bio-oil at biorefineries. Woody biomass is one of the widely used resources to produce bio-oil.

Table 2.1: Applied conversion technologies according to the biofuel produced
[Adapted from 5].

Biomass Conversion Technologies	Biofuels
Esterification	Biodiesel
Hydrolysis / Fermentation	Bioethanol
Gasification	Bioethanol Methanol Dimethyl Ether Fischer-Tropsch Diesel Fischer-Tropsch Gasoline Biohydrogen
Pyrolysis	Aqueous Phase Bio-oil Bio-char
Carbonization	Wood charcoal
Anaerobic digestion	Biogas
Biophotolysis	Biohydrogen

2.1.1 Woody biomass

Biomass materials can be classified into two main groups; woody and non-woody biomass. Although forests are only woody biomass sources, agricultural and waste resources can provide woody and non-woody biomass, so these two groups are not entirely different [9]. Woody biomass is also a lignocellulosic biomass. By taking into consideration the competition between biomass and food sector, woody biomass researches are very important. Because, woody biomass does not compete with food crops.

Lignocellulosic biomass is composed of cellulose, hemicellulose and lignin polymers together with other components like acetyl groups, minerals and phenolic substituents [10]. Table 2.1 presents these compositions for some biomass materials. Lignocellulosic feed stocks can either be woody or non-woody biomass such as agricultural residues and forest residues.

Woody biomass feed stocks usually come from the following sources:

- Obtained from the forest residues, wood industry residues, arboricultural industry and co-products

- Energy forestry
- Agricultural applications
- Waste woods from urban and industries

Woody biomass utilization has several benefits such as social, ecological - environmental and economic benefits. Social benefits include better human health and air quality, improve rural community vitality through the provision of sustainable environments and economies over the long term. Reducing dependence on fossil fuels and reducing greenhouse gas emissions effects are in ecological and environmental benefits and decreasing energy costs by substituting woody biomass for other fuels effect is economic benefits of woody biomass utilization.

Various materials can be obtained by applying conversion technologies from woody biomass in biorefineries.

2.2 Pyrolysis

Thermal degradation occurs when the biomass is heated in the absence of air or in a limited amount of air. At the end; solid, liquid and gaseous products are recovered. Thermal decomposition is termed "fast pyrolysis" if the liquid product yield is high, "carbonization" if the solid and gas products yield is high [11].

The woody biomass reacts differently at different temperatures. This can be used to obtain value-added chemicals by pyrolysis, which is the thermal decomposition of organic material in the absence of oxygen. Pyrolysis is a versatile thermal conversion technology with various types such as slow, medium and fast pyrolysis [6]. Table 2.2 shows pyrolysis mode and output fractions at different conditions using different technologies.

Pyrolysis processes are highly developed nowadays. Formerly, fixed bed and gas recycle processes were used for large biomass particles; fluid bed and rotary kiln systems were used for pulverized grained biomass. Kinetic laws have begun to play an important role and heat transfer technologies have been developed to create diversities in pyrolysis products.

Advanced pyrolysis techniques have been recently developed according to the composition of biomass. For each raw material, different pyrolysis temperature, pressure, space time and catalyst should be applied.

Table 2.2: Pyrolysis modes and output fractions [4, adapted from 10].

Mode	Reaction Conditions				Products, %		
	Reactor Temperature	Heating Rates	Residence Types and Times	Reactor Technology	Liquid	Solid (Char)	Gas
Fast	500 °C	High (>1000°C/s)	Hot vapor residence, short ~1s	Fluidized bed, entrained flow, ablative	75	12	13
Intermediate	400 - 500 °C	1 - 1000 °C	Hot vapor residence, ~10-30s	Same as for fast pyrolysis plus auger type of reactors	50	25	25
Slow Carbonization	400 - 500 °C	Low (<1°C/s)	Solid residence, hours-days	Moving bed retorts, augers, batch fixed bed reactors	30	33	35

One of the most important points distinguishing the pyrolysis processes from each other is the reactor type. Reactor type influence that working conditions, grain size etc. So, different product can be achieved depending on the reactor type.

Fixed bed, moving bed, fluid bed and transport bed reactors can be used in pyrolysis. It is stated that the best fluid product yield at high heating rate and short residence time, using the transport bed reactors [13].

By using pyrolysis of woody biomass, substances in liquid phase are obtained. These substances are pyrolysis oil called bio-oil and aqueous phase including organic compounds.

Main distinguishing factors in biomass pyrolysis are biomass properties and process variables. Biomass properties such as organic structure, inorganic structure, water content, particle size and porosity directly affect pyrolysis [14].

In pyrolysis of biomass, firstly hemicelluloses degradation occurs in the range of 200-260 °C, followed by cellulose degradation in the range of 240-350 °C and finally lignin degradation in the range of 248-500 °C [14].

The reaction is endothermic up to 280 °C. When the pyrolysis process reaches the exothermic case, it is no longer necessary to heat externally. The temperature slowly

risks up to 400-450 °C. In order to obtain a higher temperature, the process must be heated with an external heating system [13].

2.2.1 Syngas

The synthesis gas is a gas mixture of CO and H₂. Synthesis gas is an important raw material for the chemical and energy industry. A large number of hydrocarbons obtained by conventional methods from petroleum can also be produced from synthesis gas [15].

Synthesis gas can be obtained from various hydrocarbons such as natural gas, coal, coke or biomass. The synthesis gas produced by biomass is called biosynthesis gas and is thus distinguished from the synthesis gas from fossil fuels [15].

Synthesis gas used in the production of oxygenated compounds, synthesis of methanol, production of liquid hydrocarbons by Fisher-Tropsch (F-T) synthesis, carbonylation and hydrogenation or reduction processes in reverse flow processes [16].

The traditional method of synthesis gas production is the reformulation of hydrocarbon fuels in the presence of water vapor and a catalyst (such as nickel) at a temperature of about 800 °C. However, these methods show the formation of CO₂, a gas which has the greenhouse effect. When combined with the increase in consumption of fossil fuels, this effect has led to the production of synthesis gas from alternative energy sources such as biomass [3].

As explained above, bio-oil is produced from biomass sources with thermal processes.

2.3 Bio-oil

Products formed by pyrolysis are converted into three main products, solid, liquid and char. The liquid product resulting from the pyrolysis process is defined as bio-oil and consists of tar, heavy hydrocarbons and water [17].

Bio-oils have an energy density of 20 MJ / m³, ten times that of biomass, making bio-oils an excellent alternative energy source [18].

The bio-oil consist of more than 400 highly oxygenated compounds with polymeric carbohydrates and lignin fractions. The most common chemicals in bio-oils are water,

phenols (such as phenol and cresol), furfurals, acids (such as acetic acid, formic acid, lactic acid) and aldehydes (such as acetaldehyde and formaldehyde) [3,17].

Table 2.3 shows the hydrocarbon composition present in a bio-oil content.

Table 2.3: Hydrocarbon composition in a bio-oil [adapted from 19].

Compounds	wt%
Acetaldehyde	0.27
Furan	0.04
Acetone	0.11
Methanol	1.98
2-Butanone	0.04
Isopropanol	0.02
Ethanol	<0.01
2-Pentanone	0.01
n-Propanol	0.01
1-Hydroxy-2-propanone	2.66
Glycolaldehyde	0.78
1-Hydroxy-2-butanone	0.08
Acetic acid	11.6
Furfural	0.34
2-Acetylfuran	0.02
Propanoic acid	0.02
Isobutyric acid	0.02
5-Methylfurfural	0.02
Butyric acid	0.06
Valeric acid	0.03
Caproic acid	0.01
Guaiacol	0.05
4-Methylguaiacol	0.03
o-Cresol	<0.01
Phenol	0.02
4-Ethylguaiacol	<0.01
m-Cresol	0.01

Table 2.3 (continued): Hydrocarbon composition in a bio-oil [adapted from 19].

Compounds	wt%
2-Propylphenol	<0.01
Eugenol	<0.01
4-Ethylphenol	0.01
o-Vanillin	0.02
Syringol/4-Propylphenol	0.01
Isoeugenol	0.02
5-(Hydroxymethyl) furfural	0.04
4-Methylcatechol	<0.01
4-Ethylcatechol	0.02
Sugars	4.3
Unknown GC-detectable compounds	4.7
Water	72.7

The physical and chemical properties of the bio-oils depend on the composition of the biomass. Hydrogen production is influenced by the chemical composition of the bio-oil. Therefore, the bio-oil used plays an important role in the yield of hydrogen. The biofuels are mostly acidic. However, the pH value largely depends on the type of the biomass used. For example, the pH values of the bio-oils from sawdust, rice crown and cotton stalk are 2.1, 3.2 and 3.3, respectively [20].

Physical properties of the bio-oils are given in Table 2.4 and elemental analysis in Table 2.5 [18].

Bio-oil; is an important resource for the production of chemicals, energy and fuel [21]. Bio-oils can be used as fuel for heat and energy production, and can be converted into synthesis gas by appropriate reactions (steam reforming and partial oxidation) and used in the production of chemicals [3].

The main components of the bio-oils are carbon, hydrogen and oxygen. For this reason, the chemical formula is experimentally expressed as $C_nH_mO_x.H_2O$. The bio-oils can be separated into organic and aqueous phases by adding water and it contains 60% evaporable components of the bio-oils [18].

Table 2.4: Physical properties of the bio-oils [18].

Physical Properties	Value
Water content (%)	15-30
pH	2.5
Specific gravity	1.2
Viscosity at 500 °C (cP)	40-100

Table 2.5: Elemental analysis of the bio-oils [18].

Element	wt%
C	54-58
H	5.5-7
N	0-0.2
O	35-40
Ash	0-0.2

Bio-oil is also used in the extraction and production of various substances as well as in energy and fuel sectors. Food flavors and essences, medicines, resins, environmental chemicals are produced by bio-oils. [17]

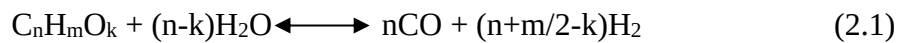
The bio-oils are used in boilers as heat and electricity sources, for the production of chemical substances such as phenol, organic acids or as fuel for engines and turbines. In addition, bio-oils are also used in H₂ production, which is another fuel source [18].

2.3.1 Bio-oil reforming

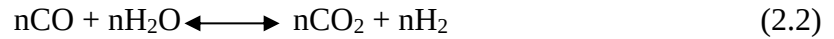
There are several methods of bio-oil reforming. These methods are explained in detail below. While studying reforming of bio-oils, a model compound is selected from the bio-oil mixture of acetic acid, acetone, di benzyl ether, ethyl lactate, ethyl propionate, ethylene glycol, hydroxy acetaldehyde, glycerol, glucose, lactic acid, m-cresol, phenol, propanoic acid, sorbitol, sucrose, xylose [3].

2.3.1.1 Steam reforming of bio-oil

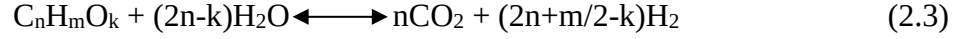
The first steam reforming facility was established in United States in 1930 and applied by the company whose name Standard Oil Co. Steam reforming is an endothermic reaction in which the materials are handled with water vapor in the presence of catalyst to synthesize carbon monoxide, carbon dioxide and hydrogen. Steam reforming has been one of the most efficient process for hydrogen production since the 1930s. Eq. 2.1 shows the reactions of bio-oil steam reforming:



If the water-gas shift reaction occurs, the CO can convert to CO₂:



Overall reaction in eq. 2.3 [13]



By adding water to the bio-oil, it is divided into bio-oils, hydrophobic-lignin-derived fraction and water fraction (approximately 50% of the bio-oils) containing monomeric components consumed from hydrocarbons. The aqueous phase of the bio-oil contains 20% organic compounds and 80% water. In recent years, steam reforming reactions have been applied to the aqueous phase to a model component of aqueous phase of the bio-oil for studying catalyst development and process investigation [22].

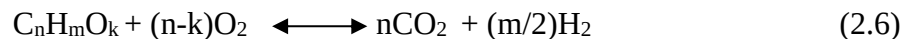
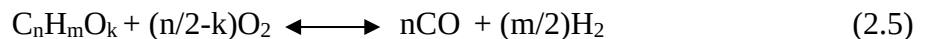
A large number of processes are deactivated due to coke accumulation. The problem of coke formation can be solved either by catalyst development that minimizes coke formation or by adding water vapor or oxygen to the inlet stream [16].

The steam reforming of oxygenates is endothermic. For this reason, high yields can be obtained at high temperatures according to Le Chateliers principle [23].

2.3.1.2 Partial oxidation

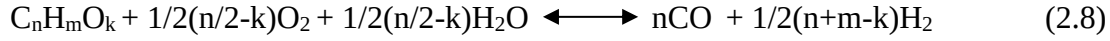
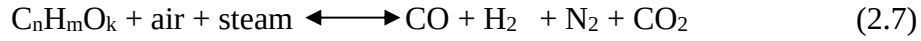
Partial oxidation is one of the hydrogen production methods. Conversion of hydrocarbons and carbon oxides in the presence of oxygen occurs the basis of partial oxidation method [23]. At the end of the reaction; heat is produced, reducing the energy requirement for the reaction to take place. However, excess air causes the oxidation to be complete forming CO₂ and H₂O [13].

Eq. 2.4 shows the partial oxidation general equation of the bio-oils, Eq. 2.5 and Eq. 2.6 show that the partial oxidation reactions.



2.3.1.3 Oxidative steam reforming

Oxidative steam reforming is generated from combination of steam reforming and partial oxidation. Eq. 2.7 shows the oxidative steam reforming general equation of the bio-oils, Eq. 2.8 and Eq. 2.9 show that the oxidative steam reforming reactions [13,18].



The most powerful advantage of this method is that energy requirement is minimized as the heat necessary for the process is produced by the partial oxidation reaction [13]. Therefore, oxidative steam reaction can be initiated quickly and continue without needing any additional heat. In addition to this, oxidative steam reforming has many advantages. Controlling of reactor temperature easier control of reactor temperature, decrease of formation hot spots and prevention of catalyst deactivation are advantages of this method [20]. However, H_2 efficiency is lower compared with steam reforming [13].

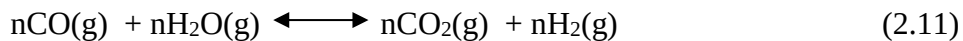
2.3.1.4 Sorption enhanced steam reforming

Sorption enhanced reforming is an alternative of the methods of hydrogen production has been recently increased by this method. In sorption enhanced steam reforming, combination of two different reactions occur, namely, steam reforming reaction and carbonation. Below equations are shown that the stages of this method.

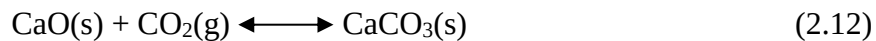
Reforming:



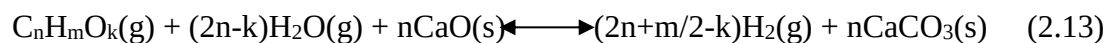
Water-Gas Shift:



Carbonation:



Overall:



General scheme of sorption enhanced reforming process is given in Figure 2.1.

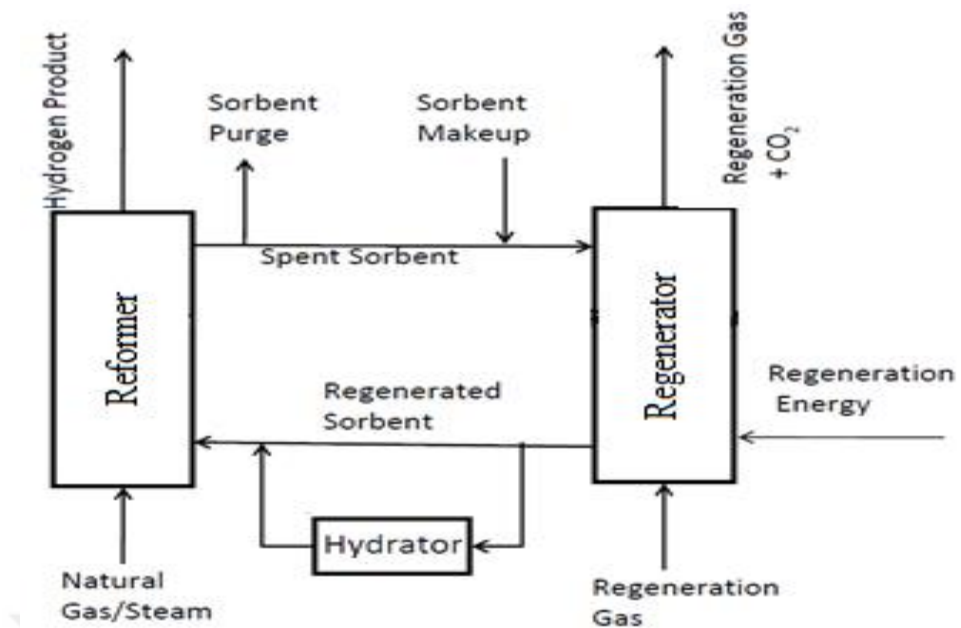


Figure 2.1: General scheme of sorption enhanced reforming process [Adapted from 24].

According to Figure 2.1, hydrogen and regeneration gas are generated from combination of natural and regeneration gas. The result of this reaction, sorbent purge and CO₂ are produced as side product.

Sorption enhanced reforming has many advantages when compared the other hydrogen production alternative methods. These advantages can be given briefly in following [24].

- Reduction of the H₂ purification process.
- Decreasing of number of equipments used (e.g. number of reactor etc.)
- Cost reduction
- Reforming reactor which used can be eliminate the carbon deposition
- Less energy requirement.
- Production of pure, sequestration ready, CO₂.

2.4 Literature Review of Bio-Oil Reforming Processes

Hydrogen is the most important element of the universe. In recent studies, researchers have found the optimum methods of the production of hydrogen are reported. According to results of these researches, via reforming of bio-oil compounds high percentages of hydrogen yields are achieved. Hydrogen production through reforming processes has also been widely reported in the literature. Reforming is affected by

various parameters such as catalyst type, temperature, reactor configuration and the residence time. To sum up, hydrogen yield produced by reforming processes, depends on complexity of process and operating parameters.

Trane et al. [25] investigated steam reforming of bio-oil and a few model compounds over a series of noble metal-based catalysts. The steam reforming of the model compounds, namely acetic acid and ethanol, was investigated in the temperature range 400-600°C over Ni, Ru and Rh supported on alumina and a ceria-zirconia sample. The supported Ni catalyst were the most abundant and cheapest for the steam reforming of these compounds, while other catalysts displayed poor performance.

Kechagiopoulos et al. [26] searched hydrogen production via aqueous phase reforming of ethylene glycol using a novel spouted bed reactor using a special design injection nozzle in combination with Olivine and Nickel of spouted bed reactor. The highest hydrogen yield was founded of %80 at 850 °C and H₂O/C ratio equal to 4.6. The known reforming problem of coke formation was not observed by investigators. According to results, Olivine assembly with Nickel is proved more efficient catalyst specifications on reforming processes.

Zhao et. Al. [27] investigated ethylene glycol steam reforming at 300°C through Pt-Ni bimetallic catalysts supported by SiO₂ and CeO₂. It is reported that catalysts with 3 wt% Pt and 7 wt% Ni were showed highest activity. While SiO₂ supported catalysts were being founded better activity and H₂ selectivity, CeO₂ supported catalysts were observed less coke formation and better stability. Furthermore, adding of Pt is showed that reducing the methanation reactions.

Wenju et al. [28] simulated the thermodynamic anlaysis of the partial oxidation of ethanol to form hydrogen rich mixture using Gibbs free energy minimization calculation through of ChemCAD simulation program. In this paper, it was investigated that effect of temperature, effect of process conditions and effect of O₂/C₂H₅OH molar ratio. According to the results, complete consuming of ethanol, 86.28%-94.98% H₂ yield and 34.69%-38.64% concentrarion of CO have been observed under optimal conditions.

According to another research [29], hydrogen production from bio-oil made by types of reforming processes such as steam reforming and partial oxidation was researchcd and chosen temperature, steam to carbon and oxygen to carbon molar feed ratios as

key operating parameters. It was analysed effect of these parameters on the performance of reforming processes by Authayanun et al.

According the literature ethylene glycol has been found more efficient hydrogen production [18].

The physical properties of ethylene glycol are given at the Table 2.6.

Table 2.6: The physical properties of ethylene glycol [30].

Properties	Ethylene glycol
Molecular formula	C ₂ H ₆ O ₂
Heat of combustion 298K (kcal/mol)	−281,9
Liquid density (gr/ml), (water:1)	1.1
Boiling point (K)	471
Melting point (K)	260
Flash point (K)	384

Steam reforming of ethylene glycol can be described as the following equation 2.14.



In the study of Vagia and Lemonidou [30], ethylene glycol has been chosen as one of the model compounds of bio-oil for hydrogen production considering efficiency and reforming conditions. The maximum stoichiometric yield is obtained as 2.5 mol H₂/mol carbon. In this study, coke has been also produced.

Vagia and Lemonidou examined ethylene glycol under several conditions such as temperature (400–1300 K), and steam to fuel ratio (1–9). In addition to these, the effect of pressure was also examined from 1 to 20 atm. It is reported that ethylene glycol was totally consumed at all reaction conditions investigated.

ASPEN simulation program was used and ethylene glycol, carbon, methane, hydrogen, carbon monoxide, carbon dioxide and steam were defined at the simulation environment. According to that research, in the case of temperature increasing, hydrogen mole fraction increasing has been observed while methane and carbon dioxide mole fraction decreased. At the same time, occurrence of carbon has been decreasing at the high temperatures and maximum hydrogen yield observed at 900 K [31].

Consequently, ethylene glycol has been chosen as a model compound of bio-oil because of the considering that above conditions are desired in this thesis.

Sladkovskiy et al. [32] presented a study about large scale process design focus on sorbitol aqueous phase reforming. Aspen HYSYS was used when simulated the plant and sorbitol syrup as a raw material, 500 kg/h production of hydrogen as output product were determined on the simulation environment. It was reported that the contribution of the selected raw material to the cost was very large. Thereof, woody biomass is seen most economic raw material for hydrogen production.

According to another research, hydrogen production has been made as regarding of the six carbon model. 1-hexanol, 1,6-hexanediol and sorbitol are on of the mostly used in literature. Sorbitol is a sugar alcohol of six-carbon fully saturated with hydroxyl group. Several biomasses such as berries and fruits or glucose can be used for sorbitol sources. Hydrogen production is provided by using sorbitol [33].



Jun et al. [33] examined steam reforming of sorbitol under various conditions such as temperature (300–1200 K), and carbon ratio (0.5–30). In addition to these, the effect of pressure was also examined from 1 to 150 atm. It is reported that increasing steam to carbon ratio promoted hydrogen formation above 500 K. Hydrogen production was observed to increase at high temperatures and low pressures. Maximum hydrogen yield was obtained at 1000 K and 1 atm [33].

2.5 Aspen Plus Process Simulation

Process engineers, process designers and researchers need simulation of during design of process. Process simulation ensure that prediction of operation performance such as thermodynamic equilibrium, energy and mass balance, chemical calculations and cost-saving calculations. These parameters and conditions are could be used by academy and plants of large number of every scale with their many stages for instance lab practises, pilot productions, middle-scaled productions and large-scaled productions [31].

Process parameters such as temperatures, rates, compositions, pressures, etc. estimated via process simulation using analysis techniques. Recently, computer-based simulation techniques have been used in all fields of science and industry. The most preferred of these simulation programs is Aspen Plus which is also used in this thesis.

Aspen Plus is so much preferred because it has a wide range of parameters, high number of components in its database, provides realistic predictions for chemical process and is easy to use for end users [31].

Aspen Plus is one of the simulation systems which developed for process engineering. Aspen is the acronym of Advanced System for Process Engineering. Aspen is based on flowsheet simulation. In the recent versions of this simulation, Aspen Plus was replaced of Aspen. Aspen is one of the computer software which is used for modelling factory process plans as using quantitative model. Aspen is a chemical process simulation which has shown all different operations (from raw material to finished product), chemical processes and input and output raw materials and energy stream with symbols. The behaviour of chemical process are modelled by Aspen utilizing basic engineering calculations. Aspen makes engineering calculations utilizing following parameters:

- Physical limits on the process
- Rate correlations for momentum, heat and mass transfer
- Thermodynamics relations between reacting and non-reacting mediums
- Reaction stoichiometry and kinetic data
- Balance equations of thermodynamics properties such as mass, mole and energy

When the parameters such as operation conditions, thermodynamic properties are given accurate and sensible, an actual plant behavior can be simulated by Aspen Plus. Performing ‘what if’ tests, controlling of plant specifications, improving process of plant, conducting analyses and making optimization studies are provided using Aspen Plus. Moreover, polymer process optimization, environmental & safety analysis, optimization with custom equipment, concurrent conceptional engineering etc. can be made in this simulation [34].

Following steps are given for conducting simulation process using Aspen Plus.

- Chemical componenets used in process should be identified to system.
- Terhmodynamic model to be represent chemical properties of components and solutions at the process should be identified to system. This model has been occured by Aspen Plus.
- Process flowsheet are identified.

- Thermodynamic conditions (such as temperature, pressure and component) of stream flows and all feed streams should be entered and identified.
- Operation conditions should be identified for making basic calculations [35].

Equipments used in Aspen has been given at the Figure 2.2.

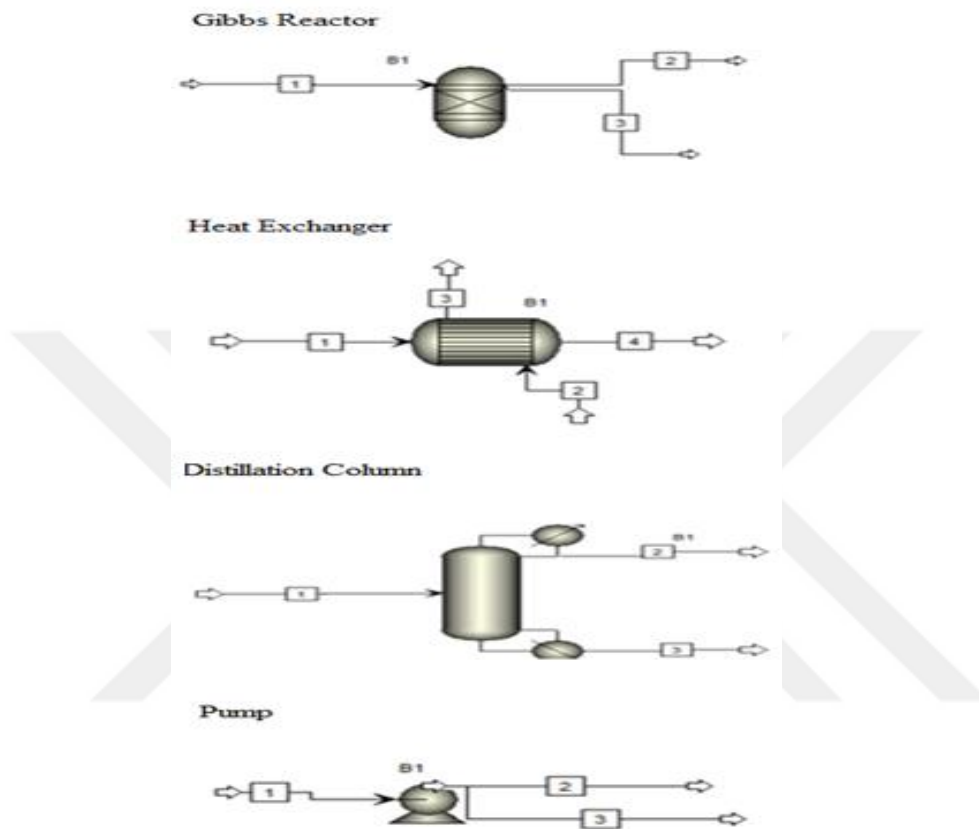


Figure 2.2: Equipments used in Aspen Plus [Adapted from 36].

3. METHODOLOGY

3.1 Thermodynamic Analysis and Gibbs Free Energy Minimization

Various performance criteria can be formulated with thermodynamic analysis. Thermal equilibria, kinetic relations, balance equations and equations of state can be calculated with thermodynamic analysis. When the thermodynamic analysis is performed, specific constraints are used for reaching the optimum solution. The methods used in thermodynamic analysis can be classified such as linear, nonlinear maximum principle and dynamic programming. Optimization problems can be occurred in the case of complexity of constraints [37].

Thermodynamic analysis includes mainly three parts. These are given respectively in this chapter. Evaluation of thermodynamic performance of operation occurring is the first part of thermodynamic analysis. The second one is the determination of improvements of object and cost saving. Thermodynamics and economic analysis of the process forms the third part. Thermodynamic analysis aims identifying, quantifying, and minimizing irreversibilities in a system. Energy conservation is significant value of such these analysis [37].

3.1.1 Gibbs free energy minimization

Gibbs free energy minimization is a thermodynamic analysis method that enables the determination of phase and component distributions of a system according to the determined working parameters [3]. The basis of the Gibbs free energy minimization technique is based on the equilibrium of the reaction when it reaches the minimum value of total Gibbs free energy, which is a function of temperature, pressure and component concentration at equilibrium [16]. The most important advantage of this method is that the reaction mechanism is not required. Therefore, this technique is used in the thermodynamic analysis of non-specific systems [3].

When the Gibbs free energy is at minimum value; its differential is zero and this is shown in equation 3.1.

$$(dG^t)_{T,p} = 0 \quad (3.1)$$

Total Gibbs free energy of a system is given by the sum of the chemical potential of all components:

$$G^t = \sum_{i=1}^N n_i \mu_i \quad (3.2)$$

The chemical potential of a component is given by following equation.

$$\mu_i = \Delta G_{fi}^0 + RT \ln\left(\frac{f_i}{f_i^0}\right) \quad (3.3)$$

When the above equations are combined, the total Gibbs free energy of the system is occurred. Below equation is showed Gibbs free energy will be minimized at specified temperature-pressure-feed composition.

$$G^t = \sum_{i=1}^N n_i \Delta G_{fi}^0 = \sum_{i=1}^N n_i RT \ln\left(\frac{f_i}{f_i^0}\right) \quad (3.4)$$

3.2 Aspen Plus and Gibbs Reactor

Aspen Plus V.8.8 is considered as a suitable simulation environment in this thesis. Simulation of a single phase or multiphase of multi-component systems in equilibrium are provided in this capable simulation program.

Mathematical modeling is the most important calculation for the simulation of a chemical process. Since Aspen Plus provides the best solutions for these mathematical models, it helps in finding the right techniques by making the most effective calculations. Phase equilibrium calculations are based on the principle of equilibrating the process by optimizing the total Gibbs Free Energy of the components in each phase in the chemical process. In order to calculate the chemical equilibrium and to minimize the Gibbs Free Energy, it is requirement to find the appropriate kinetics taking into account the molar and mass balances of the system [38].

Fundamental thermodynamic kinetic models can be classified respectively in following:

- Equation of State
- Activity Coefficient Models
- Vapour Pressure Models
- Semiempirical Models

Equation of state and activity coefficient models are used for determination of equilibrium relations with utilizing fugacity coefficients. There are several equations of state which are used for calculating equilibrium conditions in thermodynamic analysis. The widely well-know equation of states are PR (Peng - Robinson, 1976) and SRK (Soave-Redlich-Kwong, 1972).

These models need only critical properties and ideal gas enthalpies which are both cubic and used for calculating thermodynamic properties [39].

Various relations are used for calculating liquid phase activity coefficients and fugacity coefficients. The well-known activity coefficient model is NRTL (Non-Random Two Liquid) model. Ideal gas enthalpy and evaporation correlations are used for calculating enthalpy in Aspen Plus.

Peng-Robinson equation of state is advised to use in Aspen Plus V.8.8 calculations for biomass components [16]. The reasons of this are given in following:

- able to calculate in broad range
- the broadest binary interaction database
- this equation can also be used in calculation of hydrocarbon, H₂O, air and fuel gas

Semiempirical equations of state representation as the sum of repulsion pressure P_R and attraction pressure P_A [40].

$$P = P_R + P_A \quad (3.5)$$

Redlich and Kwong (1949), Soave (1972) and van der Waals (1873) have expressed the repulsion pressure by the van der Waals hard sphere equation, which is

$$P_R = \frac{RT}{v-b} \quad (3.6)$$

The attraction pressure can be expressed as equation 3.7 where $g(v)$ is a function of molar volume.

$$P_A = - \frac{a}{g(v)} \quad (3.7)$$

Peng and Robinson suggest an equation for pressure in equation 3.8 and this equation of state was used in calculations of fugacity coefficients in this thesis. The relationship between Peng-Robinson equation of state and ideal gas behaviour disclosed by Peng and Robinson in 1976. The parameters such as pressure (P), temperature (T), ideal gas

constant (R), molar volume (v), temperature at critical point (T_c), pressure at critical point (P_c) and Peng-Robinson special critical parameters (a and b) are given [40]:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)} \quad (3.8)$$

$$a = 0.457235 \frac{(RT_c)^2}{P_c} \quad (3.9)$$

$$b = 0.077796 \frac{(RT_c)}{P_c} \quad (3.10)$$

Gibbs free energy minimization method was used as utilizing Aspen Plus v.8.8 in thermodynamic equilibrium calculations. RGibbs reactor was used in simulation program. Composition of compounds in reaction system were calculated Gibbs free energy minimization method by RGibbs reactor. RGibbs Reactor calculates the Gibbs free energy of all components in reaction system according to reaction mechanism by used energy minimization principle. Figure 3.1 shows that a simulation with using RGibbs reactor.

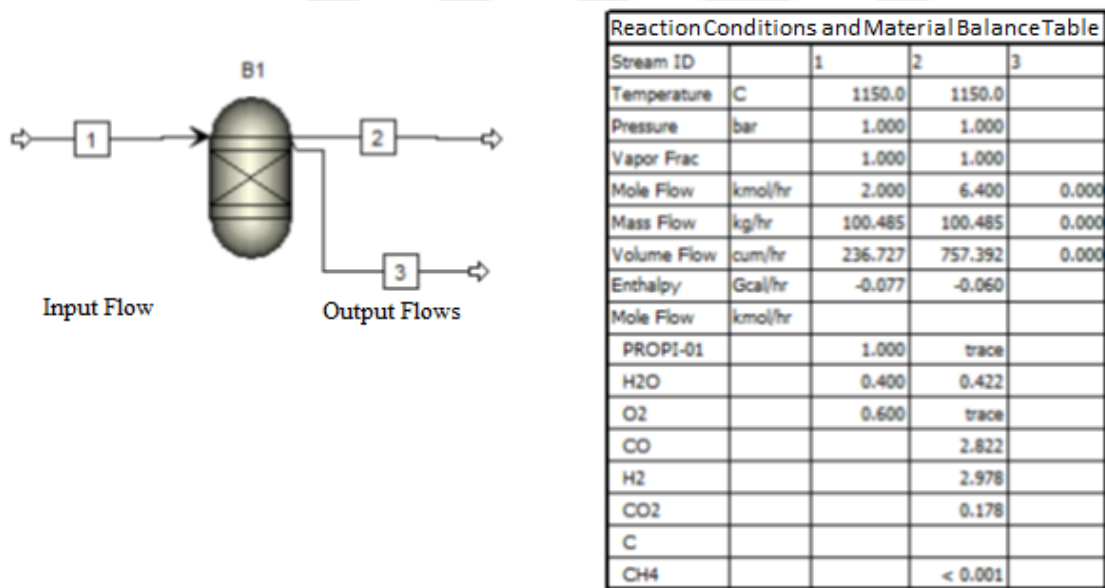


Figure 3.1: A simulation example with using RGibbs reactor [Adapted from 36].

Aspen Plus Gibbs Reactor is used for volatile compounds reactions. C, H, O, N, S, ash and humidity are fundamental biomass components. Carbon is founded in gas phase and divided from top flow. The reminded carbon is divided from bottom flow as a char [41].

3.3 Chemical Reaction Analysis

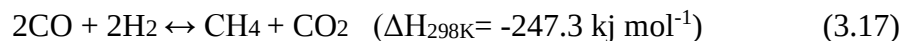
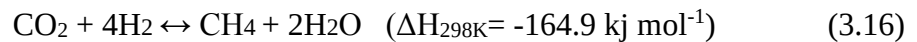
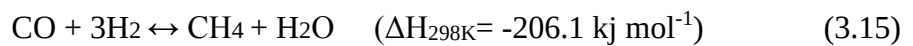
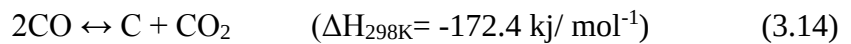
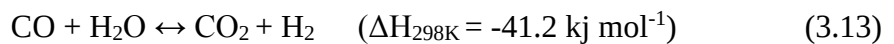
Thermodynamic equilibrium analysis is a useful tool for analyzing the complex reaction mechanism. Thermodynamic limits of the system are determined by thermodynamic equilibrium analysis. It is therefore a useful guide in the development of experiments and processes. Since the steam reforming reactions are usually carried out at higher temperatures, thermodynamic simulation provides results close to experimental or commercial data [23].

Reactions and enthalpy of formation values for steam reforming, oxidative steam reforming and sorption enhanced steam reforming for bio-oil model components, ethylene glycol and sorbitol are given in this section. Negative values of enthalpy, called as exothermic and positive values of enthalpy, called as endothermic.

Complete steam reforming reactions of ethylene glycol and sorbitol are shown by the following equations 3.11 and 3.12 [30,42,43].

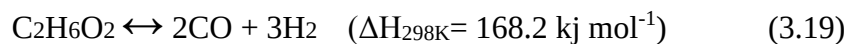
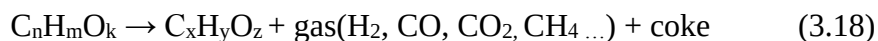


In addition to the basic reaction, side reactions also occur. Ethylene glycol and sorbitol are degraded by side reactions because they have low stability. Side reactions, which are water gas shift reaction (WGS) (equation 3.13), Boudouard reaction (equation 3.14) and methanation reactions (reactions 3.15, 3.16 and 3.17) are shown by following equations [30].

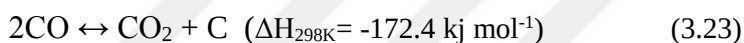
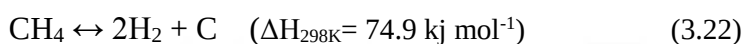
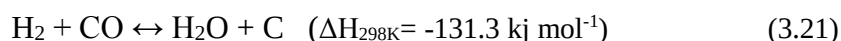


Besides all these reactions, thermal decomposition reactions which form a gas mixture and coke formation under the influence of temperature are also realized. General thermal decomposition reaction for most oxygenates is given in equation 3.18 [30].

Specific thermal decomposition reactions for ethylene glycol (equation 3.19) and sorbitol (equation 3.20) are shown in below [42-43]:



Other possible reactions that may lead to coke formation for both model components are given in the following equations 3.21-3.24 [42].



The conventional steam reforming reaction is endothermic, so maximum efficiency is obtained at high temperatures or low pressures according to La Chatelier's principle. All steam reactions and side reactions, mentioned at above, have shown in Table 3.1 as schematic view with general information about these reactions.

3.4 Calculations

3.4.1 Conversion and yield formulas for ethylene glycol

$C_2H_6O_2$, CH_4 , CO_2 , H_2 , CO , H_2O and C were used as components of steam reforming of ethylene glycol. CaO and $CaCO_3$ were described to simulation environment in the sorption enhanced reforming.

Moreover, in the oxidative steam reforming of ethylene glycol $C_2H_6O_2$, O_2 , CH_4 , CO_2 , H_2 , CO , H_2O and C were used. In the case of sorption enhanced reforming, CaO and $CaCO_3$ were described to simulation environment.

The conversions of feed stream ($C_2H_6O_2$, H_2O , O_2) and the yields of output stream (CH_4 , CO_2 , H_2 , CO , H_2O and C) are expressed from equations 3.5 to 3.12.

Tablo 3.1: Main reactions and side reactions for EG and Sorbitol.

<i>Main Reactions</i>	<i>Intermediate Reactions</i>	<i>Coking Reactions</i>
<i>Complete Steam Reforming Reactions</i>	<i>Water-Gas Shift Reaction</i>	<i>Boudouard Reaction</i>
EG: $\text{C}_2\text{H}_6\text{O}_2 + 2\text{H}_2\text{O} \leftrightarrow 2\text{CO}_2 + 5\text{H}_2$ $\Delta H_{298\text{K}} = 85.9 \text{ kJ mol}^{-1}$ Sorbitol: $\text{C}_6\text{H}_{14}\text{O}_6 + 6\text{H}_2\text{O} \leftrightarrow 6\text{CO}_2 + 13\text{H}_2$ $\Delta H_{298\text{K}} = 230.1 \text{ kJ mol}^{-1}$	$\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$ $\Delta H_{298\text{K}} = -41.2 \text{ kJ mol}^{-1}$	$2\text{CO} \leftrightarrow \text{C} + \text{CO}_2$ $\Delta H_{298\text{K}} = -172.4 \text{ kJ mol}^{-1}$
<i>Thermal Decomposition</i>	<i>Methanation</i>	<i>Coke Formations</i>
EG: $\text{C}_2\text{H}_6\text{O}_2 \leftrightarrow 2\text{CO} + 3\text{H}_2$ $\Delta H_{298\text{K}} = 168.2 \text{ kJ mol}^{-1}$ Sorbitol: $\text{C}_6\text{H}_{14}\text{O}_6 \leftrightarrow 6\text{CO} + 7\text{H}_2$ $\Delta H_{298\text{K}} = 450.6 \text{ kJ mol}^{-1}$	$\text{CO} + 3\text{H}_2 \leftrightarrow \text{CH}_4 + \text{H}_2\text{O}$ $\Delta H_{298\text{K}} = -206.1 \text{ kJ mol}^{-1}$ $\text{CO}_2 + 4\text{H}_2 \leftrightarrow \text{CH}_4 + 2\text{H}_2\text{O}$ $\Delta H_{298\text{K}} = -164.9 \text{ kJ mol}^{-1}$ $2\text{CO} + 2\text{H}_2 \leftrightarrow \text{CH}_4 + \text{CO}_2$ $\Delta H_{298\text{K}} = -247.3 \text{ kJ mol}^{-1}$	$\text{H}_2 + \text{CO} \leftrightarrow \text{H}_2\text{O} + \text{C}$ $\Delta H_{298\text{K}} = -131.3 \text{ kJ mol}^{-1}$ $\text{CH}_4 \leftrightarrow 2\text{H}_2 + \text{C}$ $\Delta H_{298\text{K}} = 74.9 \text{ kJ mol}^{-1}$ $2\text{CO} \leftrightarrow \text{CO}_2 + \text{C}$ $\Delta H_{298\text{K}} = -172.4 \text{ kJ mol}^{-1}$ $\text{CO}_2 + 2\text{H}_2 \leftrightarrow 2\text{H}_2\text{O} + \text{C}$ $\Delta H_{298\text{K}} = -90.13 \text{ kJ mol}^{-1}$

$$\text{The conversion of \% } \mathbf{C_2H_6O_2} = \frac{[\mathbf{C_2H_6O_2}]_{\text{input}} - [\mathbf{C_2H_6O_2}]_{\text{output}}}{[\mathbf{C_2H_6O_2}]_{\text{input}}} \times 100 \quad (3.5)$$

$$\text{The conversion of \% } \mathbf{H_2O} = \frac{[\mathbf{H_2O}]_{\text{input}} - [\mathbf{H_2O}]_{\text{output}}}{[\mathbf{H_2O}]_{\text{input}}} \times 100 \quad (3.6)$$

$$\text{The conversion of \% } \mathbf{O_2} = \frac{[\mathbf{O_2}]_{\text{input}} - [\mathbf{O_2}]_{\text{output}}}{[\mathbf{O_2}]_{\text{input}}} \times 100 \quad (3.7)$$

$$\text{The yield of \% } \mathbf{H_2} = \frac{[\mathbf{H_2}]_{\text{output}}}{3 \times [\mathbf{C_2H_6O_2}]_{\text{input}} + [\mathbf{H_2O}]_{\text{input}}} \times 100 \quad (3.8)$$

$$\text{The yield of \% } \mathbf{CO} = \frac{[\mathbf{CO}]_{\text{output}}}{2 \times [\mathbf{C_2H_6O_2}]_{\text{input}}} \times 100 \quad (3.9)$$

$$\text{The yield of \% } \mathbf{CO_2} = \frac{[\mathbf{CO_2}]_{\text{output}}}{2 \times [\mathbf{C_2H_6O_2}]_{\text{input}}} \times 100 \quad (3.10)$$

$$\text{The yield of \% } \mathbf{C} = \frac{[\mathbf{C}]_{\text{output}}}{2 \times [\mathbf{C_2H_6O_2}]_{\text{input}}} \times 100 \quad (3.11)$$

$$\text{The yield of \% } \mathbf{CH_4} = \frac{[\mathbf{CH_4}]_{\text{output}}}{2 \times [\mathbf{C_2H_6O_2}]_{\text{input}}} \times 100 \quad (3.12)$$

3.4.2 Conversion and yield formulas for sorbitol

$\text{C}_6\text{H}_{14}\text{O}_6$, CH_4 , CO_2 , H_2 , CO , H_2O and C were used as components of steam reforming of ethylene glycol. CaO and CaCO_3 were described to simulation environment in the sorption enhanced reforming.

Moreover, in the autothermal reforming of ethylene glycol $\text{C}_2\text{H}_6\text{O}_2$, O_2 , CH_4 , CO_2 , H_2 , CO , H_2O and C were used. In the case of sorption enhanced reforming, CaO and CaCO_3 were described to simulation environment.

The conversions of feed stream ($\text{C}_6\text{H}_{14}\text{O}_6$, H_2O , O_2) and the yields of output stream (CH_4 , CO_2 , H_2 , CO , H_2O and C) are expressed as following.

$$\text{The conversion of \% } \mathbf{C_6H_{14}O_6} = \frac{[\mathbf{C_6H_{14}O_6}]_{\text{input}} - [\mathbf{C_6H_{14}O_6}]_{\text{output}}}{[\mathbf{C_6H_{14}O_6}]_{\text{input}}} \times 100 \quad (3.13)$$

$$\text{The conversion of \% } \mathbf{H_2O} = \frac{[\mathbf{H_2O}]_{\text{input}} - [\mathbf{H_2O}]_{\text{output}}}{[\mathbf{H_2O}]_{\text{input}}} \times 100 \quad (3.14)$$

$$\text{The conversion of \% } \mathbf{O_2} = \frac{[\mathbf{O_2}]_{\text{input}} - [\mathbf{O_2}]_{\text{output}}}{[\mathbf{O_2}]_{\text{input}}} \times 100 \quad (3.15)$$

$$\text{The yield of \% } \mathbf{H_2} = \frac{[\mathbf{H_2}]_{\text{output}}}{7 \times [\mathbf{C_6H_{14}O_6}]_{\text{input}} + [\mathbf{H_2O}]_{\text{input}}} \times 100 \quad (3.16)$$

$$\text{The yield of \% CO} = \frac{[\text{CO}]_{\text{output}}}{6 \times [\text{C}_6\text{H}_{14}\text{O}_6]_{\text{input}}} \times 100 \quad (3.17)$$

$$\text{The yield of \% CO}_2 = \frac{[\text{CO}_2]_{\text{output}}}{6 \times [\text{C}_6\text{H}_{14}\text{O}_6]_{\text{input}}} \times 100 \quad (3.18)$$

$$\text{The yield of \% C} = \frac{[\text{C}]_{\text{output}}}{6 \times [\text{C}_6\text{H}_{14}\text{O}_6]_{\text{input}}} \times 100 \quad (3.19)$$

$$\text{The yield of \% CH}_4 = \frac{[\text{CH}_4]_{\text{output}}}{6 \times [\text{C}_6\text{H}_{14}\text{O}_6]_{\text{input}}} \times 100 \quad (3.20)$$

3.5 Simulation Sets

The properties of reactants and products were described as the first step into Aspen Plus simulation program at the specified temperature and pressure while executing simulation sets. After that, the second step is minimization were run to obtain compositions of reactants and products at the equilibrium state. 5 sets of both ethylene glycol and sorbitol were performed using RGibbs reactor at the simulation. Then, 2 more sets were studied to see effect of ethylene glycol and sorbitol mixture.

3.5.1 Ethylene glycol simulation sets

The steam reforming reaction of ethylene glycol was performed in set 1. In Table 3.2, the feed flow compositions defined in Aspen were given in below during the steam reforming reaction of ethylene glycol. The simulation executed in between 200-1000 °C temperature range ($\Delta T=50$ °C) and under pressure 1 bar.

Table 3.2: Molar composition of feed stream at the steam reforming of ethylene glycol.

Components	Mole number of feed stream			
C ₂ H ₆ O ₂	1	1	1	1
H ₂ O	2	3	4	5

Oxidative steam reforming was performed in the Set 2. The compositions of feed stream were given in the following Table 3.3 for the oxidative steam reforming of ethylene glycol at the constant $\text{C}_2\text{H}_6\text{O}_2/(\text{H}_2\text{O}+\text{O}_2)=1/2$. The simulation was executed in between 200-1000 °C temperature range ($\Delta T=50$ °C) and under pressure 1 bar.

Sorption enhanced reforming of ethylene glycol was performed in Set 3. The compositions of feed stream were given in the following Table 3.4 and Table 3.5 in the sorption enhanced reforming of ethylene glycol.

Table 3.3: Molar composition of feed stream at the oxidative steam reforming of ethylene glycol ($\text{H}_2\text{O}+\text{O}_2=2$ moles).

Components	Mole number of feed stream			
$\text{C}_2\text{H}_6\text{O}_2$	1.0	1.0	1.0	1.0
H_2O	1.5	1.0	0.5	2.0
O_2	0.5	1.0	1.5	0.0

CaO which used as adsorbent of CO_2 , was taken as 1-3 mole in all conditions. The simulation was executed in between 200-1000 $^\circ\text{C}$ temperature range ($\Delta T=50$ $^\circ\text{C}$) and under pressure 1 bar. Temperature were changed as 200-1000 $^\circ\text{C}$ for each feed stream. The effect of CaO adsorbent into the steam reforming process was researched as making this simulation.

Table 3.4: Molar composition of feed stream at the sorption enhanced steam reforming of ethylene glycol ($\text{CaO}=1$ mole).

Components	Mole number of feed stream			
$\text{C}_2\text{H}_6\text{O}_2$	1	1	1	1
H_2O	2	3	4	5
CaO	1	1	1	1

Table 3.5: Molar composition of feed stream at the sorption enhanced steam reforming of ethylene glycol ($\text{CaO}=3$ moles).

Components	Mole number of feed stream			
$\text{C}_2\text{H}_6\text{O}_2$	1	1	1	1
H_2O	2	3	4	5
CaO	3	3	3	3

Set 4 was executed regarding the effect of CaO adsorbent into the oxidative steam reforming of ethylene glycol. The compositions of feed stream were determined in the following Table 3.6 and Table 3.7 in the sorption enhanced steam reforming of ethylene glycol. CaO was taken as 1-3 mole in all conditions. The simulation was executed in between 200-1000 $^\circ\text{C}$ temperature range ($\Delta T=50$ $^\circ\text{C}$) and under pressure 1 bar. Temperature was changed as 200-1000 $^\circ\text{C}$ for each feed stream. The effect of CaO adsorbent into the oxidative steam reforming process was researched as making this simulation.

Table 3.6: Molar composition of feed stream at the sorption enhanced oxidative steam reforming of ethylene glycol. ($\text{CaO}=1$ mole).

Components	Mole number of feed stream			
$\text{C}_2\text{H}_6\text{O}_2$	1.0	1.0	1.0	1.0
H_2O	1.5	1.0	0.5	2.0
O_2	0.5	1.0	1.5	0.0
CaO	1	1	1	1

Table 3.7: Molar composition of feed stream at the sorption enhanced oxidative steam reforming of ethylene glycol. (CaO=3 moles).

Components	Mole number of feed stream			
C ₂ H ₆ O ₂	1.0	1.0	1.0	1.0
H ₂ O	1.5	1.0	0.5	2.0
O ₂	0.5	1.0	1.5	0.0
CaO	3	3	3	3

Set 5 was executed regarding the effect of pressure on the steam reforming of ethylene glycol. In feed stream, C₂H₆O₂ was taken as 1 mole, H₂O was taken as 2 moles in this set. Pressure was changed as 1 bar, 10 bars and 20 bars, respectively. Temperature was changed as 200-1000 °C for each feed stream.

3.5.2 Sorbitol simulation sets

The steam reforming reaction of sorbitol was performed in set 1. In Table 3.8 the feed flow compositions defined in Aspen were given in below during the steam reforming reaction of sorbitol. The simulation executed in between 200-1000 °C temperature range ($\Delta T=50$ °C) and under pressure 1 bar.

Table 3.8: Molar composition of feed stream at the steam reforming of sorbitol.

Components	Mole number of feed stream				
C ₆ H ₁₄ O ₆	1	1	1	1	1
H ₂ O	6	7	8	9	10

Oxidative steam reforming was performed in the Set 2. The compositions of feed stream were given in the following Table 3.9 for the oxidative steam reforming of sorbitol at the constant C₆H₁₄O₆/(H₂O+O₂)=1/6. The simulation was executed in between 200-1000 °C temperature range ($\Delta T=50$ °C) and under pressure 1 bar.

Table 3.9: Molar composition of feed stream at the oxidative steam reforming of sorbitol (H₂O+O₂=6 moles).

Components	Mole number of feed stream				
C ₆ H ₁₄ O ₆	1.0	1.0	1.0	1.0	1.0
H ₂ O	5.0	4.0	3.0	2.0	1.0
O ₂	1.0	2.0	3.0	4.0	5.0

Sorption enhanced reforming of sorbitol was performed in Set 3. The compositions of feed stream were given in the following Table 3.10 and Table 3.11 in the sorption enhanced steam reforming of sorbitol. CaO which used as adsorbent of CO₂, was taken as 1-3 mole in all conditions. The simulation was executed in between 200-1000 °C

temperature range ($\Delta T=50$ °C) and under pressure 1 bar. Temperature were changed as 200-1000 °C for each feed stream. The effect of CaO adsorbent into the steam reforming process was researched as making this simulation.

Table 3.10: Molar composition of feed stream at the sorption enhanced steam reforming of sorbitol (CaO=1 mole).

Components	Mole number of feed stream				
C ₆ H ₁₄ O ₆	1	1	1	1	1
H ₂ O	6	7	8	9	10
CaO	1	1	1	1	1

Table 3.11: Molar composition of feed stream at the sorption enhanced steam reforming of sorbitol (CaO=3 moles).

Components	Mole number of feed stream				
C ₆ H ₁₄ O ₆	1	1	1	1	1
H ₂ O	6	7	8	9	10
CaO	3	3	3	3	3

Set 4 was executed regarding the effect of CaO adsorbent into the oxidative steam reforming of sorbitol. The compositions of feed stream were determined in the following Table 3.12 and Table 3.13 in the sorption enhanced steam reforming of sorbitol. CaO was taken as 1-3 mole in all conditions. The simulation was executed in between 200-1000 °C temperature range ($\Delta T=50$ °C) and under pressure 1 bar. Temperature was changed as 200-1000 °C for each feed stream. The effect of CaO adsorbent into the oxidative steam reforming process was researched as making this simulation.

Table 3.12: Molar composition of feed stream at the sorption enhanced oxidative steam reforming of sorbitol. (CaO=1 mole).

Components	Mole number of feed stream				
C ₆ H ₁₄ O ₆	1.0	1.0	1.0	1.0	1.0
H ₂ O	5.0	4.0	3.0	2.0	1.0
O ₂	1.0	2.0	3.0	4.0	5.0
CaO	1.0	1.0	1.0	1.0	1.0

Table 3.13: Molar composition of feed stream at the sorption enhanced oxidative steam reforming of sorbitol. (CaO=3 moles).

Components	Mole number of feed stream				
C ₆ H ₁₄ O ₆	1.0	1.0	1.0	1.0	1.0
H ₂ O	5.0	4.0	3.0	2.0	1.0
O ₂	1.0	2.0	3.0	4.0	5.0
CaO	3.0	3.0	3.0	3.0	3.0

Set 5 was executed regarding the effect of pressure on the steam reforming of sorbitol. In feed stream, $C_6H_{14}O_6$ was taken as 1 mole, H_2O was taken as 6 moles in this set. Pressure was changed as 1 bar, 10 bars and 20 bars, respectively. Temperature was changed as 200-1000 $^{\circ}C$ for each feed stream.

3.5.3 Ethylene glycol and sorbitol mixture simulation sets

In mixture studies, after separate studies for ethylene glycol and sorbitol, the effect of mixing these two components was investigated. The steam reforming reaction of mixture was performed in set 1. In Table 3.14, the feed flow compositions defined in Aspen were given in below during the steam reforming reaction of constant feed mixture (1 mol). The simulation executed in between 200-1000 $^{\circ}C$ temperature range ($\Delta T=50$ $^{\circ}C$) and under pressure 1 bar.

Table 3.14: Molar composition of feed stream at the steam reforming of mixture ($C_2H_6O_2 + C_6H_{14}O_6 = 1$ mole).

Components	Mole number of feed stream			
$C_2H_6O_2$	0.5	0.5	0.5	0.5
$C_6H_{14}O_6$	0.5	0.5	0.5	0.5
H_2O	3	4	5	6

Sorption enhanced steam reforming of mixture was performed in Set 2. The compositions of feed stream were given in the following Table 3.15 in the sorption enhanced steam reforming of mixture. H_2O was taken constant stream as 3 moles and CaO which used as adsorbent of CO_2 , was taken as 1-3 mole in all conditions. The simulation was executed in between 200-1000 $^{\circ}C$ temperature range ($\Delta T=50$ $^{\circ}C$) and under pressure 1 bar. Temperature were changed as 200-1000 $^{\circ}C$ for each feed stream. The effect of CaO adsorbent into the steam reforming process was researched as making this simulation.

Table 3.15: Molar composition of feed stream at the sorption enhanced reforming of mixture.

Components	Mole number of feed stream	
$C_2H_6O_2$	0.5	0.5
$C_6H_{14}O_6$	0.5	0.5
H_2O	3	3
CaO	1	3

In the simulation, a single flow was sent to the Gibbs reactor ($C_2H_6O_2$, $C_6H_{14}O_6$, H_2O and CaO) and the upper and lower flows as output flows were obtained.

While the upper output flow is H_2 , H_2O , O_2 , H_2O , CO , CO_2 or CH_4 , the lower flow is obtained as C (coke) or CaCO_3 . The gas products obtained as a result of the simulation were obtained from the upper stream and the solid products from the upper stream.

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4. RESULTS AND DISCUSSION

4.1 Thermodynamic Analysis of Ethylene Glycol Steam Reforming

The steam reforming reaction of ethylene glycol was performed in set 1. In Table 3.2, the feed flow compositions defined in Aspen were given in below during the steam reforming reaction of ethylene glycol. The simulation executed in between 200-1000 °C temperature range ($\Delta T=50$ °C) and under pressure 1 bar. Ethylene glycol was consumed at every operational conditions. The reason of this ethylene glycol has lower stability. In endothermic equations, equation moves to right side in the higher temperatures; otherwise in the exothermic equations, steam reforming equation moves the right side at the lower temperature. Due to these reactions, ethylene glycol is consumed in each operational conditional.

Conversion of H_2O has negative values under the 400 °C in steam reforming reaction of ethylene glycol and this is given in Figure 4.1. Temperature which are above 400 °C steam reforming reaction moves the right side and conversion of H_2O is affected positively. While the mole of H_2O is increasing in the input flow, decreasing of H_2O conversion is observed.

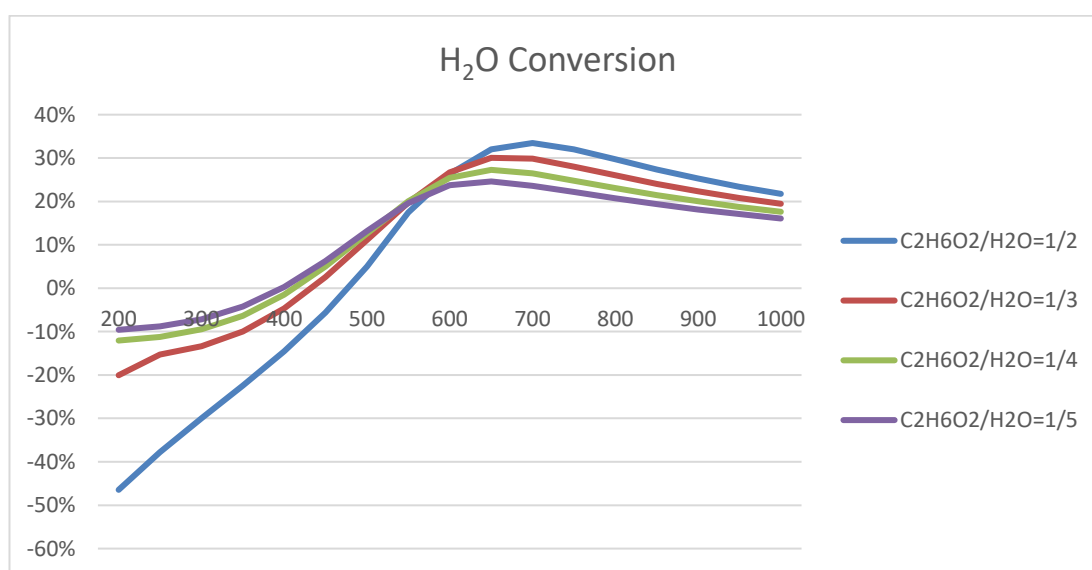


Figure 4.1: The effect of temperature and H_2O concentration on H_2O conversion in steam reforming reaction of ethylene glycol.

Figure 4.2 shows that H_2O quantity in input flow does not affect to H_2 yield at the below temperatures of 550 C. While the temperature is increasing, the yield of H_2 is affected negatively. While H_2O addition is increased, decreasing of H_2 yield is observed. The reason of that is originated from equation 3.16.

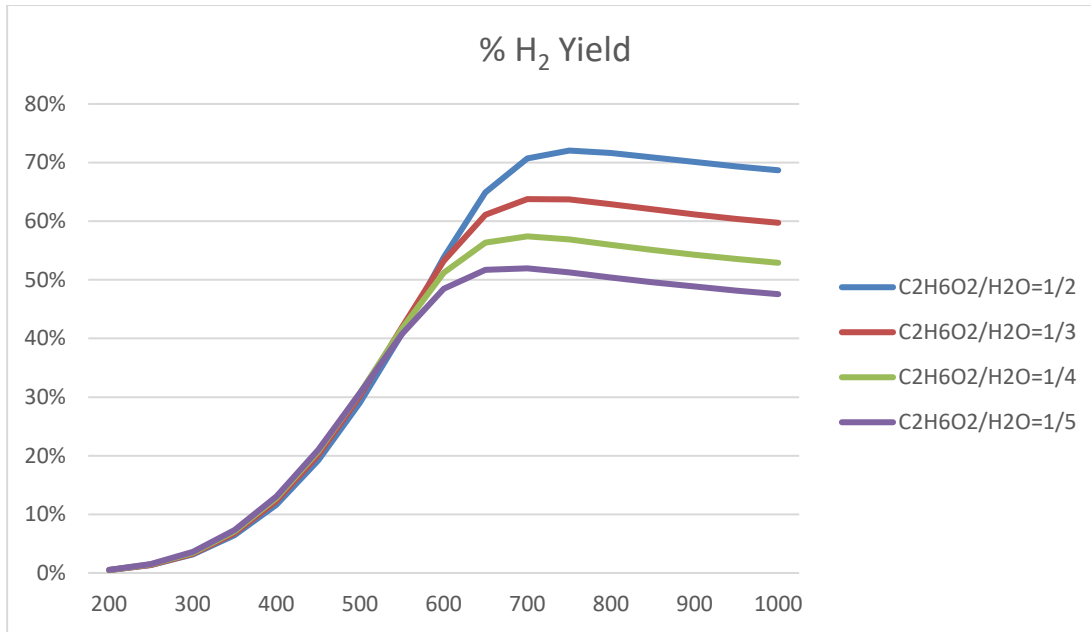


Figure 4.2: The effect of temperature and H_2O concentration on % H_2 yield in steam reforming reaction of ethylene glycol.

Figure 4.3 shows that while the temperature is increasing the yield of CO conversion was affected positively. There are many reasons which are provided that. These can be counted such as steam reforming reaction, coking reaction water-gas shift reaction etc.

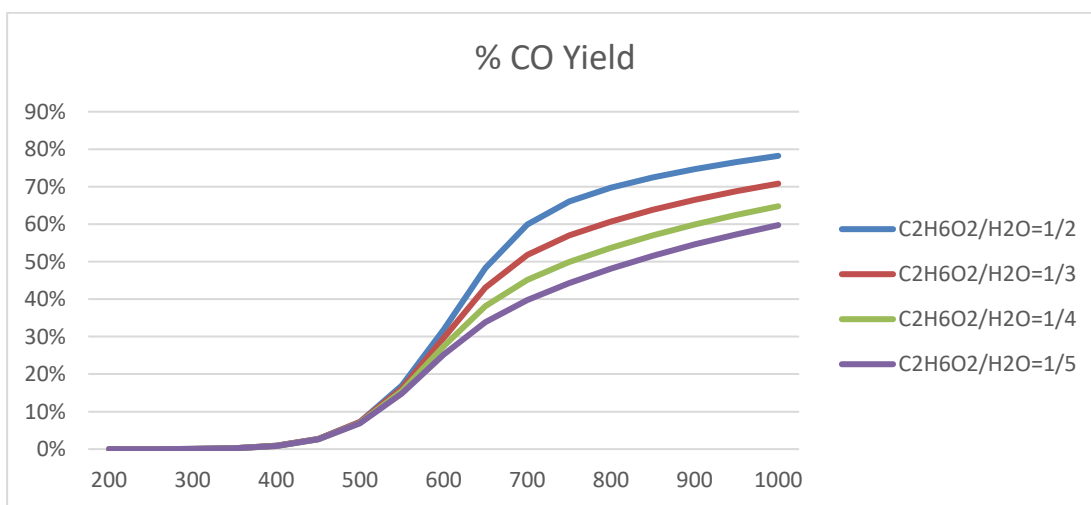


Figure 4.3: The effect of temperature and H_2O concentration on % CO yield in steam reforming reaction of ethylene glycol.

Figure 4.4 shows that the yield of CO_2 was affected positively until the temperature was 550°C . This affect can be derived exothermic water-gas shift reaction and reverse Boudouard reaction. The production of CO_2 was decreased at higher temperature because the steam reform reaction moved the left side. Moreover, the increase of CO_2 yield was observed while the mole of H_2O is increasing in input flow. Water-gas shift reaction can be cause of this result.

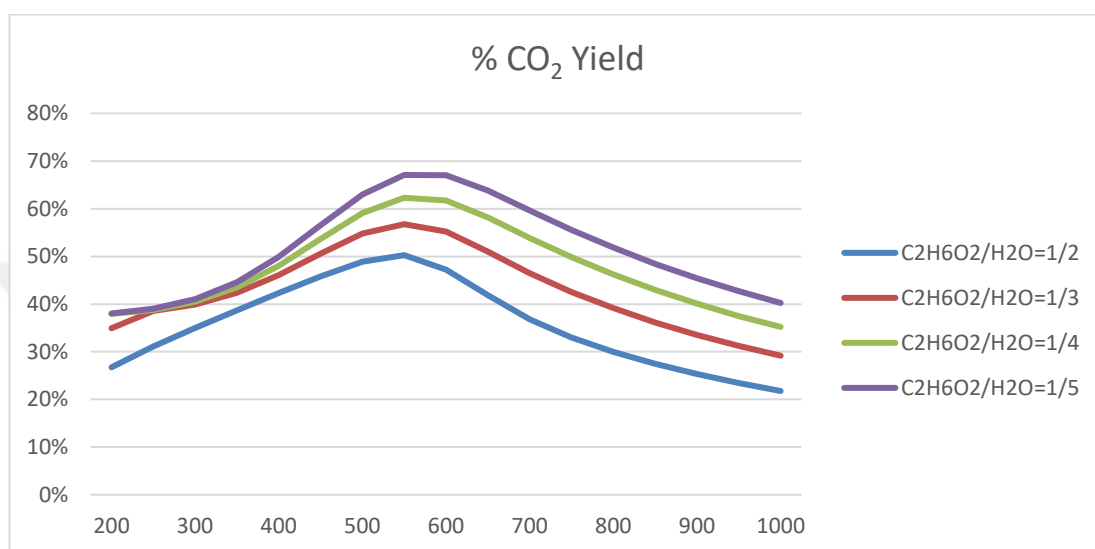


Figure 4.4: The effect of temperature and H_2O concentration on % CO_2 yield in steam reforming reaction of ethylene glycol.

Decreasing of coke generation was observed when the temperature increasing and increasing of H_2O mole in input flow. This situation is given in Figure 4.5. The reason of this can be reverse Boudouard reaction and CO reduction equation. Decreasing of C was observed while adding H_2 .

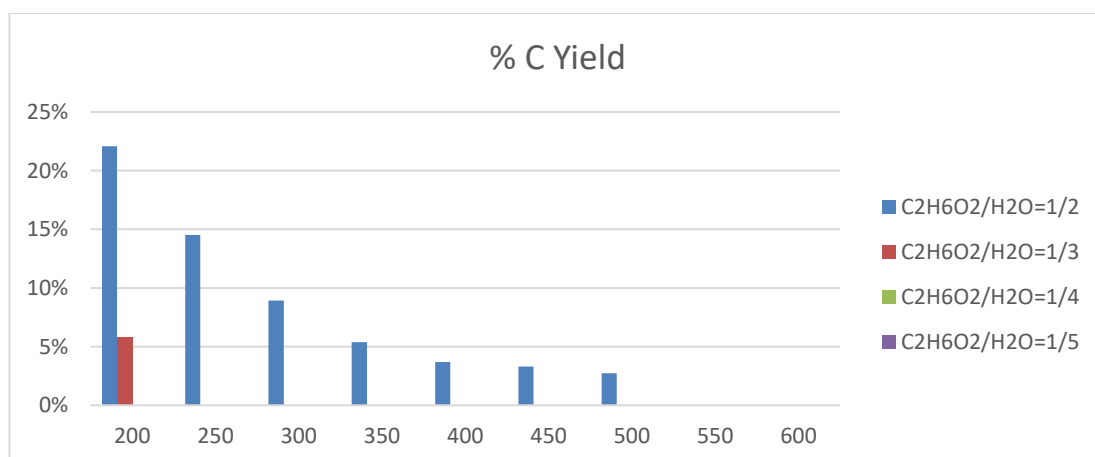


Figure 4.5: The effect of temperature and H_2O concentration on % C yield in steam reforming reaction of ethylene glycol.

Figure 4.6 shows that the increasing of CH_4 yield was observed until the 350°C , upper temperatures than 350°C decreasing of CH_4 yield was observed. Moreover, the increasing of CH_4 yield was observed while the mole of H_2O was decreasing. The inverse proportion of temperature and CH_4 yield can be originated from methanation reaction.

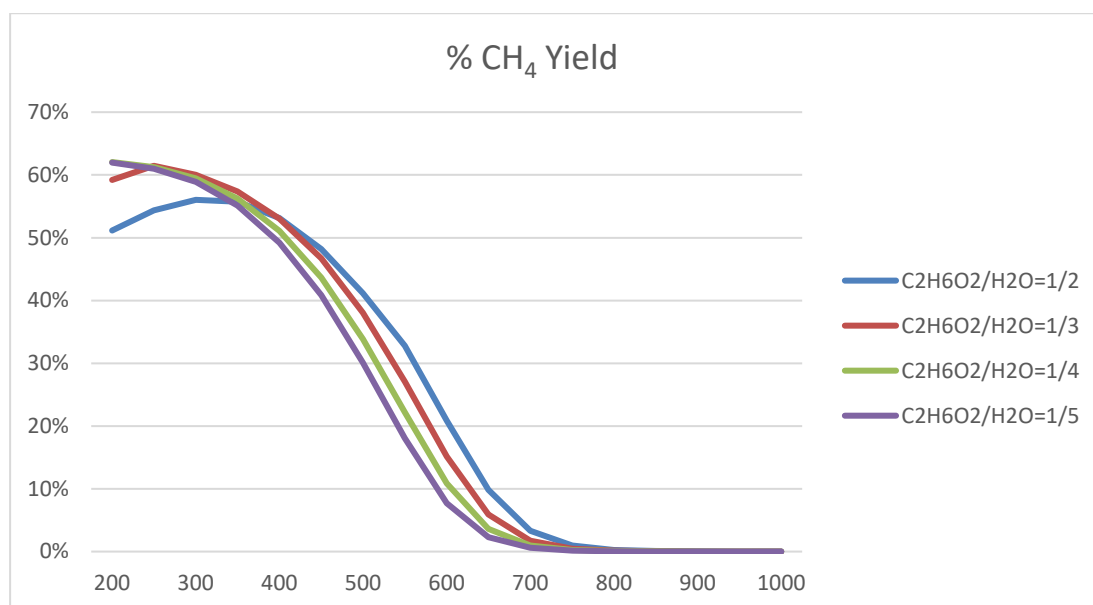


Figure 4.6: The effect of temperature and H_2O concentration on % CH_4 yield in steam reforming reaction of ethylene glycol.

Figure 4.7 shows that there is a very high H_2 / CO ratio at temperatures below 600°C . At temperatures below 600°C , the water-gas shift reaction, expressed in equation 2.2, to the H_2 product side resulted in an increase in the H_2 / CO ratio. At high temperatures, the H_2 / CO ratio reaches lower values due to reverse water-gas shift reaction. When the results are considered, it can be determined that the H_2 / CO ratio is close to a constant value at temperatures above 1000°C . The $\text{H}_2\text{O} / \text{C}_2\text{H}_6\text{O}_2$ ratio in the feed stream also affects the H_2 / CO ratio. H_2 / CO ratio increases as H_2O increases in feed flow.

H_2/CO ratio, % C yield and % CH_4 yield as side reaction products under different feed flow ratio and different temperatures at 1 bar for ethylene glycol steam reforming calculated using Aspen Plus are given in Table 4.1. It is proposed that the H_2 / CO ratio in the feed stream used in commercial processes such as the synthesis of Fischer-Tropsch is 2 and that the synthesis gas mixture does not contain any side reaction products such as CO_2 and CH_4 [3].

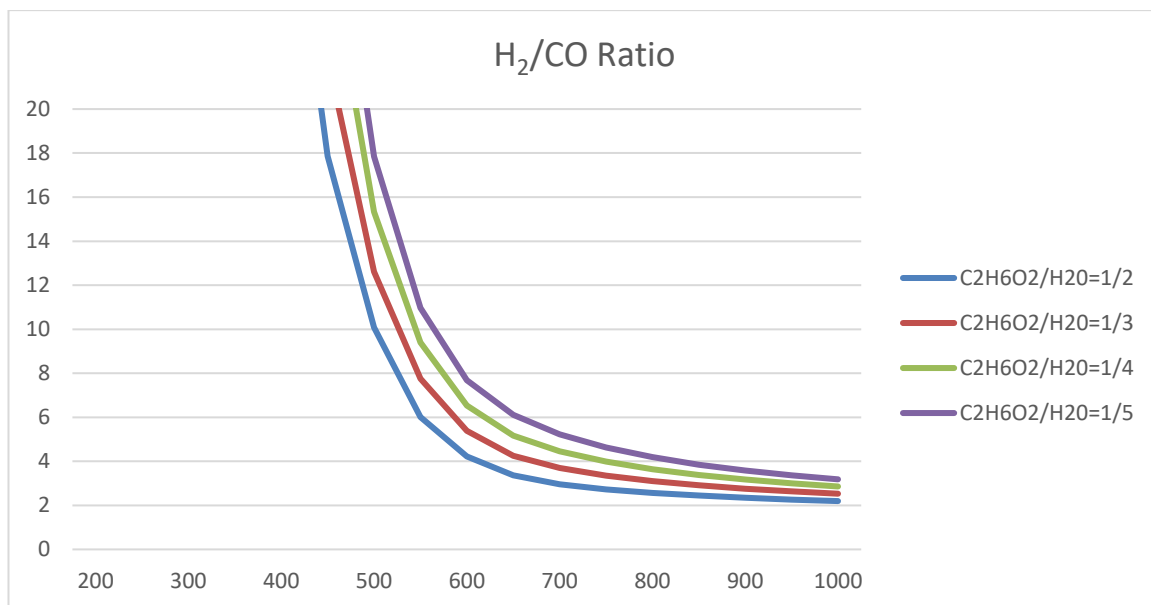


Figure 4.7: The effect of temperature and H₂O concentration on H₂/CO ratio in steam reforming reaction of ethylene glycol.

According to Table 4.1, while the molar ratio of ethylene glycol/H₂O is 1/2 at 1000 °C and under 1 bar, is close to 2 (2.19) and the yield of side reaction products is low.

4.2 Thermodynamic Analysis of Ethylene Glycol Oxidative Steam Reforming

1. The oxidative steam reforming reaction of ethylene glycol was performed in set 2. In Table 3.3, the feed flow compositions defined in Aspen were given in below during the oxidative steam reforming reaction of ethylene glycol. The simulation executed at the fixed mol number for C₂H₆O₂ is 1 and fixed mol number H₂O+O₂ is 2. The number of H₂O moles and O₂ moles were changed individually total moles to be 2 moles, in between 200-1000 °C temperature range ($\Delta T=50$ °C) and under pressure 1 bar.

Components C₂H₆O₂, H₂O, O₂, CO, H₂, CO₂, C, CH₄ were defined in the simulation environment. Ethylene glycol and oxygen were consumed at every operational conditions. The reason of this ethylene glycol has lower stability. It is thought that all of O₂ consumed because the O₂ is used to energetically neutralize the environment in the oxidative steam reforming. Furthermore, O₂ has been reacted to provide a part of the energy required for the endothermic process of steam reforming. Likewise, ethylene glycol has been formed a complete combustion reaction at low temperatures with O₂, while at high temperatures it has been formed both complete combustion and partial combustion reactions. Due to all these described circumstances, all of the O₂ could be consumed.

Table 4.1: H₂/CO ratio, % C yield and % CH₄ yield at different temperatures and H₂O concentrations in steam reforming reaction of ethylene glycol.

C ₂ H ₆ O ₂ /H ₂ O (mol/mol)	H ₂ /CO Ratio				C Yield (%)				CH ₄ Yield (%)			
	400°C	600°C	800°C	1000°C	400°C	600°C	800°C	1000°C	400°C	600°C	800°C	1000°C
1/2	33.49	4.21	2.56	2.19	3.69	0.00	0.00	0.00	53.15	20.88	0.27	0.00
1/3	42.12	5.38	3.10	2.52	0.00	0.00	0.00	0.00	53.05	15.14	0.14	0.00
1/4	52.23	6.52	3.64	2.85	0.00	0.00	0.00	0.00	51.09	10.85	0.08	0.00
1/5	61.70	7.68	4.19	3.18	0.00	0.00	0.00	0.00	49.22	7.72	0.05	0.00

As shown in Figure 4.8, as the number of O₂/H₂O ratio in the feed stream increased, the H₂O conversion decreased. This effect is estimated to be due to the increased use of O₂ in the complete combustion reaction and the production of more H₂O. When the general trends in the graph are taken into account, the temperature increase up to 600°C contributes to H₂O conversion and after these temperatures, the conversion decreases.

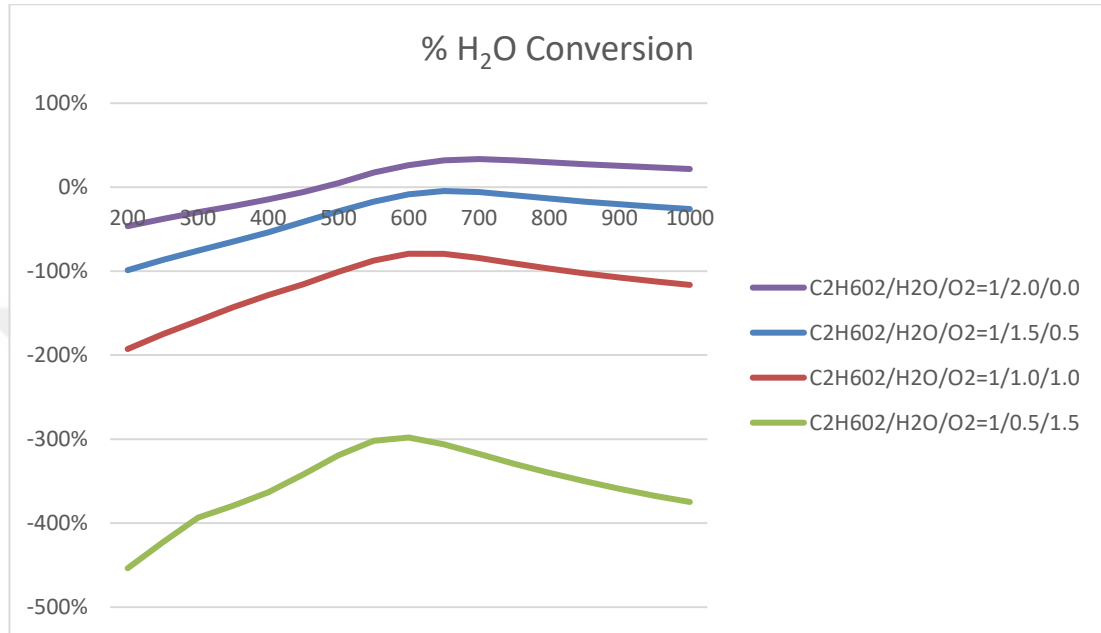


Figure 4.8: The effect of temperature and O₂/H₂O ratio on H₂O conversion in oxidative steam reforming reaction of ethylene glycol.

Figure 4.9 shows that increasing the number of O₂ moles in the feed stream has a negative effect on the H₂ yield. This negative effect may be thought to be due to the use of a portion of the ethylene glycol in oxidation, resulting in less H₂ production as a result of the process of steam reforming. In addition, O₂ in the medium reacts with the produced H₂, causing H₂O production and thus decreasing H₂ efficiency. The O₂ is increased in the feed stream up to 400 °C has no effect on the H₂ yield. While the temperature increases up to 550-700 °C contributed to the H₂ yield, the yields were adversely affected after these temperatures. This adversely effect may have been observed because the water-gas shift reaction at high temperatures shifts in the direction of the entrants and increases H₂ consumption. In the case of C₂H₆O₂ / H₂O / O₂ = 1/0.0/2.0, H₂ yield is considered to be the lowest because full combustion is the dominant reaction. C₂H₆O₂ / (H₂O+O₂)= ½ constant ratio and H₂O / O₂ change were not affected by H₂ yield up to 400 °C. This situation can be explained by the fact that after 400 °C the reforming reactions come to the fore.

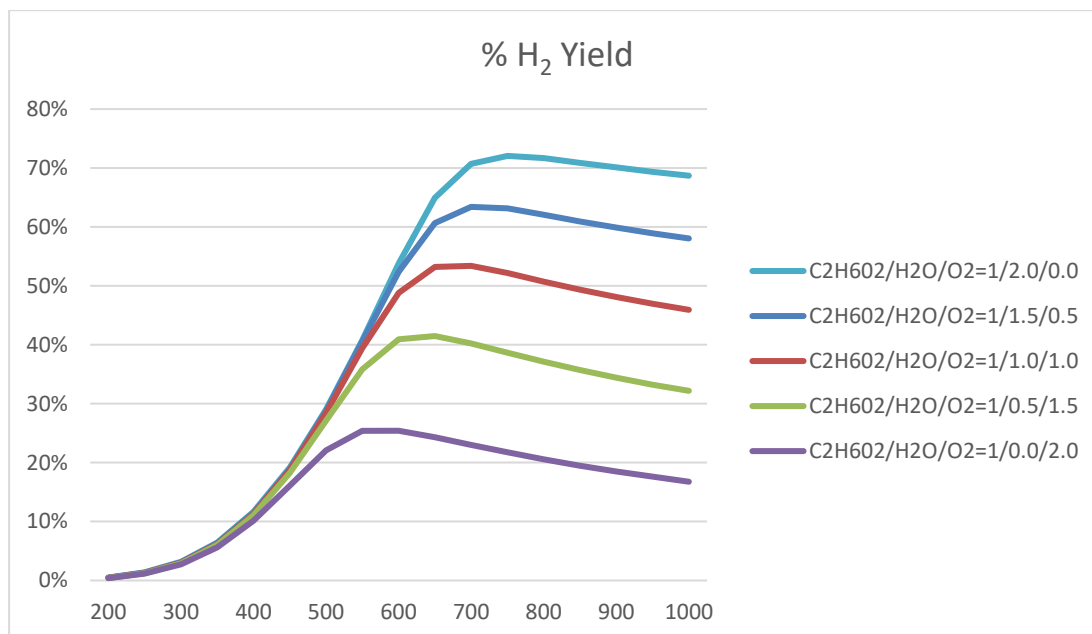


Figure 4.9: The effect of temperature and O₂/H₂O ratio on % H₂ yield in oxidative steam reforming reaction of ethylene glycol.

The increase in O₂/ H₂O in the feed stream up to 450 °C according to Figure 4.10 does not affect CO efficiency. The graph of the oxidative steam reforming reaction obtained for CO yield was found to be similar to the steam reforming process as a general trend. The steam reforming reaction and the coking reaction of the ethylene glycol which are endothermic processes shifts towards the product side and increase the CO efficiency. As the water-gas shift reaction, methanation, reverse Boudouard and CO reduction reactions which are in the exothermic processes, in the side of the reactants, it can be said that the CO efficiency is affected positively as the temperature increases. It is determined that the CO efficiency obtained as a result of the steam reforming process is higher at temperatures above 700 °C.

The CO₂ yield is given in Figure 4.11 shows the same general trend as CO₂ as a result of the steam reforming process. It is observed that the increase in the amount of O₂ in the feed stream increases the CO₂ efficiency. The use of O₂ in oxidation reactions and the production of product CO₂ as the cause may be the cause of this effect. Higher CO₂ yield was obtained in the oxidative steam reforming reaction if the steam reforming values are compared. At temperatures higher than 550 °C, the oxidation reaction and the complete combustion reaction, which are exothermic reactions can be said to be decreasing in CO₂ yield due to the shifts towards the reactants.

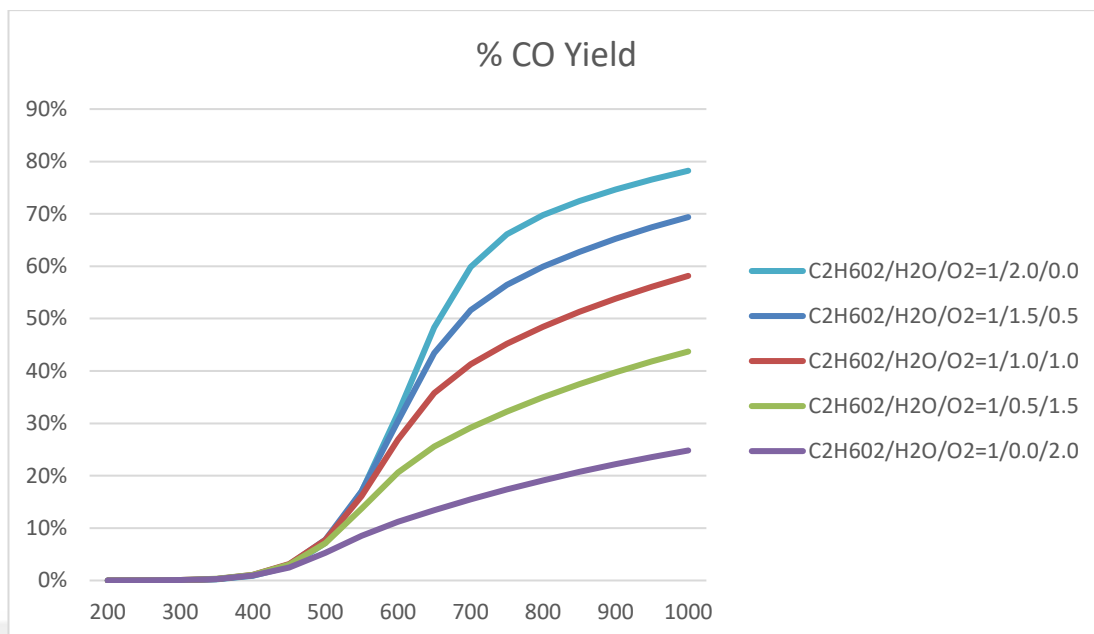


Figure 4.10: The effect of temperature and O₂/H₂O ratio on % H₂ yield in oxidative steam reforming reaction of ethylene glycol.

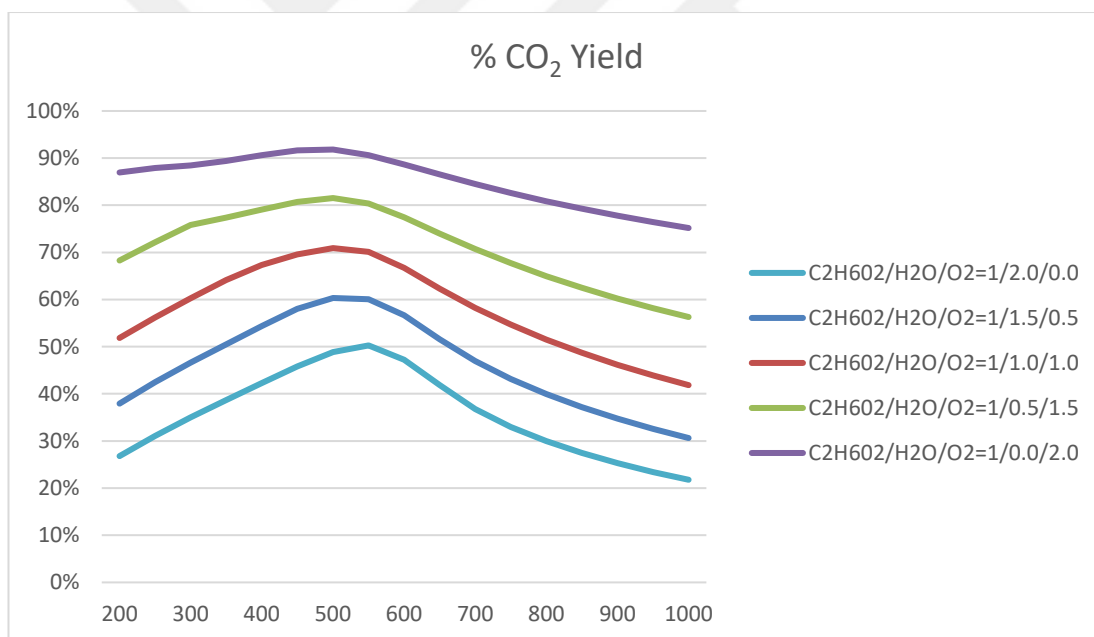


Figure 4.11: The effect of temperature and O₂/H₂O ratio on % CO₂ yield in oxidative steam reforming reaction of ethylene glycol.

The general trend of C (coke) yield as shown in Figure 4.12 was found to be the same as the C yield general trend obtained as a result of steam reforming process. However, a lower coke yield was obtained in the oxidative steam reforming reaction if the steam reforming reaction values are compared. In the case of C₂H₆O₂ / H₂O / O₂ = 1/2/0, the coke yield was 22.08% at 200 °C, while at the same temperature C₂H₆O₂ / H₂O / O₂ = 1/2/1, was found to be 1.36%. Increased O₂ in the feed stream, decreased the coke

formation. The reason for this; It is thought that CO_2 and H_2O are the result of complete combustion of O_2 with ethylene glycol and the reaction is shifted to the entrants and decreases in the formation of C (coke) by the increase of CO_2 in the reverse Boudouard reaction which is the side reaction. In addition, the coke reacts with O_2 to form CO_2 , which is also a cause.

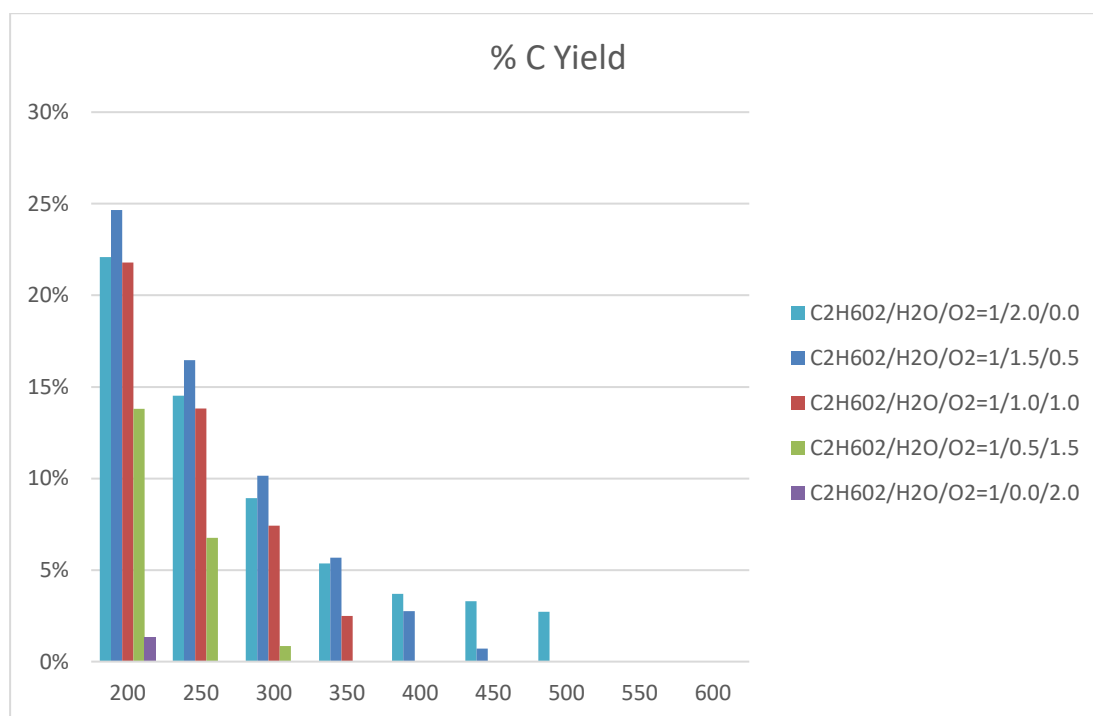


Figure 4.12: The effect of temperature and $\text{O}_2/\text{H}_2\text{O}$ ratio on % C yield in oxidative steam reforming reaction of ethylene glycol.

The general trend of CH_4 (methane) yield as shown in Figure 4.13 was found to be the same as the CH_4 yield general trend obtained as a result of steam reforming. However, the yield of CH_4 in the oxidative steam reforming lower than the yield of CH_4 in the steam reforming. In the case of $\text{C}_2\text{H}_6\text{O}_2 / \text{H}_2\text{O} / \text{O}_2 = 1/2.0/0.0$, the CH_4 yield was 53.15% at 400 °C, while at the same temperature $\text{C}_2\text{H}_6\text{O}_2 / \text{H}_2\text{O} / \text{O}_2 = 1/0.0/2.0$, was found to be 8.46%. CH_4 formation with increasing temperature up to 300-350 °C, except in the absence of H_2O in the environment, shows an increasing trend, however after this temperature CH_4 yield is decreased. This situation has been happened because the methanization reaction, which is exothermic at low temperatures, shifted the products side and increased the efficiency of forming CH_4 , and at high temperature decreased the CH_4 yield while the reaction was shifting reactants side.

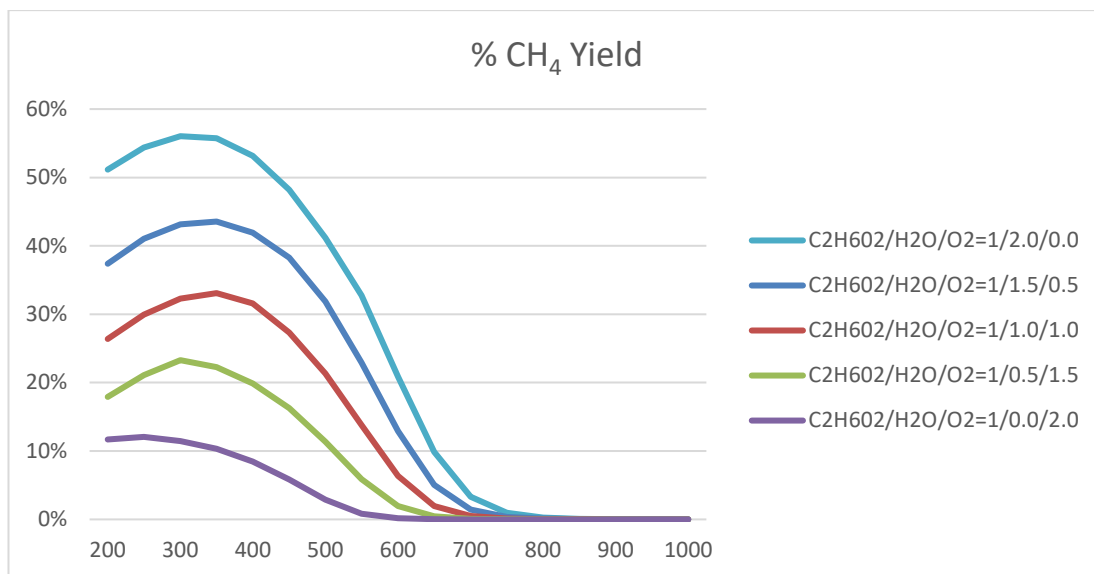


Figure 4.13: The effect of temperature and O₂/H₂O ratio on % CH₄ yield in oxidative steam reforming reaction of ethylene glycol.

The general trend of H₂/CO yield as shown in Figure 4.14 was found to be the same as the H₂/CO yield general trend obtained as a result of steam reforming. At temperatures below 600 °C, a very high H₂/CO ratio is observed. This effect can be seen due to the water-gas shift reaction shifted toward H₂ product side at temperatures 600 °C. At high temperature, H₂/CO ratio observed lower values because of the reverse water-gase shift reaction. Higher than at 1000 °C, it could be said that the graph trend is beginning to the linear. Table 4.2 shows that the H₂/CO ratio, C yield and CH₄ yield for different feed stream mole fraction and and different temperatures.

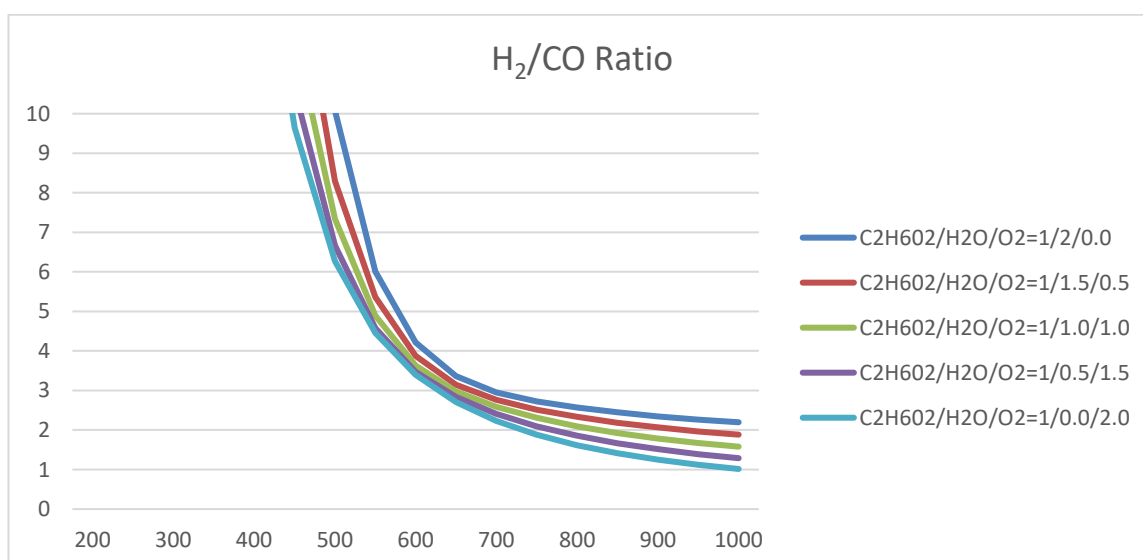


Figure 4.14: The effect of temperature and O₂/H₂O ratio on H₂/CO ratio in oxidative steam reforming reaction of ethylene glycol.

Table 4.2: H₂/CO ratio, % C yield and % CH₄ yield at different temperatures and H₂O concentrations in oxidative steam reforming reaction of ethylene glycol.

C ₂ H ₆ O ₂ /H ₂ O/O ₂ (mol/mol/mol)	H ₂ /CO Ratio				C Yield (%)				CH ₄ Yield (%)			
	400°C	600°C	800°C	1000°C	400°C	600°C	800°C	1000°C	400°C	600°C	800°C	1000°C
1.0/2.0/0.0	33.49	4.21	2.56	2.19	3.69	0.00	0.00	0.00	53.15	20.88	0.27	0.00
1.0/1.5/0.5	26.24	3.87	2.33	1.88	2.75	0.00	0.00	0.00	41.93	12.90	0.11	0.00
1.0/1.0/1.0	20.97	3.62	2.09	1.58	0.00	0.00	0.00	0.00	31.58	6.36	0.03	0.00
1.0/0.5/1.5	18.11	3.47	1.85	1.28	0.00	0.00	0.00	0.00	19.88	1.95	0.01	0.00
1.0/0.0/2.0	16.08	3.40	1.61	1.01	0.00	0.00	0.00	0.00	8.46	0.17	0.00	0.00

According to Table 4.2, it is proposed that the H_2 / CO ratio in the feed stream used in commercial processes such as the synthesis of Fischer-Tropsch is 2 and that the synthesis gas mixture does not contain any side reaction products such as CO_2 and CH_4 . In the case of oxidative steam reforming, while the molar ratio of $C_2H_6O_2/H_2O/O_2$ is 1/1/1 at 800 °C and under 1 bar, is close to 2 (2.09) and the yield of side reaction products is low. Usage of O_2 in the reforming process reduced the H_2/CO ratio. It was observed that the steam reforming reaction of ethylene glycol had a more ideal H_2/CO ratio for the produced of Fischer-Tropsch more than oxidative steam reforming process.

4.3 Thermodynamic Analysis of Ethylene Glycol Sorption Enhanced Steam Reforming

The sorption enhanced steam reforming reaction of ethylene glycol was performed in set 3. In Table 3.4 and in Table 3.5, the feed flow compositions defined in Aspen were given in below during the sorption enhanced steam reforming reaction of ethylene glycol. The simulation executed with 1 mole and 3 moles CaO in between 200-1000 °C temperature range ($\Delta T=50$ °C) and under pressure 1 bar. Components $C_2H_6O_2$, H_2O , CaO , CO , H_2 , CO_2 , C , CH_4 , $CaCO_3$, $Ca(OH)_2$ were defined in the simulation environment. Ethylene glycol was consumed at every operational conditions.

In Table 4.3, CaO conversion and $CaCO_3$ yield values of sorption enhanced ethylene glycol steam reforming process at different temperatures are given. $Ca(OH)_2$ is defined in the simulation environment due to the possibility of reacting with H_2O as a side reaction and the formation of $Ca(OH)_2$ by the reaction of CaO with CO_2 . However, in the case of CaO 1 mole using, CaO has not been reacted with H_2O under any circumstances and CaO produced only $CaCO_3$ by adsorption of CO_2 . Therefore, CaO conversion and $CaCO_3$ yield values were obtained as the same. In the case of CaO 3 moles using, it is observed that the $Ca(OH)_2$ up to 400 °C. According to the simulation results in Table 4.3, it is observed that all of the CaO reacts with CO_2 and form $CaCO_3$, regardless of the H_2O molar number in the feed stream up to 700°C. CaO conversion at temperatures above 700 °C was not observed. This negative effect may be due to the fact that the adsorption reaction of CaO with CO_2 is exothermic, the adsorption at temperatures higher than 700 °C does not occur while the reaction is performed at full temperatures at low temperatures and the CaO is deactivated. It is seen that the increase of H_2O in the feed stream at 700°C contributes to the conversion of CaO . This effect may have been due to the fact that the H_2O mole number in the feed stream is too high, the water-gas exchange reaction.

Table 4.3: %CaO conversion at different temperatures and 1-3 moles CaO feeding in sorption enhanced steam reforming reaction of ethylene glycol.

$C_2H_6O_2/H_2O$ (mol/mol)	300 °C		400 °C		500 °C		600 °C		700 °C		800 °C		900 °C		1000 °C	
	CaO 1 mole	CaO 3 moles	CaO 1 mole	CaO 3 moles	CaO 1 mole	CaO 3 moles	CaO 1 mole	CaO 3 moles	CaO 1 mole	CaO 3 moles	CaO 1 mole	CaO 3 moles	CaO 1 mole	CaO 3 moles	CaO 1 mole	CaO 3 moles
1/2	100.0	100.0	100.0	81.6	100.0	55.7	100.0	54.4	83.6	27.85	0.0	0.0	0.0	0.0	0.0	0.0
1/3	100.0	100.0	100.0	100.0	100.0	61.8	100.0	60.5	100.0	34.7	0.0	0.0	0.0	0.0	0.0	0.0
1/4	100.0	100.0	100.0	100.0	100.0	64.6	100.0	63.1	100.0	37.7	0.0	0.0	0.0	0.0	0.0	0.0
1/5	100.0	100.0	100.0	100.0	100.0	65.6	100.0	64.0	100.0	38.6	0.0	0.0	0.0	0.0	0.0	0.0

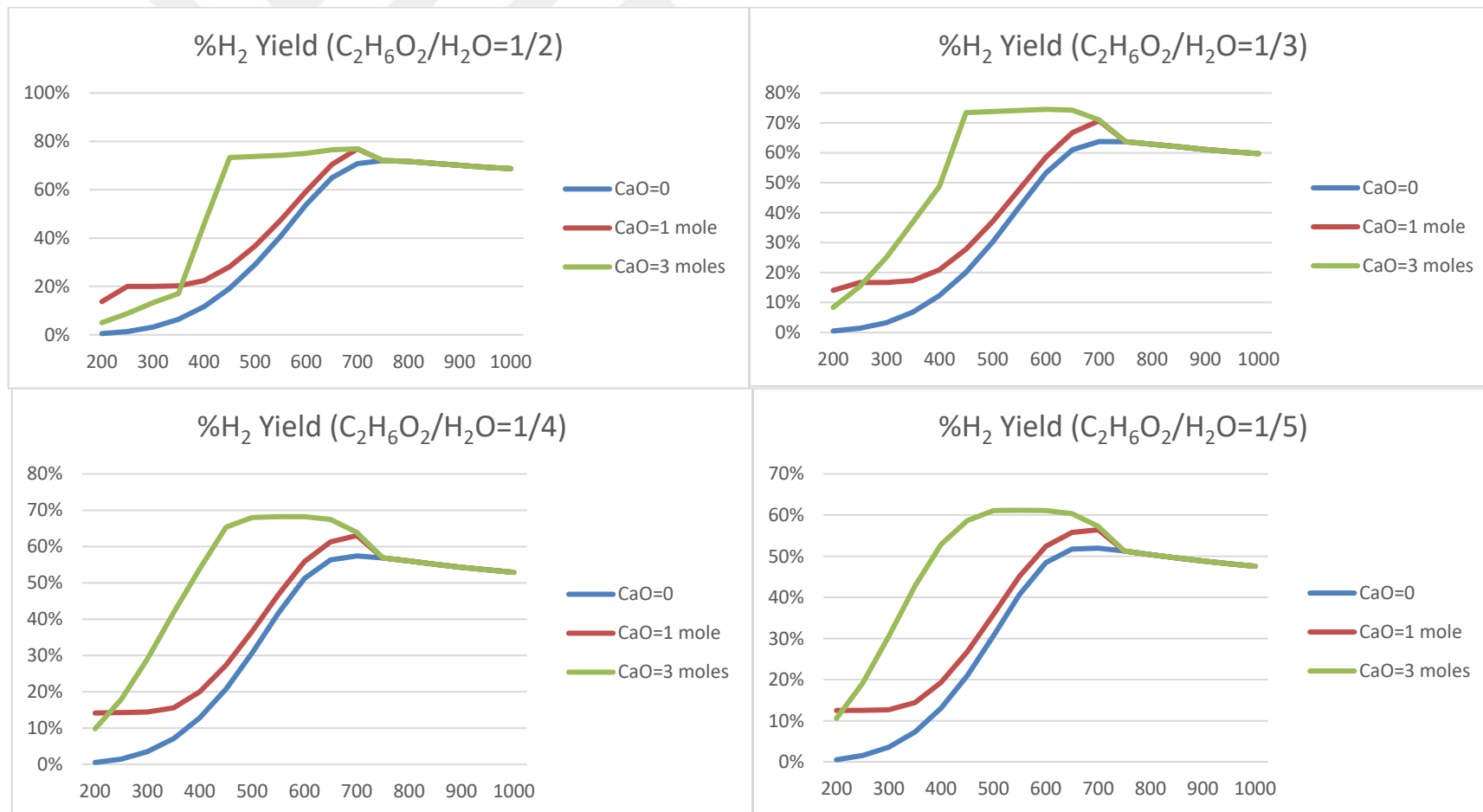


Figure 4.15: The effect of temperature and 1-3 moles CaO feeding on % H₂ yield with different H₂O concentration in sorption enhanced steam reforming reaction of ethylene glycol.

As indicated in the graphs in Figure 4.15, CO₂ adsorption of ethylene glycol with CaO to the steam reforming process positively affected the H₂ yield for both 1 mole and 3 moles CaO. This may be the reason for the decrease in the number of CO₂ moles due to adsorption in the reaction medium and the increase in H₂ formation of the water-gas shift reaction towards the products direction. In the case of temperatures higher than 700 °C, CaO does not adsorb CO₂, so the H₂O values of steam reforming process and the sorption enhanced steam reforming process are the same. The endothermic steam reforming process is thought to contribute to the H₂ yield due to shifted toward products side by increasing temperature.

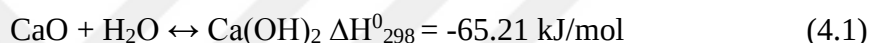
In Table 4.4, the sorption enhanced process was observed to be higher than the H₂ / CO ratio compared to the steam reforming process. The reason for this is that the water-gas shift reaction due to the CO₂ adsorption has a positive effect on H₂ formation and decreases CO formation at low temperatures. At below 700 °C temperatures, CaO is not effected H₂/CO ratio.

Table 4.4: Comparison chart of H₂/CO ratio between steam reforming of ethylene glycol and sorption enhanced steam reforming of ethylene glycol at different temperatures and 1-3 moles CaO feeding.

C ₂ H ₆ O ₂ /H ₂ O (mol/mol)	H ₂ /CO Ratio					
	600 °C			1000 °C		
	CaO 0 mole	CaO 1 mole	CaO 3 moles	CaO 0 mole	CaO 1 mole	CaO 3 moles
1/2	4.22	10.88	84.57	2.20	2.20	2.20
1/3	5.38	12.31	134.64	2.53	2.53	2.53
1/4	6.53	14.0	189.19	2.86	2.86	2.86
1/5	7.68	15.90	238.12	3.18	3.18	2.86

In the simulation results, no coke formation was observed under any conditions of sorption enhanced reforming. CaO is absorbed CO₂ and caused the water-gas shift reaction to shift the product side. For this reason, the reverse Boudouard and CO reduction reactions have not been occurred due to decreased amount of CO. Therefore, no coke formation was observed. According to the simulation results, since CO₂ adsorption at temperatures higher than 700 °C is not realized, the coke formation values of the steam reforming process and the sorption enhanced reforming were the same. In conclusion, the use of CaO in steam reforming processes is contributed to process as coke formation was not desired.

In addition, in the case of the use 1 mole of CaO, the Ca(OH)₂ forming reaction shown below is not occurred; when CaO was used 3 moles, this side reaction was observed up to 400-450 °C temperature.



It is thought that this side reaction, which is exothermic, increased the H₂O conversion by shift to the direction of the reactants at low temperatures and therefore, due to the increased H₂O conversion, the reforming reactions shift to the direction of the products and increase the H₂ yield.

4.4 Thermodynamic Analysis of Ethylene Glycol Sorption Enhanced Oxidative Steam Reforming

The sorption enhanced oxidative steam reforming reaction of ethylene glycol was performed in set 4. In Table 3.6 and in Table 3.7, the feed flow compositions defined in Aspen were given in below during the sorption enhanced steam reforming reaction of ethylene glycol. The simulation executed with 1 mole and 3 moles CaO, at the fixed mol number for C₂H₆O₂ is 1 and fixed mol number H₂O+O₂ is 2. The number of H₂O moles and O₂ moles were changed individually total moles to be 2 moles, in between 200-1000 °C temperature range (ΔT=50 °C) and under pressure 1 bar. Components C₂H₆O₂, H₂O, O₂, CO, H₂, CO₂, C, CH₄ were defined in the simulation environment. Thereby ethylene glycol has low stability, it is completely consumed as in previous operations. In fixed H₂O/O₂ case, as the oxidation reaction is performed primarily due to enhance the oxidation steam reforming process, O₂ is completely consumed.

In Table 4.5, CaO conversion and CaCO₃ yield values of sorption enhanced ethylene glycol steam reforming process at different temperatures are given. Ca(OH)₂ is defined in the simulation environment due to the possibility of reacting with H₂O as a side reaction and the formation of Ca(OH)₂ by the reaction of CaO with CO₂. However, in the case of CaO 1 mole using, CaO has not been reacted with H₂O under any circumstances and CaO produced only CaCO₃ by adsorption of CO₂. Therefore, CaO conversion and CaCO₃ yield values were obtained as the same. In the case of CaO 3 moles using, it is observed that the Ca(OH)₂ up to 400 °C. According to the simulation results in Table 4.5, it is observed that all of the CaO reacts with CO₂ and form CaCO₃, regardless of the H₂O molar number in the feed stream up to 700°C. CaO conversion at temperatures above 700 °C was not observed. As in the sorption enhanced steam reforming process, the sorption enhanced oxidative steam reforming process is not CaO converted at temperatures above 700 °C.

As indicated in the graphs in Figure 4.16, CO₂ adsorption of ethylene glycol with CaO to the steam reforming process positively affected the H₂ yield for both 1 mole and 3 moles CaO. This may be the reason for the decrease in the number of CO₂ moles due to adsorption in the reaction medium and the increase in H₂ formation of the water-gas shift reaction towards the products direction. In the case of temperatures higher than 700 – 800 °C, CaO does not adsorb CO₂, so the H₂O values of steam reforming process and the sorption enhanced steam reforming process are the same. It has been found that while the mole number of O₂ was increasing in the feed stream, H₂ yield decreased. This is because by the use of ethylene glycol with oxidation reaction, occur the more less H₂ production.

In Table 4.6, the sorption enhanced oxidative steam reforming process was observed to be higher than the H₂ / CO ratio compared to the oxidative steam reforming process. While the mole number of O₂ and temperature increased, H₂/CO ratio decreased. At below 750 - 800 °C temperatures, CaO is not effected H₂/CO ratio.

Table 4.5: %CaO conversion at different temperatures and 1-3 moles CaO feeding in sorption enhanced oxidative steam reforming reaction of ethylene glycol.

C₂H₆O₂/H₂O/O₂ (mol/mol/mol)	300 °C		400 °C		500 °C		600 °C		700 °C		800 °C		900 °C		1000 °C	
	CaO	CaO	CaO	CaO	CaO	CaO	CaO	CaO	CaO	CaO	CaO	CaO	CaO	CaO	CaO	CaO
	1	3	1	3	1	3	1	3	1	3	1	3	1	3	1	3
	mole	moles	mole	moles	mole	moles	mole	moles	mole	moles	mole	moles	mole	moles	mole	moles
1.0/2.0/0.0	100.0	100.0	100.0	81.6	100.0	55.7	100.0	54.4	83.6	27.85	0.0	0.0	0.0	0.0	0.0	0.0
1.0/1.5/0.5	100.0	100.0	100.0	95.3	100.0	61.3	100.0	60.4	100.0	39.5	0.0	0.0	0.0	0.0	0.0	0.0
1.0/1.0/1.0	100.0	100.0	100.0	100.0	100.0	65.0	100.0	64.2	100.0	48.9	0.0	0.0	0.0	0.0	0.0	0.0
1.0/0.5/1.5	100.0	100.0	100.0	100.0	100.0	66.4	100.0	63.4	100.0	55.4	0.0	0.0	0.0	0.0	0.0	0.0
1.0/0.0/2.0	100.0	100.0	100.0	100.0	100.0	66.6	100.0	66.1	100.0	59.6	0.0	0.0	0.0	0.0	0.0	0.0

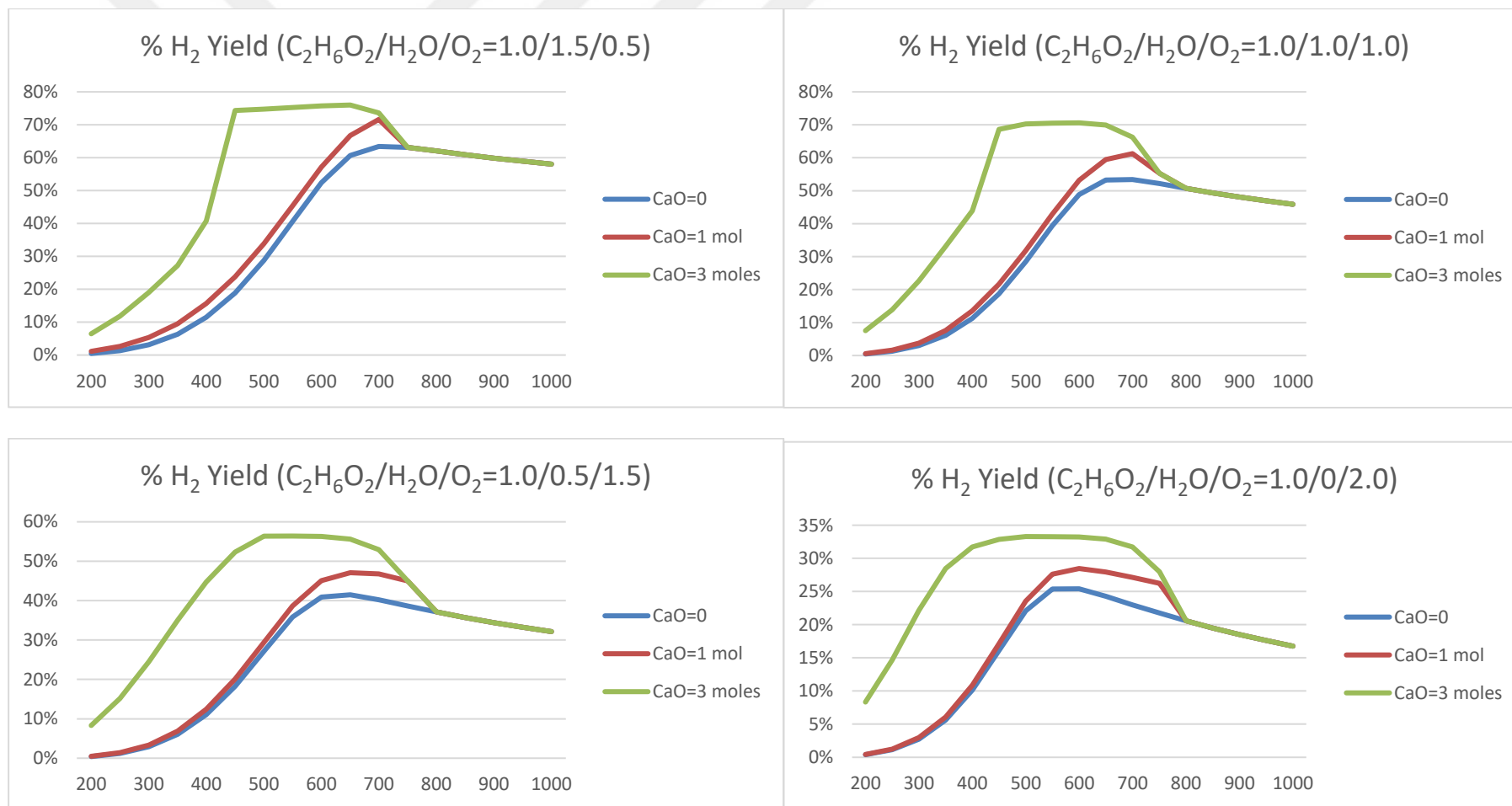


Figure 4.16: The effect of temperature and 1-3 moles CaO feeding on % H₂ yield with different H₂O concentration in sorption enhanced oxidative steam reforming reaction of ethylene glycol

Table 4.6: Comparison chart of H₂/CO ratio between steam reforming of ethylene glycol and sorption enhanced steam reforming of ethylene glycol at different temperatures and 1-3 moles CaO feeding.

C ₂ H ₆ O ₂ /H ₂ O/O ₂ (mol/mol/mol)	H ₂ /CO Ratio					
	600 °C			1000 °C		
	CaO 0 mole	CaO 1 mole	CaO 3 moles	CaO 0 mole	CaO 1 mole	CaO 3 moles
1.0/2.0/0.0	4.22	10.88	84.57	2.20	2.20	2.20
1.0/1.5/0.5	3.87	8.73	114.72	1.88	1.88	1.88
1.0/1.0/1.0	3.63	7.49	171.27	1.58	1.58	1.58
1.0/0.5/1.5	3.47	6.84	269.35	1.29	1.29	1.29
1.0/0.0/2.0	3.40	6.65	414.26	1.01	1.01	1.01

4.5 Thermodynamic Analysis of Pressure Effect of Ethylene Glycol Steam Reforming

The pressure effect on steam reforming reaction of ethylene glycol was performed in set 5. In this set, ethylene glycol is simulated with 1 mol, H₂O is simulated with 2 moles and the simulation is executed in between 200-1000 °C temperature range ($\Delta T=50$ °C) and pressure was changed as 1 bar, 10 bars and 20 bars, respectively. Pressure is also an important variable in reforming processes [22]. Under all temperature and pressure conditions, the ethylene glycol was completely consumed. Figure 4.17 shows that the H₂ yield, C yield, CH₄ yield and H₂/CO ratio under different temperatures and different pressures.

4.6 Thermodynamic Analysis of Sorbitol Steam Reforming

The steam reforming reaction of sorbitol was performed in set 1. In Table 3.7, the feed flow compositions defined in Aspen were given in below during the steam reforming reaction of sorbitol. The simulation executed in between 200-1000 °C temperature range ($\Delta T=50$ °C) and under pressure 1 bar. Sorbitol was consumed at every

operational conditions. The reason of this sorbitol has lower stability. In endothermic equations, equation moves to right side in the higher temperatures; otherwise in the exothermic equations, steam reforming equation moves the right side at the lower temperature. Due to these reactions, sorbitol is consumed in each operational conditional.

Conversion of H_2O has negative values under the 400 °C in steam reforming reaction of sorbitol and this is given in Figure 4.17. Temperature which are above 400 °C steam reforming reaction moves the right side and conversion of H_2O is affected positively. While the mole of H_2O is increasing in the input flow, decreasing of H_2O conversion is observed.

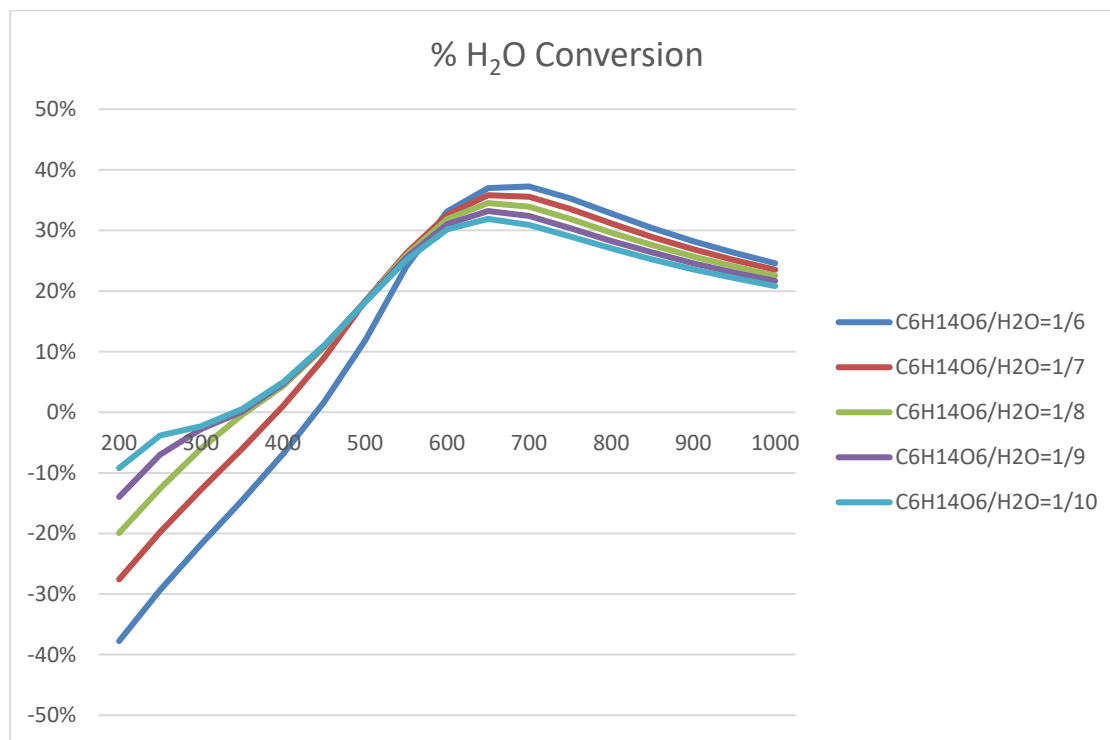


Figure 4.17: The effect of temperature and H_2O concentration on H_2O conversion in steam reforming reaction of sorbitol.

Figure 4.19 shows that H_2O quantity in input flow does not affect to H_2 yield at the below temperatures of 600 °C. While the temperature is increasing, the yield of H_2 is affected negatively. While H_2O addition is increased, decreasing of H_2 yield is observed. The reason of that is originated from equation 3.16.

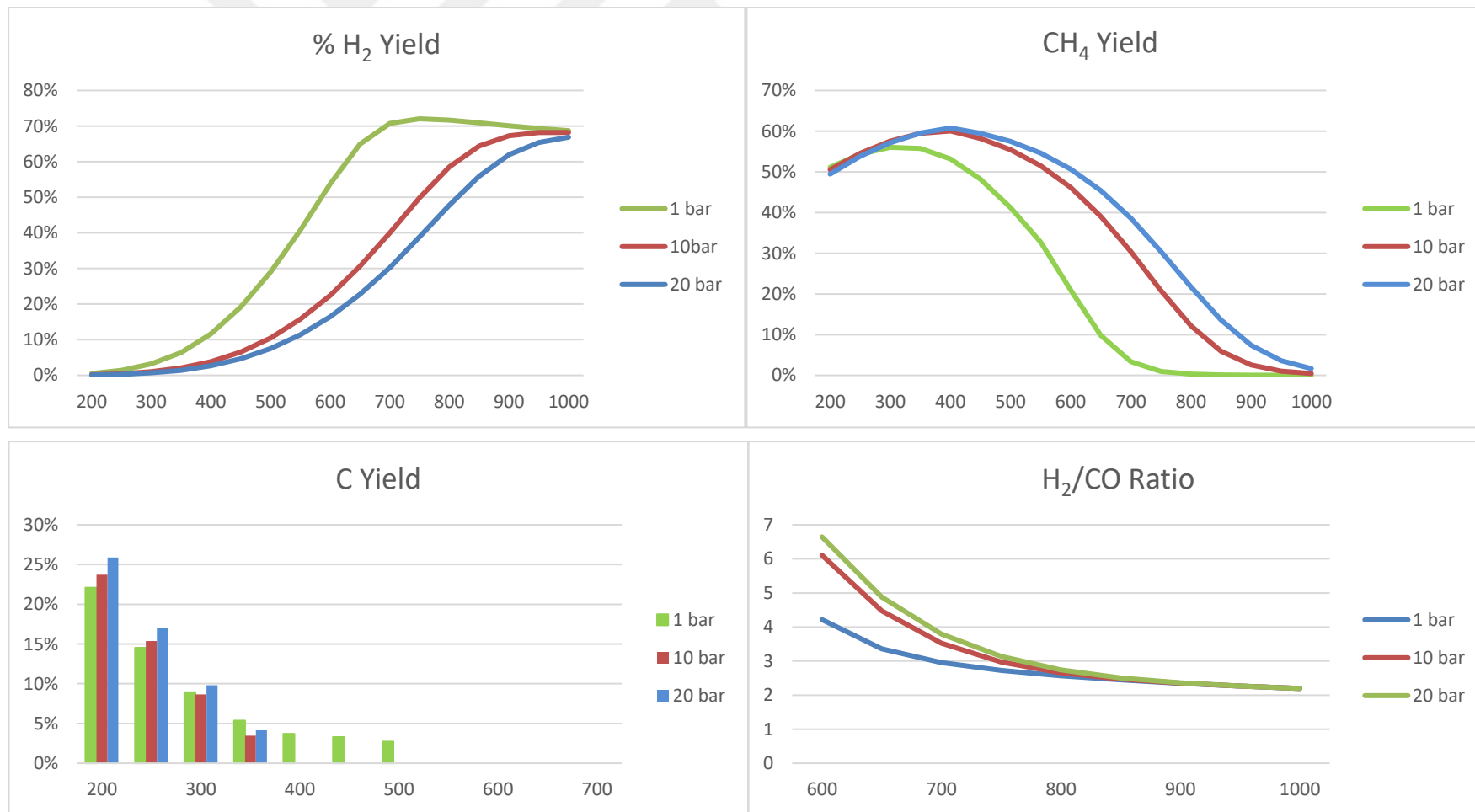


Figure 4.18: Pressure effect of ethylene glycol steam reforming with H₂ yield, C yield, CH₄ yield and H₂/CO ratio under 1 bar, 10 bars and 20 bars.

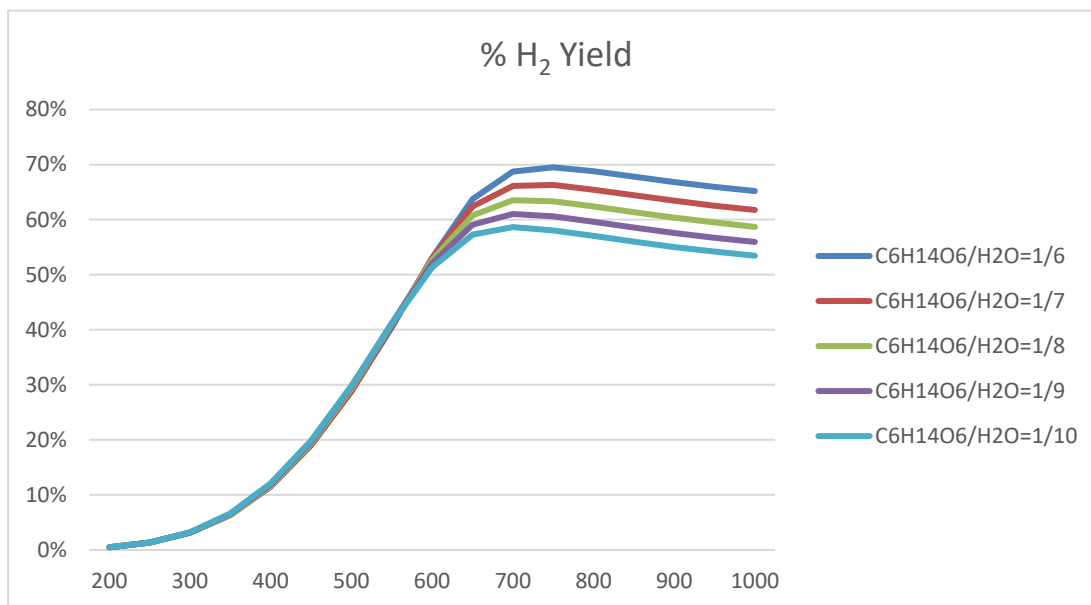


Figure 4.19: The effect of temperature and H₂O concentration on % H₂ yield in steam reforming reaction of ethylene glycol.

Figure 4.20 shows that while the temperature is increasing the yield of CO conversion was affected positively. There are many reasons which are provided that. These can be counted such as steam reforming reaction, coking reaction water-gas shift reaction etc.

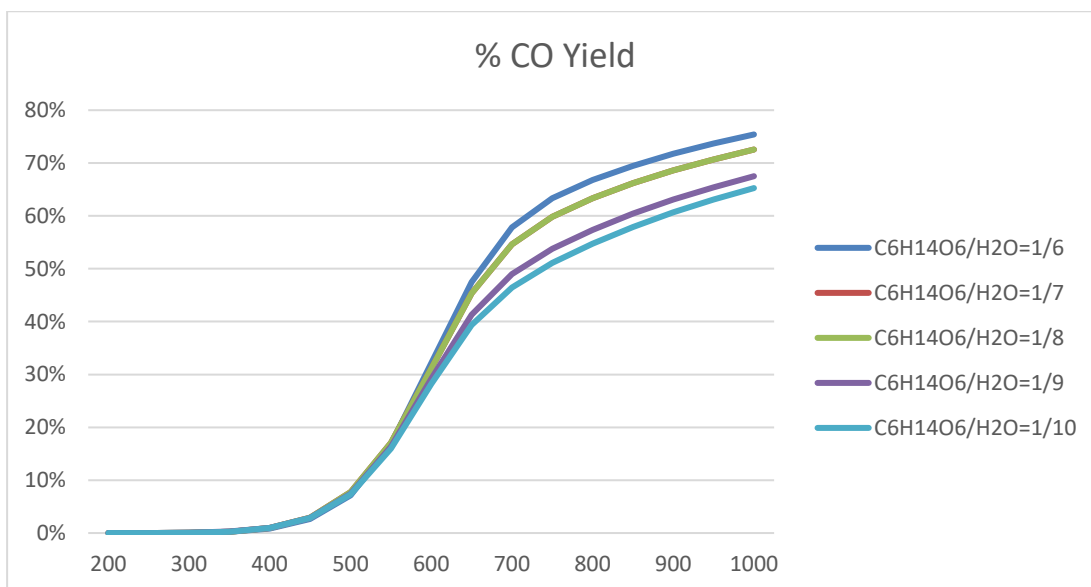


Figure 4.20: The effect of temperature and H₂O concentration on % CO yield in steam reforming reaction of sorbitol.

Figure 4.21 shows that the yield of CO₂ was affected positively until the temperature was 550 °C. This affect can be derived exothermic water-gas shift reaction and reverse

Boudouard reaction. The production of CO_2 was decreased at higher temperature because the steam reform reaction moved the left side. Moreover, the increase of CO_2 yield was observed while the mole of H_2O is increasing in input flow. Water-gas shift reaction can be cause of this result.

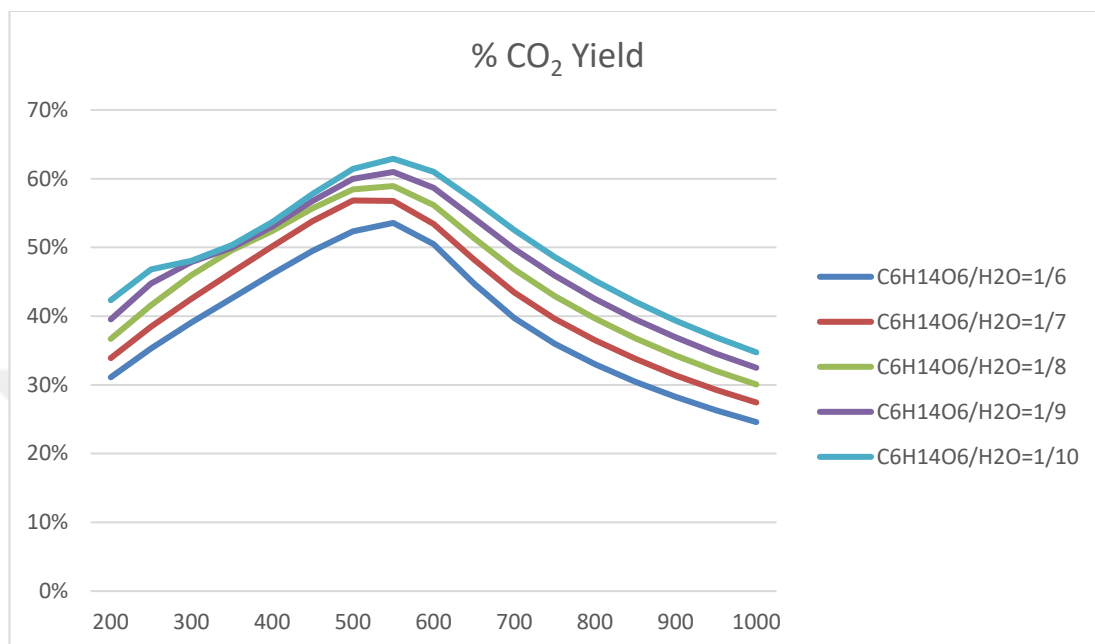


Figure 4.21: The effect of temperature and H_2O concentration on % CO_2 yield in steam reforming reaction of sorbitol.

Decreasing of coke generation was observed when the temperature increasing and increasing of H_2O mole in input flow. This situation is given in Figure 4.22. The reason of this can be reverse Boudouard reaction and CO reduction equation. Decreasing of C was observed while adding H_2 .

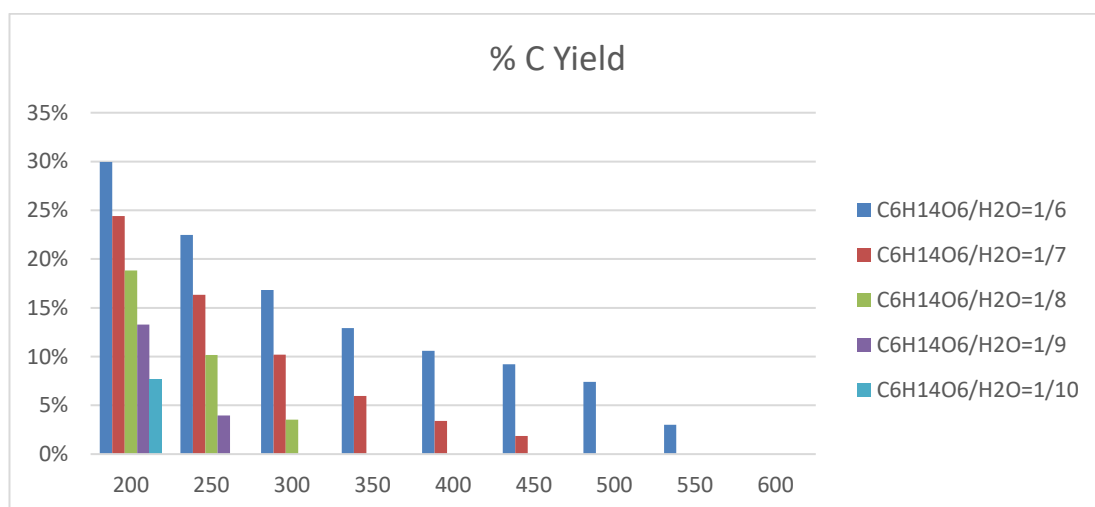


Figure 4.22: The effect of temperature and H_2O concentration on % C yield in steam reforming reaction of sorbitol.

Figure 4.23 shows that the increasing of CH_4 yield was observed until the $350\text{ }^\circ\text{C}$, upper temperatures than $350\text{ }^\circ\text{C}$ decreasing of CH_4 yield was observed. The inverse proportion of temperature and CH_4 yield can be originated from methanation reaction. Moreover, CH_4 yield at temperatures higher than $500\text{ }^\circ\text{C}$ shows values close to each other in all feeding H_2O amounts, so it can be said that CH_4 yield at higher temperatures is not affected by the amount of H_2O feeding for steam reforming of sorbitol.

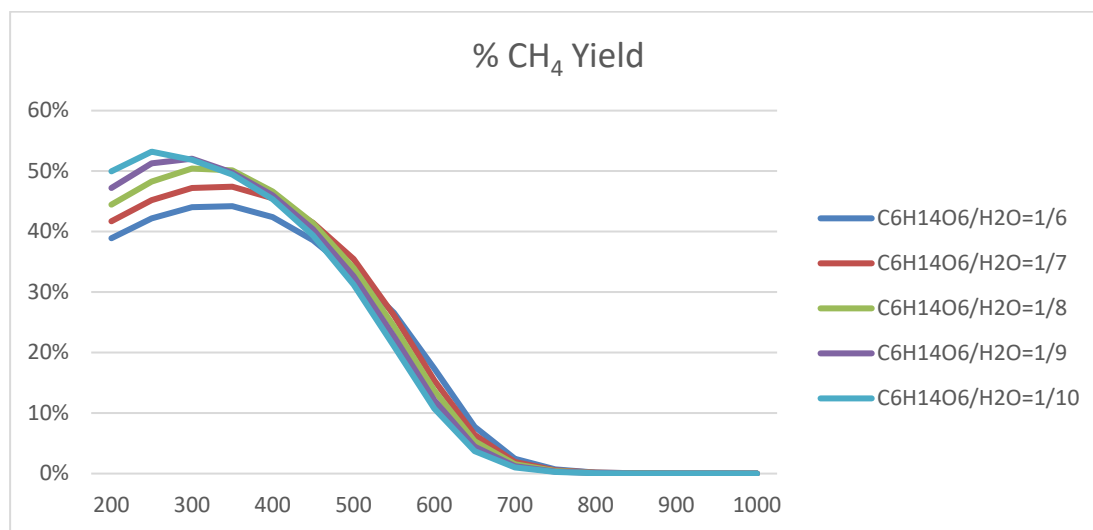


Figure 4.23: The effect of temperature and H_2O concentration on % CH_4 yield in steam reforming reaction of sorbitol.

Figure 4.24 shows that there is a very high H_2 / CO ratio at temperatures below $600\text{ }^\circ\text{C}$. At temperatures below $600\text{ }^\circ\text{C}$, the water-gas shift reaction, expressed in equation 2.2, to the H_2 product side resulted in an increase in the H_2 / CO ratio. At high temperatures, the H_2 / CO ratio reaches lower values due to reverse water-gas shift reaction. When the results are considered, it can be determined that the H_2 / CO ratio is close to a constant value at temperatures above $1000\text{ }^\circ\text{C}$.

H_2/CO ratio, % C yield and % CH_4 yield as side reaction products under different feed flow ratio and different temperatures at 1 bar for sorbitol steam reforming calculated using Aspen Plus are given in Table 4.7. It is proposed that the H_2 / CO ratio in the feed stream used in commercial processes such as the synthesis of Fischer-Tropsch is 2 and that the synthesis gas mixture does not contain any side reaction products such as CO_2 and CH_4 [3]. According to Table 4.7, while the molar ratio of sorbitol/ H_2O is 1/7 at $1000\text{ }^\circ\text{C}$ and under 1 bar, is close to 2 (1.99) and the yield of side reaction products is low.

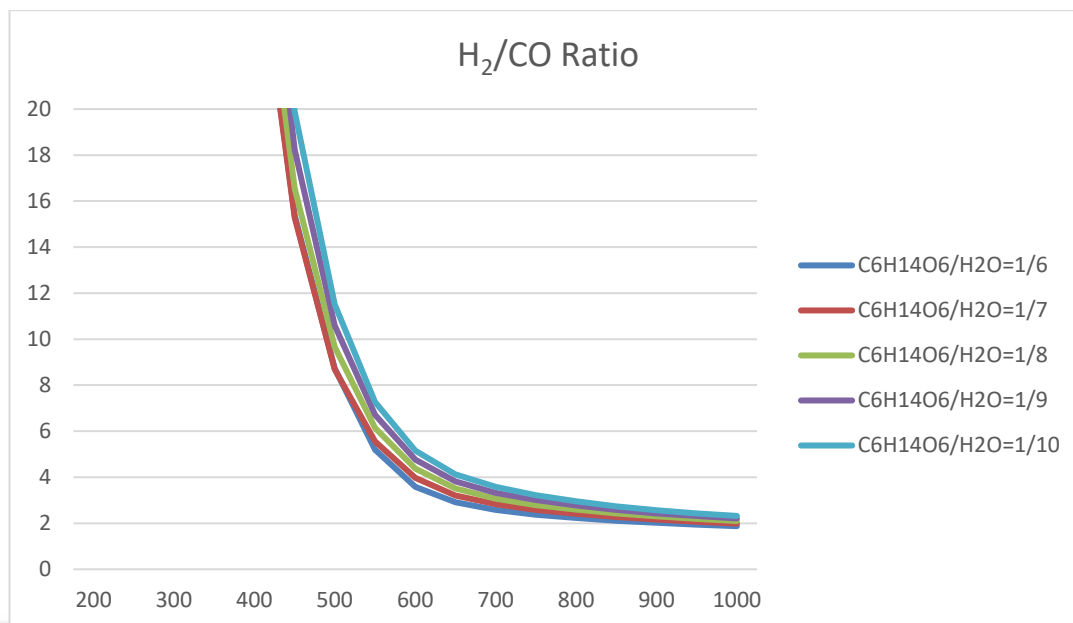


Figure 4.24: The effect of temperature and H₂O concentration on H₂/CO ratio in steam reforming reaction of sorbitol.

4.7 Thermodynamic Analysis of Sorbitol Oxidative Steam Reforming

The oxidative steam reforming reaction of sorbitol was performed in set 2. In Table 3.8, the feed flow compositions defined in Aspen were given in below during the oxidative steam reforming reaction sorbitol. The simulation executed at the fixed mol number for C₆H₁₄O₆ is 1 and fixed mol number H₂O+O₂ is 6. The number of H₂O moles and O₂ moles were changed individually total moles to be 6 moles, in between 200-1000 °C temperature range ($\Delta T=50$ °C) and under pressure 1 bar. Components C₂H₆O₂, H₂O, O₂, CO, H₂, CO₂, C, CH₄ were defined in the simulation environment. Sorbitol and oxygen were consumed at every operational conditions. The reason of this sorbitol has lower stability. It is thought that all of O₂ consumed because the O₂ is used to energetically neutralize the environment in the oxidative steam reforming. Furthermore, O₂ has been reacted to provide a part of the energy required for the endothermic process of steam reforming. Likewise, sorbitol has been formed a complete combustion reaction at low temperatures with O₂, while at high temperatures it has been formed both complete combustion and partial combustion reactions. Due to all these described circumstances, all of the O₂ could be consumed.

Table 4.7: H₂/CO ratio, % C yield and % CH₄ yield at different temperatures and H₂O concentrations in steam reforming reaction of sorbitol.

C ₆ H ₁₄ O ₆ /H ₂ O (mol/mol)	H ₂ /CO Ratio				C Yield (%)				CH ₄ Yield (%)			
	400°C	600°C	800°C	1000°C	400°C	600°C	800°C	1000°C	400°C	600°C	800°C	1000°C
1/6	28.64	3.58	2.31	1.87	10.60	0.00	0.00	0.00	42.40	17.35	0.19	0.00
1/7	28.46	3.98	2.41	1.99	3.41	0.00	0.00	0.00	45.50	15.43	0.15	0.00
1/8	30.09	4.37	2.59	2.10	0.00	0.00	0.00	0.00	46.63	13.70	0.12	0.00
1/9	33.31	4.76	2.77	2.21	0.00	0.00	0.00	0.00	46.00	12.13	0.09	0.00
1/10	36.46	5.15	2.95	2.32	0.00	0.00	0.00	0.00	45.37	10.73	0.08	0.00

As shown in Figure 4.25, as the number of O_2/H_2O ratio in the feed stream increased, the H_2O conversion decreased. This effect is estimated to be due to the increased use of O_2 in the complete combustion reaction and the production of more H_2O . When the general trends in the graph are taken into account, the temperature increase up to $600^\circ C$ contributes to H_2O conversion and after these temperatures, the conversion decreases. In the steam reforming process, the H_2O conversion rate is higher than that of the oxidative steam reforming process, because it is thought that a part of the ethylene glycol reacts with O_2 , so that it is produced smaller amount of H_2O conversion. Extremely, in the case of $C_2H_6O_2/H_2O/O_2=1/0.5/1.5$, H_2O conversion is considered to be the least because of very high rate of oxidation reaction.

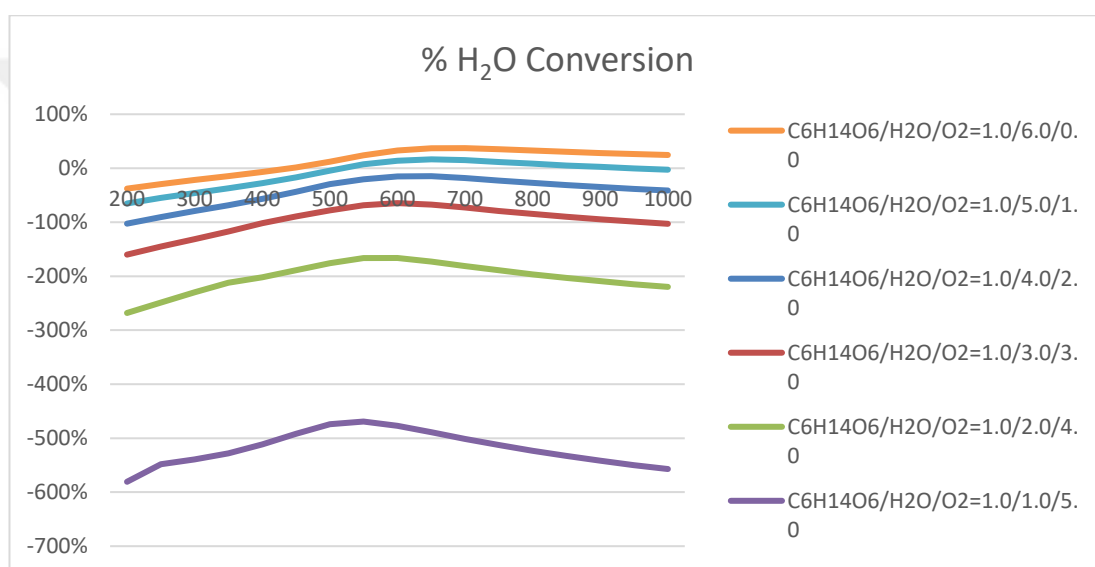


Figure 4.25: The effect of temperature and O_2/H_2O ratio on H_2O conversion in oxidative steam reforming reaction of sorbitol.

Figure 4.26 shows that increasing the number of O_2 moles in the feed stream has a negative effect on the H_2 yield. This negative effect may be thought to be due to the use of a portion of the sorbitol in oxidation, resulting in less H_2 production as a result of the process of steam reforming. In addition, O_2 in the medium reacts with the produced H_2 , causing H_2O production and thus decreasing H_2 efficiency. The O_2 is increased in the feed stream up to $450^\circ C$ has no effect on the H_2 yield. While the temperature increases up to $550-650^\circ C$ contributed to the H_2 yield, the yields were adversely affected after these temperatures. This adversely effect may have been observed because the water-gas shift reaction at high temperatures shifts in the direction of the entrants and increases H_2 consumption.

$C_6H_{14}O_6 / (H_2O+O_2) = 1/6$ constant ratio and H_2O / O_2 change were not affected by H_2 yield up to 400 °C. This situation can be explained by the fact that after 400 °C the reforming reactions come to the fore.

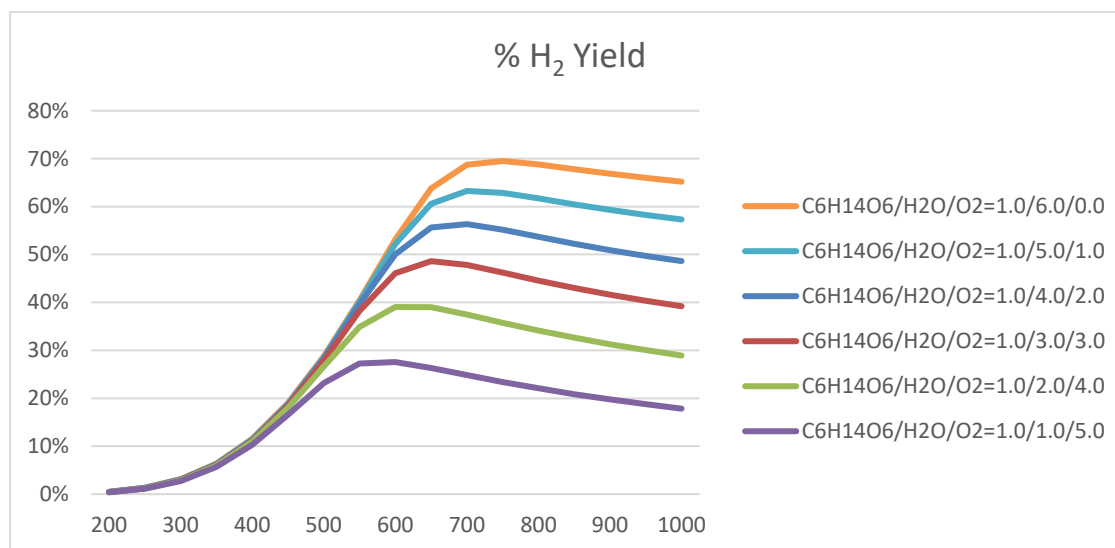


Figure 4.26: The effect of temperature and O_2/H_2O ratio on % H_2 yield in oxidative steam reforming reaction of sorbitol.

The increase in O_2 / H_2O in the feed stream up to 500 °C according to Figure 4.27 does not affect CO efficiency. The graph of the oxidative steam reforming reaction obtained for CO yield was found to be similar to the steam reforming process as a general trend. The steam reforming reaction and the coking reaction of the sorbitol which are endothermic processes shifts towards the product side and increase the CO efficiency. As the water-gas shift reaction, methanation, reverse Boudouard and CO reduction reactions which are in the exothermic processes, in the side of the reactants, it can be said that the CO efficiency is affected positively as the temperature increases. It is determined that the CO efficiency obtained as a result of the steam reforming process is higher at temperatures above 650 °C.

The CO_2 yield is given in Figure 4.28 shows the same general trend as CO_2 as a result of the steam reforming process. It is observed that the increase in the amount of O_2 in the feed stream increases the CO_2 efficiency. The use of O_2 in oxidation reactions and the production of product CO_2 as the cause may be the cause of this effect. It is thought that CO_2 efficiency increases due to the water-gas shift reaction which is exothermic up to 550 °C and the temperature increase of the oxidation reactions.

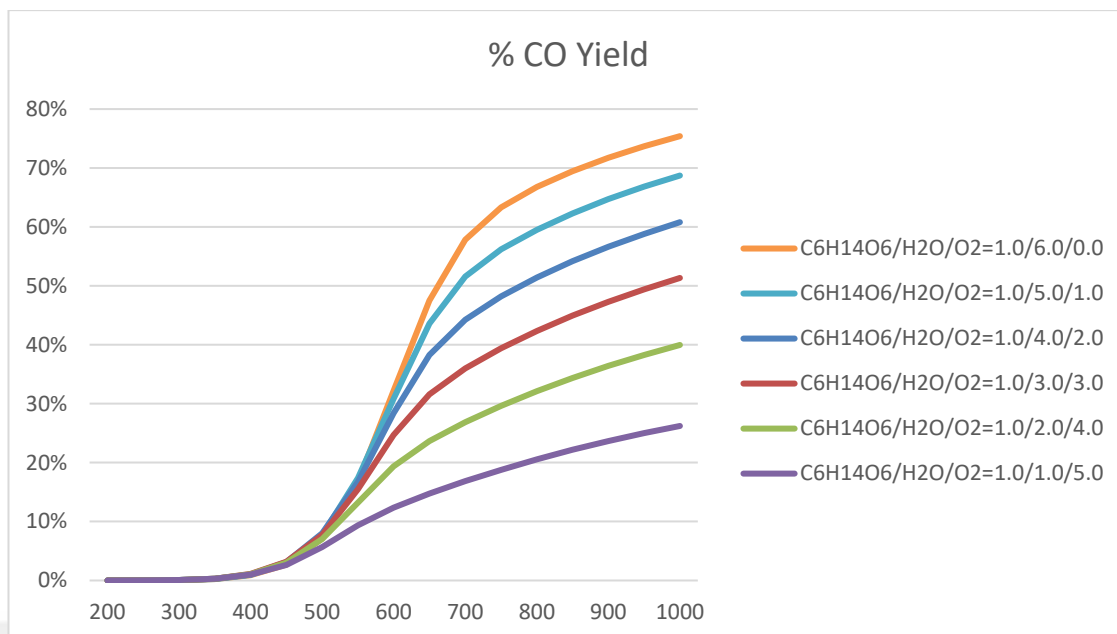


Figure 4.27: The effect of temperature and O_2/H_2O ratio on % H_2 yield in oxidative steam reforming reaction of ethylene glycol.

At temperatures higher than 550 °C, the oxidation reaction and the complete combustion reaction, which are exothermic reactions can be said to be decreasing in CO_2 yield due to the shifts towards the reactants.

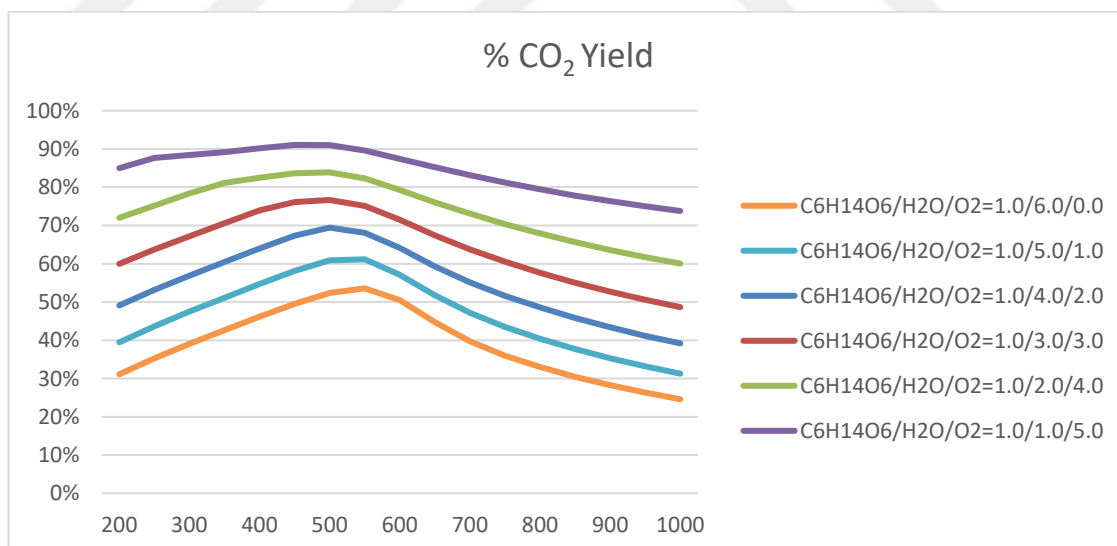


Figure 4.28: The effect of temperature and O_2/H_2O ratio on % CO_2 yield in oxidative steam reforming reaction of sorbitol.

The general trend of C (coke) yield as shown in Figure 4.29 was found to be the same as the C yield general trend obtained as a result of steam reforming process. However, a lower coke yield was obtained in the oxidative steam reforming reaction if the steam reforming reaction values are compared.

In the case of $C_6H_{14}O_6 / H_2O / O_2 = 1.0/6.0/0.0$, the coke yield was 29.95% at 200 °C, while at the same temperature $C_6H_{14}O_6 / H_2O / O_2 = 1.0/1.0/5.0$, was found to be 5.38%. Increased O_2 in the feed stream, decreased the coke formation. The reason for this; It is thought that CO_2 and H_2O are the result of complete combustion of O_2 with sorbitol and the reaction is shifted to the entrants and decreases in the formation of C (coke) by the increase of CO_2 in the reverse Boudouard reaction which is the side reaction. In addition, the coke reacts with O_2 to form CO_2 , which is also a cause.

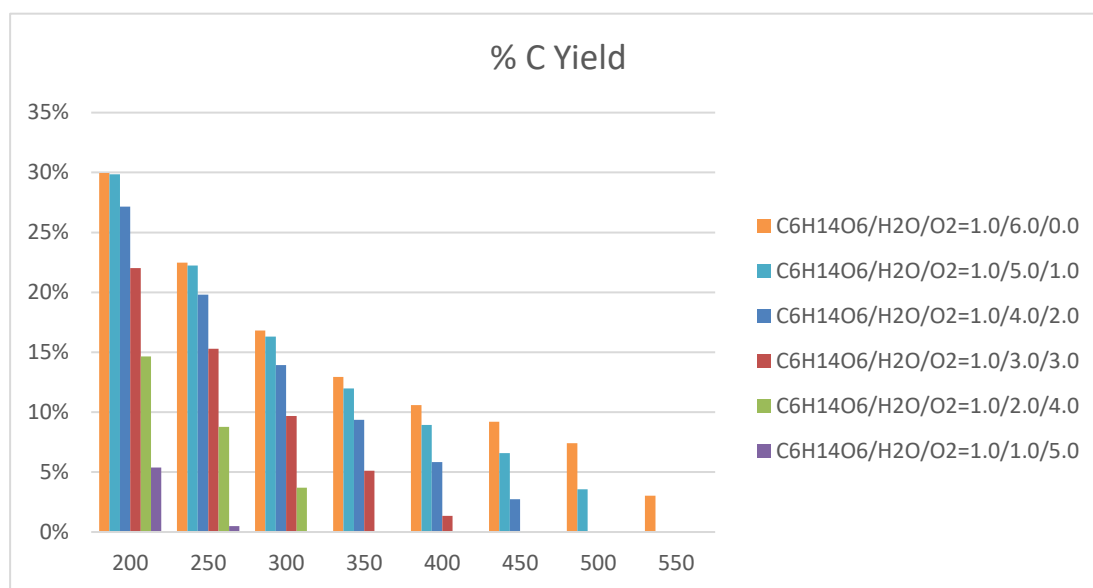


Figure 4.29: The effect of temperature and O_2/H_2O ratio on % C yield in oxidative steam reforming reaction of sorbitol.

The general trend of CH_4 (methane) yield as shown in Figure 4.30 was found to be the same as the CH_4 yield general trend obtained as a result of steam reforming. However, the yield of CH_4 in the oxidative steam reforming lower than the yield of CH_4 in the steam reforming. In the case of $C_6H_{14}O_6 / H_2O / O_2 = 1.0/6.0/0.0$, the CH_4 yield was 42.40% at 400 °C, while at the same temperature $C_6H_{14}O_6 / H_2O / O_2 = 1.0/1.0/5.0$, was found to be 8.82%. CH_4 formation with increasing temperature up to 300-350 °C, except in the absence of H_2O in the environment, shows an increasing trend, however after this temperature CH_4 yield is decreased. This situation has been happened because the methanization reaction, which is exothermic at low temperatures, shifted the products side and increased the efficiency of forming CH_4 , and at high temperature decreased the CH_4 yield while the reaction was shifting reactans side. The general trend of H_2/CO yield as shown in Figure 4.31 was found to be the same as the H_2/CO yield general trend obtained as a result of steam reforming.

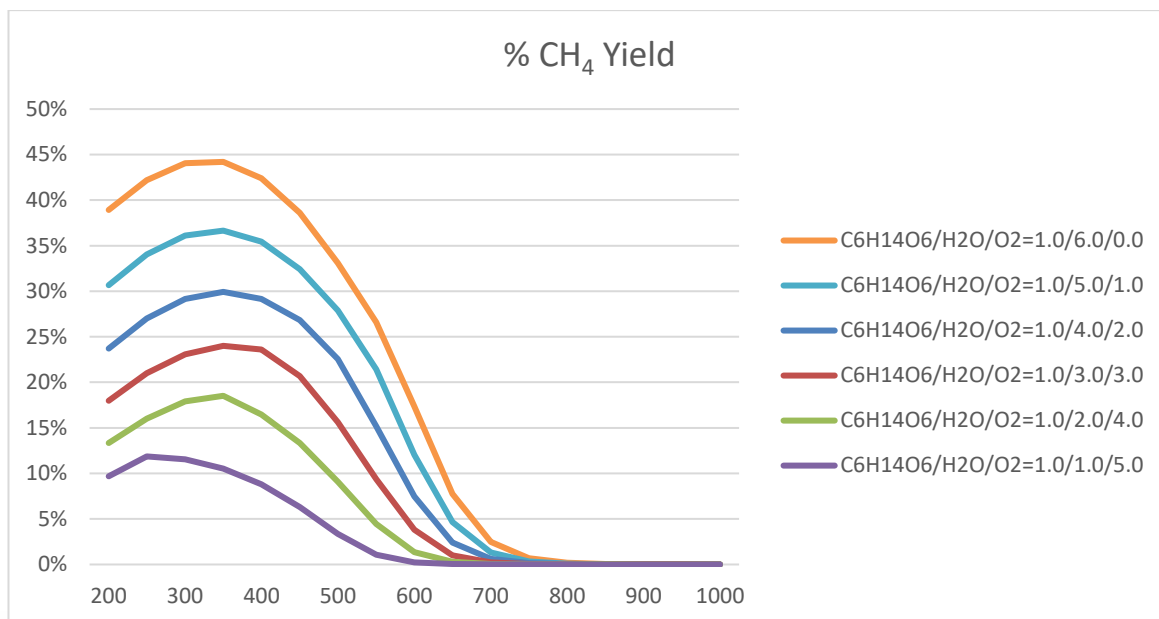


Figure 4.30: The effect of temperature and O₂/H₂O ratio on % CH₄ yield in oxidative steam reforming reaction of sorbitol.

At temperatures below 600 °C, a very high H₂/CO ratio is observed. This effect can be seen due to the water-gas shift reaction shifted toward H₂ product side at temperatures 600 °C. At high temperature, H₂/CO ratio observed lower values because of the reverse water-gas shift reaction. Higher than at 1000 °C, it could be said that the graph trend is beginning to the linear. Table 4.8 shows that the H₂/CO ratio, C yield and CH₄ yield for different feed stream mole fraction and and different temperatures. According to Table 4.8, it is proposed that the H₂ / CO ratio in the feed stream used in commercial processes such as the synthesis of Fischer-Tropsch is 2 and that the synthesis gas mixture does not contain any side reaction products such as CO₂ and CH₄.

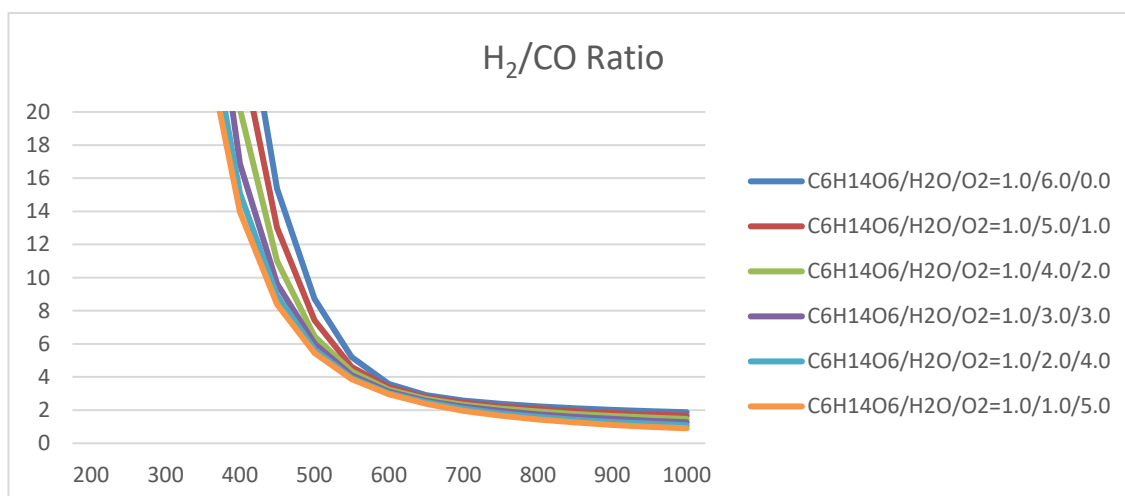


Figure 4.31: The effect of temperature and O₂/H₂O ratio on H₂/CO ratio in oxidative steam reforming reaction of sorbitol.

Table 4.8: H₂/CO ratio, % C yield and % CH₄ yield at different temperatures and H₂O concentrations in oxidative steam reforming reaction of sorbitol.

C ₆ H ₁₄ O ₆ /H ₂ O/O ₂ (mol/mol/mol)	H ₂ /CO Ratio				C Yield (%)				CH ₄ Yield (%)			
	400°C	600°C	800°C	1000°C	400°C	600°C	800°C	1000°C	400°C	600°C	800°C	1000°C
1.0/6.0/0.0	28.64	3.58	2.31	1.87	10.60	0.00	0.00	0.00	42.40	17.35	0.19	0.00
1.0/5.0/1.0	24.04	3.38	2.07	1.67	8.95	0.00	0.00	0.00	35.43	12.06	0.10	0.00
1.0/4.0/2.0	20.17	3.23	1.91	1.47	5.85	0.00	0.00	0.00	29.17	7.46	0.04	0.00
1.0/3.0/3.0	16.87	3.11	1.75	1.27	1.33	0.00	0.00	0.00	23.60	3.80	0.02	0.00
1.0/2.0/4.0	15.10	3.02	1.59	1.08	0.00	0.00	0.00	0.00	16.46	1.35	0.00	0.00
1.0/1.0/5.0	13.97	2.97	1.43	0.91	0.00	0.00	0.00	0.00	8.82	0.22	0.00	0.00

In the case of oxidative steam reforming, while the molar ratio of $C_6H_{14}O_6/H_2O/O_2$ is 1.0/5.0/1.0 at 800 °C and under 1 bar, is close to 2 (2.07) and the yield of side reaction products is low. Usage of O_2 in the reforming process reduced the H_2/CO ratio. It was observed that the steam reforming reaction of sorbitol had a more ideal H_2/CO ratio for the produced Fischer-Tropsch more than oxidative steam reforming process.

4.8 Thermodynamic Analysis of Sorbitol Sorption Enhanced Steam Reforming

The sorption enhanced steam reforming reaction of sorbitol was performed in set 3. In Table 3.9 and in Table 3.10, the feed flow compositions defined in Aspen were given in below during the sorption enhanced steam reforming reaction of sorbitol. The simulation executed with 1 mole and 3 moles CaO in between 200-1000 °C temperature range ($\Delta T=50$ °C) and under pressure 1 bar. Components $C_6H_{14}O_6$, H_2O , CaO, CO, H_2 , CO_2 , C, CH_4 , $CaCO_3$, $Ca(OH)_2$ were defined in the simulation environment. Sorbitol was consumed at every operational conditions.

In Table 4.9, CaO conversion and $CaCO_3$ yield values of sorbitol sorption enhanced steam reforming process at different temperatures are given. $Ca(OH)_2$ is defined in the simulation environment due to the possibility of reacting with H_2O as a side reaction and the formation of $Ca(OH)_2$ by the reaction of CaO with CO_2 . However, CaO has not been reacted with H_2O under any circumstances and CaO produced only $CaCO_3$ by adsorption of CO_2 . Therefore, CaO conversion and $CaCO_3$ yield values were obtained as the same. According to the simulation results in Table 4.9, it is observed that all of the CaO reacts with CO_2 and form $CaCO_3$, regardless of the H_2O molar number in the feed stream up to 700°C. CaO conversion at temperatures above 700 °C was not observed. This negative effect may be due to the fact that the adsorption reaction of CaO with CO_2 is exothermic, the adsorption at temperatures higher than 700 °C does not occur while the reaction is performed at full temperatures at low temperatures and the CaO is deactivated. It is seen that the increase of H_2O in the feed stream at 700°C contributes to the conversion of CaO. This effect may have been due to the fact that the H_2O mole number in the feed stream is too high, the water-gas exchange reaction.

Table 4.9: %CaO conversion at different temperatures and 1-3 moles CaO feeding in sorption enhanced steam reforming reaction of sorbitol.

C₆H₁₄O₆/H₂O (mol/mol)	300 °C		400 °C		500 °C		600 °C		700 °C		800 °C		900 °C		1000 °C	
	CaO 1 mole	CaO 3 moles	CaO 1 mole	CaO 3 moles	CaO 1 mole	CaO 3 moles	CaO 1 mole	CaO 3 moles	CaO 1 mole	CaO 3 moles	CaO 1 mole	CaO 3 moles	CaO 1 mole	CaO 3 moles	CaO 1 mole	CaO 3 moles
1/6	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	99.10	0.0	0.0	0.0	0.0	0.0	0.0
1/7	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0
1/8	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0
1/9	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0
1/10	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0

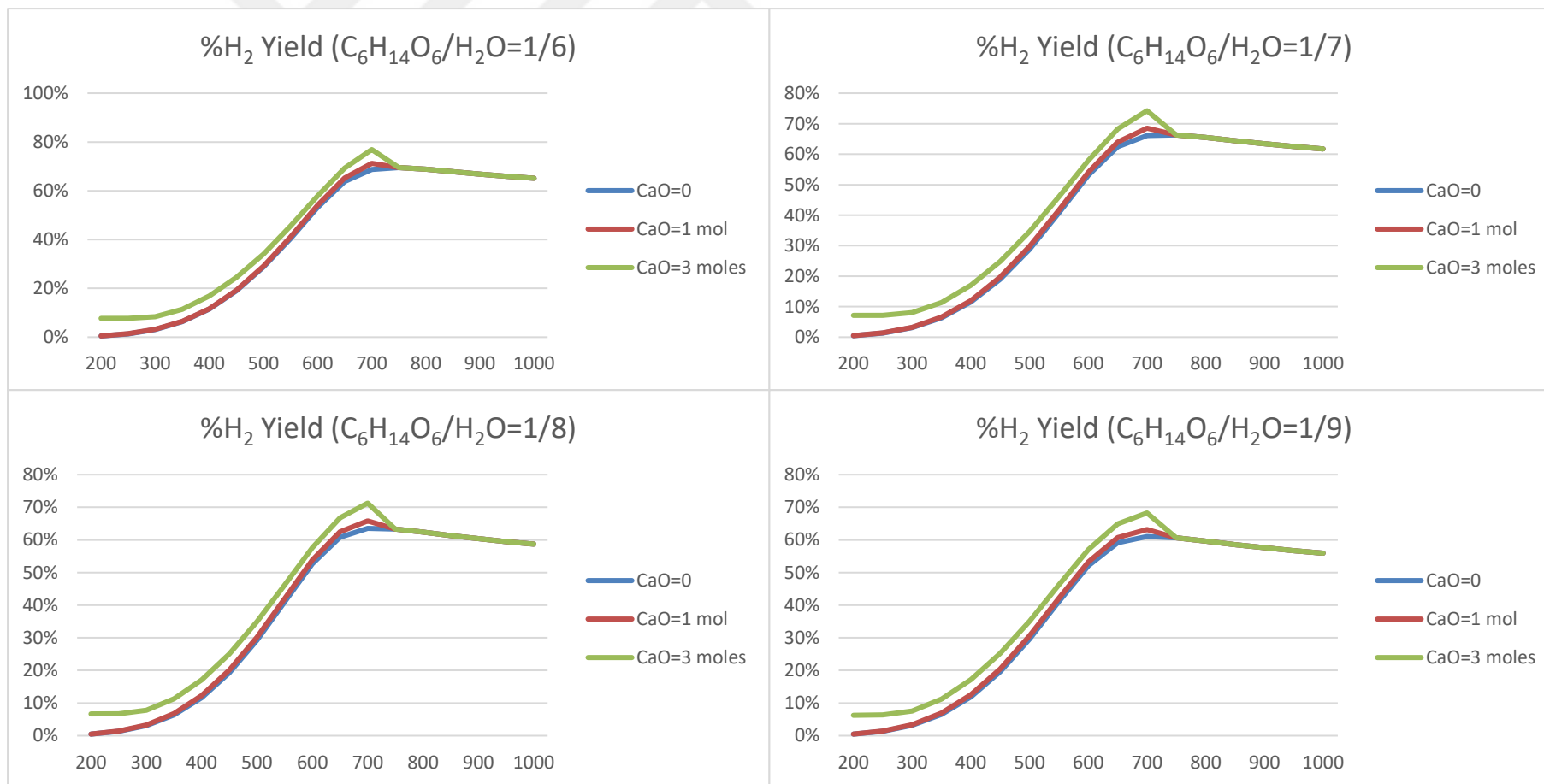


Figure 4.32: The effect of temperature and 1-3 moles CaO feeding on % H₂ yield with different H₂O concentration in sorption enhanced steam reforming reaction of sorbitol.

As indicated in the graphs in Figure 4.32, CO₂ adsorption of sorbitol with CaO to the steam reforming process positively affected the H₂ yield for both 1 mole and 3 moles CaO. This may be the reason for the decrease in the number of CO₂ moles due to adsorption in the reaction medium and the increase in H₂ formation of the water-gas shift reaction towards the products direction. In the case of temperatures higher than 700 °C, CaO does not adsorb CO₂, so the H₂O values of steam reforming process and the sorption enhanced steam reforming process are the same. The endothermic steam reforming process is thought to contribute to the H₂ yield due to shifted toward products side by increasing temperature.

In Table 4.10, the sorption enhanced process was observed to be higher than the H₂ / CO ratio compared to the steam reforming process. The reason for this is that the water-gas shift reaction due to the CO₂ adsorption has a positive effect on H₂ formation and decreases CO formation at low temperatures. At below 700 °C temperatures, CaO is not effected H₂/CO ratio.

Table 4.10: Comparison chart of H₂/CO ratio between steam reforming of sorbitol and sorption enhanced steam reforming of sorbitol at different temperatures and 1-3 moles CaO feeding.

C ₂ H ₆ O ₂ /H ₂ O (mol/mol)	H ₂ /CO Ratio					
	600 °C			1000 °C		
	CaO 0 mole	CaO 1 mole	CaO 3 moles	CaO 0 mole	CaO 1 mole	CaO 3 moles
1/6	3.58	4.41	8.72	1.87	1.87	1.87
1/7	3.98	4.89	9.31	1.99	1.99	1.99
1/8	4.37	5.34	9.91	2.10	2.10	2.10
1/9	4.76	5.80	10.52	2.21	2.21	2.21
1/10	5.15	6.26	11.14	2.32	2.32	2.32

In the simulation results, no coke formation was observed under any conditions of sorption enhanced reforming. CaO is absorbed CO₂ and caused the water-gas shift reaction to shift the product side. For this reason, the reverse Boudouard and CO

reduction reactions have not been occurred due to decreased amount of CO. Therefore, no coke formation was observed. According to the simulation results, since CO₂ adsorption at temperatures higher than 700 °C is not realized, the coke formation values of the steam reforming process and the sorption enhanced reforming were the same. In conclusion, the use of CaO in steam reforming processes is contributed to process as coke formation was not desired.

4.9 Thermodynamic Analysis of Sorbitol Sorption Enhanced Oxidative Steam Reforming

The sorption enhanced oxidative steam reforming reaction of sorbitol was performed in set 4. In Table 3.11 and in Table 3.12, the feed flow compositions defined in Aspen were given in below during the sorption enhanced steam reforming reaction of sorbitol. The simulation executed with 1 mole and 3 moles CaO, at the fixed mol number for C₆H₁₄O₆ is 1 and fixed mol number H₂O+O₂ is 6. The number of H₂O moles and O₂ moles were changed individually total moles to be 6 moles, in between 200-1000 °C temperature range ($\Delta T=50$ °C) and under pressure 1 bar. Components C₆H₁₄O₆, H₂O, O₂, CO, H₂, CO₂, C, CH₄ were defined in the simulation environment. Thereby sorbitol has low stability, it is completely consumed as in previous operations. In fixed H₂O/O₂ case, as the oxidation reaction is performed primarily due to enhance the oxidation steam reforming process, O₂ is completely consumed.

In Table 4.11, CaO conversion and CaCO₃ yield values of sorption enhanced sorbitol steam reforming process at different temperatures are given. Ca(OH)₂ is defined in the simulation environment due to the possibility of reacting with H₂O as a side reaction and the formation of Ca(OH)₂ by the reaction of CaO with CO₂. However, CaO has not been reacted with H₂O under any circumstances and CaO produced only CaCO₃ by adsorption of CO₂. Therefore, CaO conversion and CaCO₃ yield values were obtained as the same. According to the simulation results in Table 4.11, it is observed that all of the CaO reacts with CO₂ and form CaCO₃, regardless of the H₂O molar number in the feed stream up to 700°C. CaO conversion at temperatures above 700 °C was not observed. As in the sorption enhanced steam reforming process, the sorption enhanced oxidative steam reforming process is not CaO converted at temperatures above 700 °C.

Table 4.11: %CaO conversion at different temperatures and 1-3 moles CaO feeding in sorption enhanced oxidative steam reforming reaction of sorbitol.

C₆H₁₄O₆/H₂O/O₂ (mol/mol/mol)	300 °C		400 °C		500 °C		600 °C		700 °C		800 °C		900 °C		1000 °C	
	CaO	CaO	CaO	CaO	CaO	CaO	CaO	CaO	CaO	CaO	CaO	CaO	CaO	CaO	CaO	CaO
	1	3	1	3	1	3	1	3	1	3	1	3	1	3	1	3
	mole	moles	mole	moles	mole	moles	mole	moles	mole	moles	mole	moles	mole	moles	mole	moles
1.0/6.0/0.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	99.10	0.0	0.0	0.0	0.0	0.0	0.0
1.0/5.0/1.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0
1.0/4.0/2.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0
1.0/3.0/3.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0
1.0/2.0/4.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0
1.0/1.0/5.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	0.0	0.0	0.0	0.0	0.0	0.0

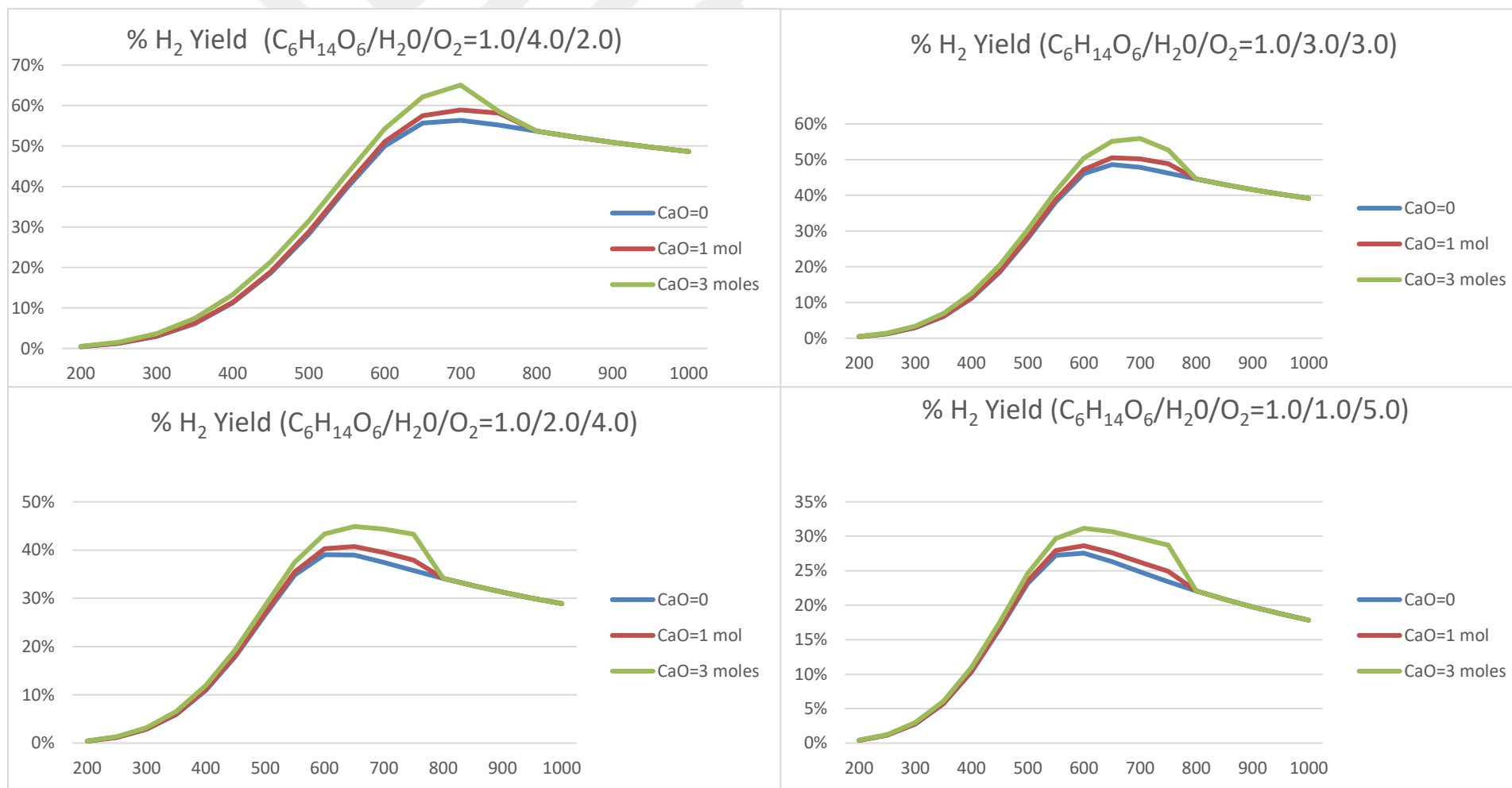


Figure 4.33: The effect of temperature and 1-3 moles CaO feeding on % H₂ yield with different H₂O concentration in sorption enhanced oxidative steam reforming reaction of sorbitol.

As indicated in the graphs in Figure 4.33, CO₂ adsorption of sorbitol with CaO to the steam reforming process positively affected the H₂ yield for both 1 mole and 3 moles CaO. This may be the reason for the decrease in the number of CO₂ moles due to adsorption in the reaction medium and the increase in H₂ formation of the water-gas shift reaction towards the products direction. In the case of temperatures higher than 700 – 800 °C, CaO does not adsorb CO₂, so the H₂O values of steam reforming process and the sorption enhanced steam reforming process are the same. It has been found that while the mole number of O₂ was increasing in the feed stream, H₂ yield decreased. This is because by the use of ethylene glycol with oxidation reaction, occur the more less H₂ production.

In Table 4.12, the sorption enhanced oxidative steam reforming process was observed to be higher than the H₂ / CO ratio compared to the oxidative steam reforming process. While the mole number of O₂ and temperature increased, H₂/CO ratio decreased. At below 750 - 800 °C temperatures, CaO is not effected H₂/CO ratio.

Table 4.12: Comparison chart of H₂/CO ratio between steam reforming of sorbitol and sorption enhanced steam reforming of sorbitol at different temperatures and 1-3 moles CaO feeding.

C ₆ H ₁₄ O ₆ /H ₂ O/O ₂ (mol/mol/mol)	H ₂ /CO Ratio					
	600 °C			1000 °C		
	CaO 0 mole	CaO 1 mole	CaO 3 moles	CaO 0 mole	CaO 1 mole	CaO 3 moles
1.0/6.0/0.0	3.58	4.41	8.72	1.87	1.87	1.87
1.0/5.0/1.0	3.38	4.11	7.56	1.67	1.67	1.67
1.0/4.0/2.0	3.23	3.88	6.76	1.47	1.47	1.47
1.0/3.0/3.0	3.11	3.71	6.22	1.27	1.27	1.27
1.0/2.0/4.0	3.02	3.59	5.91	1.08	1.08	1.08
1.0/1.0/5.0	2.97	3.53	5.79	0.91	0.91	0.91

4.10 Thermodynamic Analysis of Pressure Effect of Sorbitol Steam Reforming

The pressure effect on steam reforming reaction of sorbitol was performed in set 5. In this set, sorbitol is simulated with 1 mol, H₂O is simulated with 6 moles and the simulation is executed in between 200-1000 °C temperature range ($\Delta T=50$ °C) and pressure was changed as 1 bar, 10 bars and 20 bars, respectively. Pressure is also an important variable in reforming processes [22]. Under all temperature and pressure conditions, the sorbitol was completely consumed. Figure 4.34 shows that the H₂ yield, C yield, CH₄ yield and H₂/CO ratio under different temperatures and different pressures.



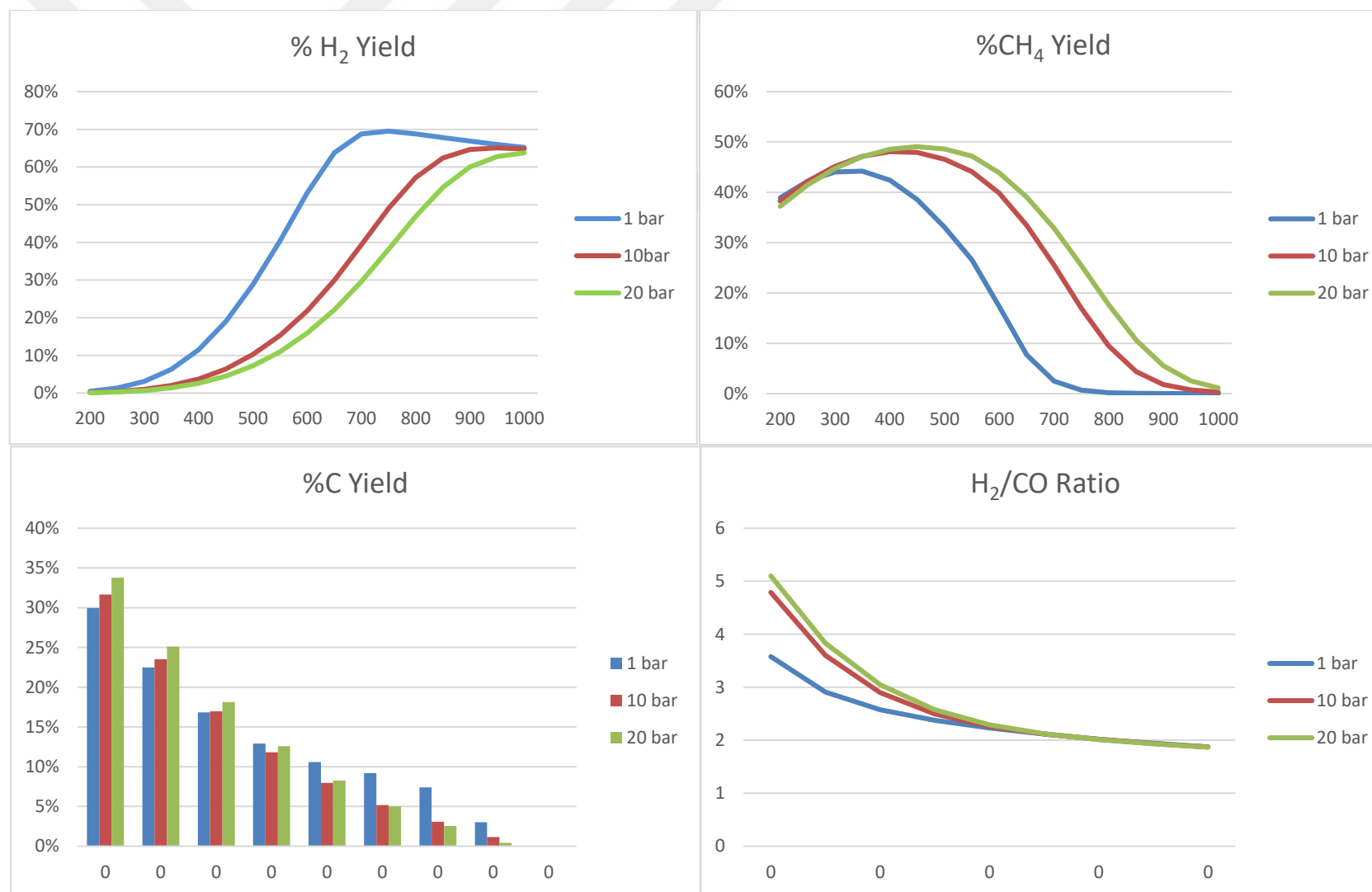


Figure 4.34: Pressure effect of sorbitol steam reforming with H₂ yield, C yield, CH₄ yield and H₂/CO ratio under 1 bar, 10 bars and 20 bars.

5. CONCLUSIONS AND RECOMMENDATIONS

- In this thesis, ethylene glycol and sorbitol were chosen as a model compound of bio-oil to produce syngas and hydrogen gas using Aspen Plus V8.8. Thermodynamic analysis of model compounds was performed and examined. Optimum conditions were purposed to choose such as temperature, pressure. Many reforming process of ethylene glycol and sorbitol were performed to examine different feed stream compounds effect at specified temperature range. These simulation studies were performed using Gibbs free minimization energy method.
- H_2 , CO_2 , CO , CH_4 were produced as gas product and coke was produced as solid product in all processes. In sorption enhanced reforming, $CaCO_3$ was produced in addition to the coke generation. Product mix differentiated according to process conditions and feed steam compound.
- The biggest advantage of oxidative steam reforming is that the process does not need any energy. according to simulation results, O_2 addition to feed steam decreases energy need. Increasing of temperature or H_2O mole has not been effected process.
- According to thermodynamic analysis of ethylene glycol and sorbitol, steam reforming was observed as the best process to produce H_2 .
- Temperature is the most critical point of H_2 production.
- Coke production can be decreased in some conditions such as higher temperature, lower pressure.
- The yield of H_2 can be increased with higher temperature, lower pressure and lower H_2O and O_2 molar feed steam.
- Technical and economic conditions should be considered to determine optimum conditions of real reforming process of ethylene glycol and sorbitol.
- Reforming process of ethylene glycol and sorbitol can be studied in laboratory. In this method thermodynamic results can be compared with experimental results.

- Conversion of bio oil to syngas, another different model can be chosen to compare with ethylene glycol and sorbitol. Hence, results can be compared with each other.



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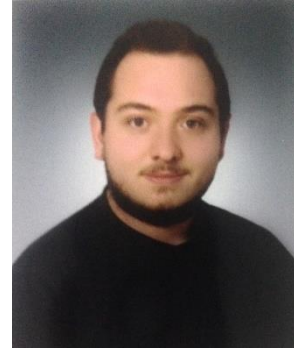
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