

**SYNTHESIS GAS CLEANING: H₂S -TAR REMOVAL AND GAS
CONDITIONING**

**M.Sc. Thesis by
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Programme : Chemical Engineering

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JUNE 2011

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**SENTEZ GAZININ TEMİZLENMESİ: H₂S – KATRANIN GİDERİMİ VE
GAZ ŞARTLANDIRMA**

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FOREWORD

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TABLE OF CONTENTS

	<u>Pages</u>
TABLE OF CONTENTS	vii
ABBREVIATIONS	ix
LIST OF TABLES	xi
LIST OF FIGURES	xiii
SUMMARY	xv
ÖZET	xvii
1. INTRODUCTION	1
2. GASIFICATION	3
2.1 Gasification And Gasification Methods	3
2.2 Gasifier Classification	6
2.2.1 Moving bed processes	7
2.2.2 Fluidized bed processes.....	8
2.2.3 Entrained flow processes.....	9
2.3 Synthetic Fuels.....	11
2.3.1 Coal to liquids	11
2.3.2 SNG from coal	13
3. GAS CLEAN UP AND PROCESSING	15
3.1 Hydrogen Sulfur Removal.....	16
3.1.1 Criteria for selecting sulfur sorption materials.....	17
3.1.2 Basic sulfidation reactions	17
3.1.3 Zinc-based materials	18
3.1.4 Copper-based materials	18
3.1.5 Calcium-based materials	19
3.1.6 Manganese-based materials	24
3.1.7 Iron-based materials	25
3.2 Tar Removal	25
3.2.1 Catalysis for tar removal	29
3.2.5 Controlling carbon accumulation and sulfur poisoning	31
3.2.5.1 Carbon accumulation	31
3.2.5.2 Sulfur poisoning	32
3.3 Synthesis Gas Conditioning.....	35
3.3.1 Fisher-Tropsch synthesis.....	35
4. EXPERIMENTAL	41
4.1 Materials And Methods	41
4.1.1 Dolomite.....	41
4.1.2 Gases	44
4.1.3 Catalysts for tar removal and gas conditioning studies.....	45
4.1.4 Experimental set up.....	45

5. RESULTS AND DISCUSSION	49
5.1 Sulfur Removal Studied With Dolomite	49
5.1.1 H ₂ S removal in N ₂ atmosphere	49
5.1.2 H ₂ S Studies with binary gas mixtures	50
5.1.3 H ₂ S Studies with tertiary gas mixtures	51
5.1.4 H ₂ S studies with real gasifier outlet gas mixtures	54
5.2 Tar Removal Studies	55
5.2.1 Tar removal studies with dolomite	55
5.2.2 Tar removal studies with Catalyst I	56
5.3 Gas Conditioning Studies	61
5.3.1 Steam reforming of methane	61
5.3.2 High temperature shift (HTS) studies	63
5.3.2.1 Simulated gas composition I	64
5.3.2.2 Simulated gas composition II	72
5.3.2.3 Simulated gas composition III	74
5.3.3 Low temperature shift (LTS) study	76
6. CONCLUSION	77
REFERENCES	81

ABBREVIATIONS

CEM	:controlled evaporator mixer unit
C_{H2S,i}	:initial H ₂ S concentration
CTL	:coal to liquid
Etmr	:Ethyl Mercaptane
FT	:Fischer Tropsch
FTS	:Fischer Tropsch Synthesis
HTS	:high temperature shift catalyst
IGCC	:Integrated Gasification Combined Cycle
LTS	:low temperature shift catalyst
MFC	:mass flow controller valve
NG	:Natural Gas
PAH	:polycyclic aromatic hydrocarbon
S	:Selectivity
SNG	:Synthetic Natural Gas
WGS	: water gas shift reaction
ppb	:parts per billion
ppm	:parts per million
ppmv	:parts per million by volume

LIST OF TABLES

	<u>Pages</u>
Table 2.1: Typical operating characteristics of coal gasifiers (Rezaiyan and Cheremisinoff, 2005).....	7
Table 2.2: Specification for Fischer-Tropsch Synthesis Gas (Higman and Van Der Burgt, 2003).....	12
Table 3.1: Characteristics of the common model tar compounds (Xu et al., 2010).	26
Table 3.2: Performance of iron catalysts for the decomposition of tars (Torres et al., 2007).....	30
Table 3.4: Heating value of syngas using various gasification agents (Url-2).	35
Table 4.1: Chemical analysis of dolomite	41
Table 4.2: Physical analysis of the original, calcined and used dolomite.	41
Table 4.3: Gases which were used in the laboratuary studies.	45
Table 4.4: Properties Of Used Commercial Catalysts.....	45
Table 5.1: Removal of H ₂ S from binary gas mixture by dolomite (dry basis), GHSV=5600 h ⁻¹ , T=750°C.....	51
Table 5.2: The results of H ₂ S removal from tertiary gas mixtures with dolomite (dry basis), GHSV=5600 h ⁻¹ , T=750 °C.....	52
Table 5.3: The results of H ₂ S removal by dolomite under simulated gasifier outlet gas composition, GHSV=5600 h ⁻¹ , T=750°C.	54
Table 5.4: Tar removal by dolomite under simulated gasifier outlet gas composition, GHSV = 5600 h ⁻¹ , T=750°C.....	55
Table 5.5: Tar reforming by Catalyst I under nitrogen atmosphere at constant Steam/C ratio, GHSV=90 000 h ⁻¹ , Steam/C=0.26, Steam/Xylene=2.1.	56
Table 5.6: Tar reforming by CatalystI under nitrogen atmosphere, GHSV=90000 h ⁻¹	57
Table 5.7: Methane reforming on Catalyst I without contaminant, GHSV =90000 h ⁻¹	58
Table 5.8: Gasoues products formed during tar reforming on Catalyst I.	59
Table 5.9: Methane reforming over Catalyst I under nitrogen atmosphere, GHSV=38000 h ⁻¹	62
Table 5.10: Outlet gas composition (v %, dry basis), T=400°C, GHSV=50000 h ⁻¹ , Catalyst: Catalyst III.....	72
Table 5.11: Outlet gas composition on dry basis as volume %, GHSV=50000 h ⁻¹ , T=400°C.	74

Table 5.17: Outlet gas composition (v%, dry) for different GHSV and Steam/CO ratios at 275 °C, Catalyst: Catalyst IV.....	76
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LIST OF FIGURES

	<u>Page</u>
Figure 2.1: Products of reaction as a function of oxygen/coal ratio (Phillips, 2006).....	3
Figure 2.2: Gasification methods (Rezaiyan and Cheremisinoff, 2005).....	4
Figure 2.3: Global syngas output by feedstock (Url-1).....	6
Figure 2.4: Gasification process (Url-1)	6
Figure 2.5: Diagram of a generic moving bed gasifier (Phillips, 2006).....	7
Figure 2.6: Diagram of a generic fluidized bed gasifier (Phillips, 2006)	8
Figure 2.7: Fluid bed regimes (Higman and Van Der Burgt, 2003)	9
Figure 2.8: Diagram of a generic entrained flow gasifier (Phillips, 2006)	10
Figure 2.9: CTL (coal-to-liquids) fuels production via coal gasification (Shen et al., 2007).	13
Figure 2.10: Block flow diagram of SNG manufacture from coal (Higman and Van Der Burgt, 2003).....	14
Figure 2.11: Concept of a poly generation plant based on the IGCC process (Clark et al., 2004).....	14
Figure 3.1: Evolution of the tar species upon gasification of sawdust with steam and oxygen (Torres et al., 2007).	26
Figure 3.2: Mechanism of tar cracking over a catalyst (e.g., Ni supported) (Xu et al., 2010).	28
Figure 3.3: Initial removal of naphthalene from a syngas on Ni/Al ₂ O ₃ catalyst (Torres et al., 2007).....	33
Figure 3.4: FTS General Process Flow Diagram (Url-3).....	36
Figure 4.1: Thermogravimetric analysis of original dolomite	42
Figure 4.2: Thermogravimetric analysis of calcined dolomite	42
Figure 4.3: Thermogravimetric analysis of used dolomite	43
Figure 4.4: Comparison of TGA curves of the original, the calcined and the used dolomite	43
Figure 4.5: The schematic of experimental setup	47
Figure 4.6: Photograph of the experimental setup	48
Figure 5.1: Change of H ₂ S concentration in the reactor outlet gas stream with temperature. Gas mixture: H ₂ S-N ₂ , C _{H2S,i} =500 ppmv, GHSV=5600 h ⁻¹	50
Figure 5.2: Changing in tar reforming extension via Catalyst I with temperature under nitrogen atmosphere	58
Figure 5.3: Changing toluene/xylene and benzene/xylene ratios with temperatures in the Catalyst I reactor under nitrogen atmosphere	60

Figure 5.4: Changing of xylene conversion with inlet tar load on a Catalyst I under nitrogen atmosphere	60
Figure 5.5: The pictures of catalyst I and bottom wool before and after tar removing process a) Catalyst, b) Bottom wool.	61
Figure 5.6: Methane conversion with temperature using Catalyst II (at 25°C and 1 atm ♦GHSV= 38000 h ⁻¹ ■GHSV= 19000 h ⁻¹).....	62
Figure 5.7: Changes in the product composition with temperature during methane reforming over Catalyst II, GHSV = 38000 h ⁻¹	63
Figure 5.8: The change in CO conversion with temperature, Steam/CO = 0.6, GHSV = 25000 h ⁻¹ , Catalyst: Catalyst III.....	65
Figure 5.9: The change in selectivity with temperature, Steam/CO = 0.6, GHSV=25000 h ⁻¹ , Catalyst: Catalyst III.....	65
Figure 5.10: Change in the H ₂ /CO ratio with temperature, Steam/CO=0,6, GHSV=25000h ⁻¹ , Catalyst: Catalyst III.....	66
Figure 5.11: The change in CO conversion as a function of inlet Steam/CO, GHSV=25000 h ⁻¹ , Catalyst: Catalyst III, ♦T=300°C , □T=360°C	67
Figure 5.14: The change in CO conversion with GHSV, T=375°C, Steam/CO=2, Catalyst: Catalyst III	69
Figure 5.15: The change in selectivity with GHSV, T=375°C, Steam/CO=2, Catalyst: Catalyst III	69
Figure 5.16: The change in H ₂ /CO ratio with GHSV, T=375°C, Steam/CO=2, Catalyst: Catalyst III	70
Figure 5.17: The change in CO conversion with temperature, GHSV=50000 h ⁻¹ , Steam/CO ratio=2, Catalyst: Catalyst III	71
Figure 5.18: The change in selectivity with temperature, GHSV=50000 h ⁻¹ , Steam/CO ratio=2, Catalyst: Catalyst III	71
Figure 5.19: The change in H ₂ /CO ratio with temperature, GHSV=50000 h ⁻¹ , Steam/CO ratio=2	72
Figure 5.20: The change in CO conversion with Steam/CO ratio, GHSV=50000 h ⁻¹ , T=400°C, Catalyst: Catalyst III.....	73
Figure 5.21: The change in selectivity with Steam/CO ratio, GHSV=50000 h ⁻¹ , T=400°C, Catalyst: Catalyst III.....	73
Figure 5.23: The change of CO conversion with GHSV h ⁻¹ , T=400°C, Steam/CO=1.28, Catalyst: Catalyst III	75

SYNTHESIS GAS CLEANING: H₂S -TAR REMOVAL AND GAS CONDITIONING

SUMMARY

The development level of a country is directly relates to its economic and social level. One of the most improtant factor is energy, which is the requirement of sustainable development. In Turkey population increases day to day and paralel to this energy demand increases. For the solution of this problem Turkey may use its lignite mine for the liquid fuel production.

For liquid fuel production firstly lignite should be gasified. Turkish lignites contains significant amount of sulfur. Gases from the gasification process mostly contain H₂S and tar. H₂S is a very corrossive and poisonous gas and causes corrosion of the pipe lines. Also the catalytic systems such as FT and tar removal catalysts are easily deactivated in the presence of sulfur higher than 1 ppmv. Generally metal oxides are used for the removal of sulfur from hot gas. Tar is the another problem for the hot gas clean up processes. It condenses in the pipelines and causes obstruction. There are physical and catalytic systems for tar removal. Catalytic systems are cheaper and there is no waste promlem for these systems.

The gas composition which is sent to the FT synthesis should have a H₂/CO ratio ≥ 1 . Therefore the gas mixture which come from the gas clean up unit should be operated before the FT synthesis and the gas composition should be adjusted. For this purpose cleansed gas mixture is sent to the gas conditioning unit before the FT synthesis. In this unit, various water gas shift catalysts are used for the adjustment of gas composition.

In this study dolomite which was supplied from Eskişehir region of Turkey was used for the sulfur and tar removal studies. The sulfur removal capacity of dolomite was investigated at different temperatures, H₂S load, GHSV and for different gas compositions. Sulfur removal efficiency seems to be highly dependent on sulfur concentration. At low sulfur concentrations, namely below 200 ppmv, 20% - 30% of sulfur was captured by dolomite. In case of high inlet H₂S concentrations of around 1500-2000 ppmv, dolomite seems to be able to remove 90% of sulfur from hot gases. Simultaneous presence of CO and CO₂ in the feed gas results in COS formation up to 8-10 ppm in sulfur soption process by dolomite. In addition, when natural gas was added to the feed gas, trace amount of ethyl mercaptane were detected in the reactor outlet gas stream. The best sulfur adsorption performance of dolomite seem to be achieved at 750°C – 800°C and with GHSV=5000 h⁻¹.

For tar removal studies tar was simulated as benzene, toluene and xylene and this mixture was sent to the clean up system after evaporated. In the studies which was performed by dolomite, xylene was converted mostly into benzene and partly into toluene at 750°C. In addition to dolomite studies tar reforming activity of a commercial precious metal based catalyst was investigated at different tar loads and temperatures. It was seen that selective steam reforming and steam dealkylation reactions were the dominant reactions in relation to steam reforming reaction. The degree of dealkylation of xylene and selective steam reforming increased with temperature in the range of 350-750°C. Also it was observed that the xylene conversion is highly dependent on inlet tar load.

After the sulfur and tar removal studies gas condition studies were performed by using four different commercial catalysts. In these studies the activity of catalysts were tested for different gas composition, temperature, GHSV and Steam/CO ratio. Studies were conducted between 20000 – 75000 h⁻¹ and the 50000 h⁻¹ was obtained as the optimum GHSV value. CO conversion increased by increasing the Steam/CO ratio. When steam/CO ratio and temperature increased water gas shift reaction has been observed as the dominant reaction instead of Boudouard reaction. Also it was seen that H₂/CO ratio is a good measure of conversion for water gas shift reaction. It was observed that Boudouard reaction and coking occurs at low temperatures, especially between 250°C and 300°C. In addition to this, at temperatures higher than 400°C catalysts loss activity because of the agglomeration on the catalyst surface.

SENTEZ GAZI TEMİZLENMESİ: H₂S –KATRAN GİDERİMİ VE GAZ ŞARTLANDIRMA

ÖZET

Ülkenin gelişmişlik düzeyi ekonomik ve sosyal seviyesiyle direk olarak ilişkilidir. En önemli faktörlerden biri, sürekli gelişme için gereklilik arz eden, enerjidir. Türkiye’de nüfus günden güne artmakta ve buna paralel olarak enerji ihtiyacı artmaktadır. Bu problemin çözümü için Türkiye sıvı yakıt üretimi için linyit madenlerini kullanabilir.

Sıvı yakıt üretimi için ilk olarak linyit gazlaştırılmalıdır. Türk linyitleri önemli miktarda sülfür ihtiva etmektedir. Gazlaştırma prosesinden gelen gazlar çoğunlukla H₂S ve katran içermektedir. H₂S oldukça korozyif ve zehirli bir gazdır ve boru hatlarında korozyona sebep olur. Ayrıca FT ve katran giderim katalizörleri gibi katalitik sistemler 1 ppmv’den yüksek sülfür varlığında kolayca etkinliğini kaybeder. Sıcak gazdan sülfürün uzaklaştırılması için genellikle metal oksitler kullanılır. Sıcak gaz temizleme prosesi için diğer bir problem de katrandır. Katran boru hatlarında yoğunlaşır ve tıkanıklığa sebebiyet verir. Katran giderimi için fiziksel ve katalitik sistemler bulunmaktadır. Katalitik sistemler daha ucuzdur ve bu sistemlerde herhangi bir atık problemi oluşmaz.

FT sentezine gönderilecek olan gaz kompozisyonunda H₂/CO oranı ≥ 1 olmalıdır. Bu yüzden gaz temizleme ünitesinden gelen gaz karışımı FT sentezinden önce işlenmeli ve gaz kompozisyonu ayarlanmalıdır. Bu amaç doğrultusunda temizlenmiş gaz karışımı FT sentezinden önce gaz şartlandırma ünitesine gönderilir. Bu üniteye gaz kompozisyonunun ayarlanması için çeşitli su gazı dönüşüm katalizörleri kullanılır.

Bu çalışmada sülfür ve tar giderimi için Türkiye’nin Eskişehir bölgesinden tedarik edilen dolomit kullanılmıştır. Dolomitin sülfür giderme kapasitesi farklı sıcaklık, farklı H₂S yüklemesi, farklı GHSV ve farklı gaz kompozisyonları için incelenmiştir. Sülfür giderim kapasitesinin sülfür konsantrasyonu ile yakından ilişkili olduğu gözlenmiştir. 200 ppmv’in altındaki düşük sülfür konsantrasyonlarında, sülfürün %20 - %30’u dolomit tarafından tutulmuştur. 1500-2000 ppmv civarındaki yüksek H₂S konsantrasyonlarında, dolomitin sıcak gazdaki sülfürün %90’ını giderebildiği görülmüştür. Dolomit ile sülfür tutma prosesi esnasında besleme gazında CO ve CO₂’nin eşzamanlı olarak bulunması 8-10 ppm değerine kadar COS oluşumuna neden olmuştur. Buna ek olarak, besleme gazında doğal gaz eklendiğinde, reaktör çıkış gazında eser miktarda etil merkaptan tespit edilmiştir. Dolomitin en iyi sülfür tutma performansının 750°C – 800°C ve GHSV=5000 h⁻¹’de olduğu görülmüştür.

Katran giderimi çalışmaları için katran benzen, toluen ve ksilen şeklinde simüle edilmiş ve bu karışım buharlaştırıldıktan sonra gaz temizleme sistemine gönderilmiştir. Dolomit ile gerçekleştirilen çalışmalarda 750°C’de ksilen çoğunlukla

benzene ve kısmen de toluene dönüşmüştür. Dolomite çalışmalarına ek olarak ticari bir değerli metal katalizörünün katran dönüştürme aktivitesi farklı sıcaklık ve katran yükünde incelenmiştir. Seçici suhar dönüşümü ve buhar dönüşümü reaksiyonlarıyla ilişkili olarak buhar dealkilasyon reaksiyonlarının baskın olduğu gözlenmiştir. Seçici buhar dönüşümü ve ksilen dealkilasyonu derecesi 350-750°C sıcaklık aralığında artmıştır. Ayrıca ksilen dönüşümünün beslenen katran yüküne son derece bağlı olduğu gözlenmiştir.

Sülfür ve katran giderim çalışmalarının ardından gaz şartlandırma çalışmaları dört farklı ticari katalizör kullanılarak gerçekleştirilmiştir. Bu çalışmalarda katalizörlerin aktiviteleri farklı gaz kompozisyonları, sıcaklık, GHSV ve Buhar/CO oranlarında test edilmiştir. Çalışmalar 20000 – 75000 h⁻¹ aralığında gerçekleştirilmiş ve 50000 h⁻¹ optimum GHSV değeri olarak belirlenmiştir. Buhar/CO oranı artırıldığında CO dönüşümü artmıştır. Buhar/CO ve sıcaklık artırıldığında su gazı dönüşüm reaksiyonunun Boudouard reaksiyonundan daha baskın olduğu tespit edilmiştir. Ayrıca H₂/CO oranının su gazı dönüşüm reaksiyonundaki dönüşüm için iyi bir ölçüt olduğu görülmüştür. Boudouard reaksiyonu ve koklaşmanın düşük sıcaklıklarda, özellikle 250°C ve 300°C arasında olduğu gözlenmiştir. Buna ek olarak, katalizör 400°C'den yüksek sıcaklıklarda yüzeyde meydana gelen aglomerasyondan dolayı aktivitesini kaybetmiştir.

1. INTRODUCTION

The development level of a country is directly related to its economical and social level. One of the most important factors is energy. Energy, which is the requirement of sustainable development, can only be an impulsive force in industrialization and overall development of societies if it is supplied on time, with sufficient quantity and under reliable economical conditions and considering the environmental impacts. The demand for energy increases rapidly parallel to the population increase, industrialization and technological developments in Turkey and the other developing countries in the world.

Currently, Turkey is not able to meet her energy requirement with its limited sources. The deficit between the energy production and energy consumption has increased rapidly. Therefore, utilizing her resources effectively is vital. Turkey has increasingly become dependent on imported fuels over years. It still imports about 70% of its primary energy need. It is now vital for Turkey to use more domestic coal, lignite and renewable energy sources, which are the largest domestic energy sources available (Yilmaz, 2008).

In Turkey there is lots of lignite mine so these should be used as a primary energy source. In addition to the combustion of lignite, liquid fuel production from lignite is a very significant process for our country. For liquid fuel production firstly lignite should be gasified. Turkish lignites contains significant amount of sulfur. Based on location the amount of sulfur in these lignites may range from 0.5% wt to 7.0% wt. It is generally accepted that nearly 50% of sulfur presented in the coal leaves the gasification system in the gas phase. This means that sulfur levels as high as 5000 - 10000 ppmv could be expected in the outlet stream of the gasifier. Sulfur, as the main contaminant in syngas is one of the main problems for the liquid fuel production from coal process. It causes pipeline corrosion and limit plant lifetime. Catalytic systems such as Fischer Tropsch are easily deactivated in the presence of sulfur higher than 1 ppmv. For removal of sulfur from the synthesis gas there are lots

of studies in the literature. Generally metal oxides are used for the removal of H_2S from hot gas.

If a scrubber system is used the syngas will loss heat and after the removal of contaminants it will be heated again for the gas conditioning. Lowering the temperature causes the tar condensation and energy loss. Also in the scrubbing process the waste chemicals should be treated accordingly to prevent the contamination of drinking water.

The other problem in the gasification process is the organic compounds which are called as tar. These are complex mixture of secondary and tertiary products (mostly aromatics). In addition to optimizing the operating conditions of gasifier there should be a tar removal system for the effective removal of tar. There are two ways of treatment for tar removal: physical systems (scrubbers, filters) and catalytic systems. In our study we prefer catalytic systems because in scrubbing systems there is large amount of liquid consumption and this methos reduces the carbon efficiency. Also the catalytic systems are cheaper than the physical systems. Catalytic systems are more efficient with the improved carbon efficiency. The main problem in the catalytic systems is easy deactivation of the catalyst in the presence of H_2S .

The gas mixture which will be sent to the FT unit should have a H_2/CO ratio ≥ 1 . So the gas clean up unit outlet gas mixture should be operated for arranging this ratio. For this reason gas clean up outlet gas is sent to the gas conditioning unit which has various catalysts.

In the present study, the performance of a Turkish dolomite as an adsorbent will be tested for high temperature sulfur and tar removal from syntethesis gases. In addition, commercial precious metal based catalysts, which are sulfur resistant to some extend, will be tried for tar removal studies. Following the gas clean up studies gas conditioning studies will performed using various commercial catalysts in order to obtained proper H_2/CO ratios for Fisher-Tropsch process.

2. GASIFICATION

2.1 Gasification And Gasification Methods

In gasification process combustible materials are partially oxidized or combusted. The product of gasification is a combustible synthesis gas, or syngas. Because gasification involves the partial, rather than complete, oxidization of the feed, gasification processes operate in an oxygen-lean environment. As Figure 2.1 indicates, the stoichiometric oxygen to coal ratio for combustion is almost four times the stoichiometric oxygen to coal ratio for gasification of coal (Phillips, 2006).

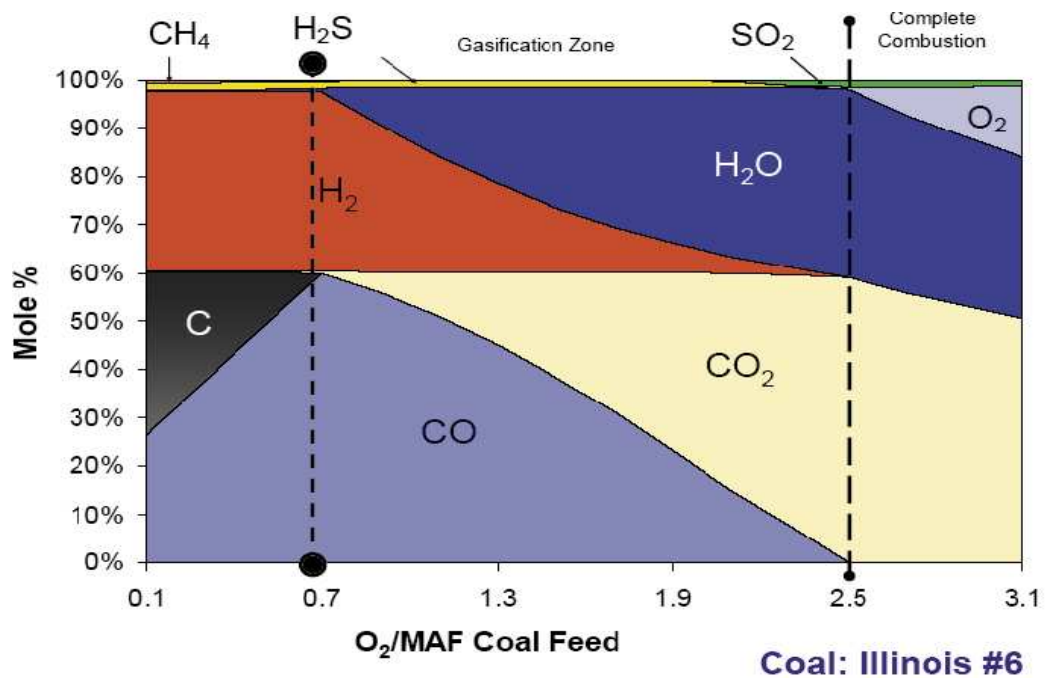


Figure 2.1: Products of reaction as a function of oxygen/coal ratio (Phillips, 2006)

Figure 2.2 shows the principal methods for gasifying a carbonaceous material.

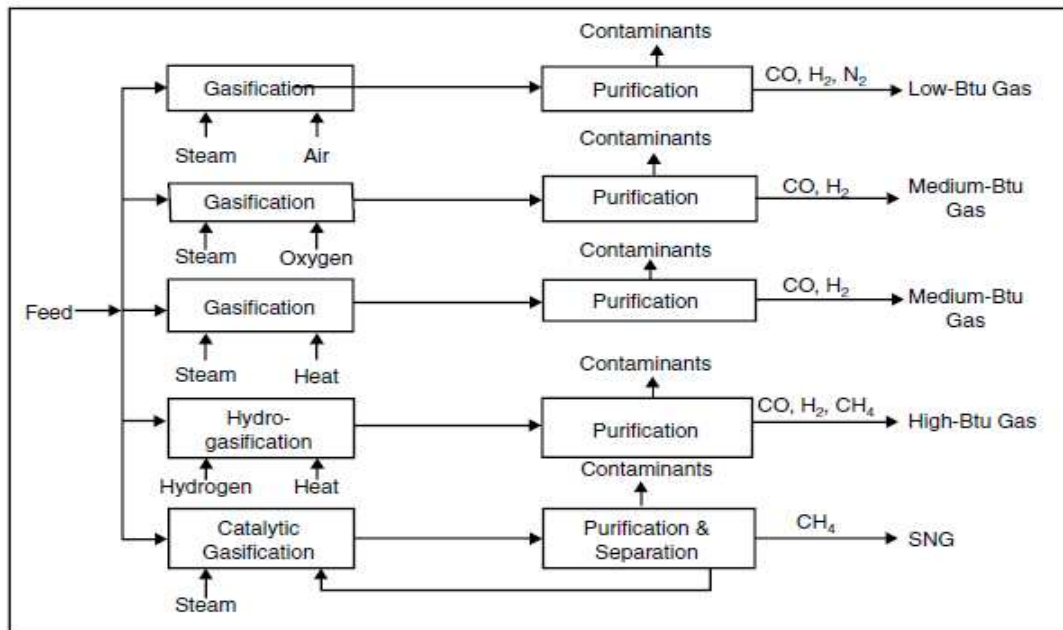
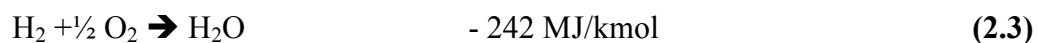
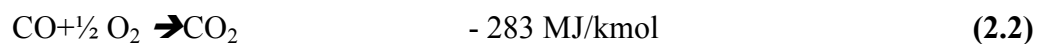
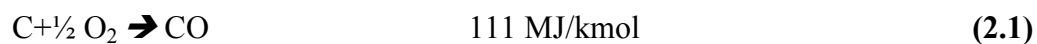


Figure 2.2: Gasification methods (Rezaiyan and Cheremisinoff, 2005)

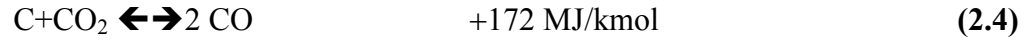
When a carbonaceous material is heated, either directly or indirectly, under gasification conditions, it is first pyrolyzed. During pyrolysis light volatile hydrocarbons, rich in hydrogen, are evolved and tars, phenols, and hydrocarbon gases are released. During pyrolysis the feedstock is thermally decomposed to yield solid carbon and a gas product stream that has higher hydrogen content than the original carbonaceous feed material (Rezaiyan and Cheremisinoff, 2005).

During the process of gasification of solid carbon whether in the form of coal, coke, or char, the principle chemical reactions are those involving carbon, carbon monoxide, carbon dioxide, hydrogen, water (or steam), and methane. These are (Higman and Van Der Burgt, 2003):

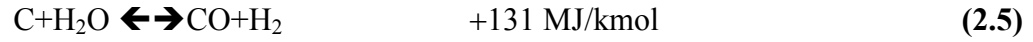
Combustion reactions,



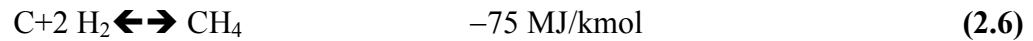
The Boudouard reaction,



The water gas reaction,



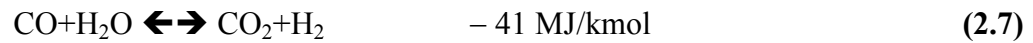
The methanation reaction,



Because reactions with free oxygen are all essentially complete under gasification conditions, reactions 2.1, 2.2, and 2.3 do not need to be considered in determining an equilibrium syngas composition. The three heterogeneous (i.e., gas and solid phase) reactions 2.4, 2.5, and 2.6 are sufficient (Higman and Van Der Burgt, 2003).

In general, we are concerned with situations where also the carbon conversion is essentially complete. Under these circumstances equations 2.4, 2.5 and 2.6 can be reduced to the following two homogeneous gas reactions (Phillips, 2006):

CO shift reaction:



and the steam methane reforming reaction:



For real fuels the overall reaction can be written as



where for gas, as pure methane, $m = 4$ and $n = 1$, hence $m/n = 4$, and

for oil, $m/n = 2$, hence $m = 2$ and $n = 1$, and

for coal, $m/n = 1$, hence $m = 1$ and $n = 1$.

Gasification temperatures are in all cases so high that, thermodynamically as well as in practice, apart from methane, no hydrocarbons can be present in any appreciable quantity (Phillips, 2006).

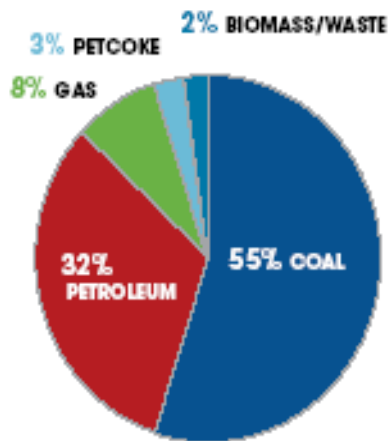


Figure 2.3:Global syngas output by feedstock (Url-1)



Figure 2.4: Gasification process (Url-1)

In Figure 2.3 the percentage of the feedstock used in syngas production are presented. Also the schematic representation of the syngas production process are given in Figure 2.4.

2.2 Gasifier Classification

Coal gasification technologies can be classified according to the flow configuration of the gasifier unit. The primary configurations are(Rezaiyan and Cheremisinoff, 2005):

- Entrained flow
- Fluidized bed
- Moving bed

Typical operating characteristics of coal gasifiers are given in Table 2.1 (Rezaiyan and Cheremisinoff, 2005).

Table 2.1: Typical operating characteristics of coal gasifiers (Rezaiyan and Cheremisinoff, 2005).

	Moving Bed	Fluidized Bed	Entrained Bed
Exit Gas Temp. (°C)	420–650	920–1050	1200
Coal Feed Size	<50 mm	<6 mm	<100 MESH
Ash Conditions	Dry/Slagging	Dry/Agglomerating	Slagging

2.2.1 Moving bed processes

A diagram of a generic moving bed gasifier is shown in Figure 2.5. Moving bed gasifiers are countercurrent flow reactors in which the coal enters at the top of the reactor and air or oxygen enters at the bottom (Phillips, 2006).

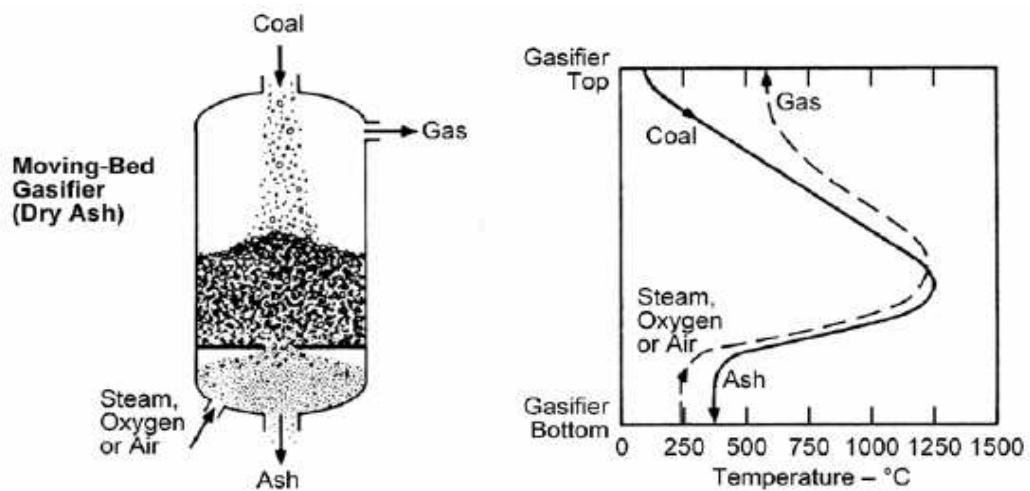


Figure 2.5: Diagram of a generic moving bed gasifier (Phillips, 2006)

The residence time of the coal within a moving bed gasifier may be on the order of hours. Moving bed gasifiers have the following characteristics (Phillips, 2006):

- Low oxidant requirements;
- Relatively high methane content in the produced gas;
- Production of hydrocarbon liquids, such as tars and oils;
- High “cold gas” thermal efficiency when the heating value of the hydrocarbon liquids are included;

- Limited ability to handle fines; and
- Special requirements for handling caking coal.

2.2.2 Fluidized bed processes

A diagram of a generic fluidized bed gasifier is shown in Figure 2.6. A fluidized bed gasifier is a back-mixed or well-stirred reactor in which there is a consistent mixture of new coal particles mixed in with older particles. The flow of gas into the reactor (oxidant, steam, recycled syngas) must be sufficient to float the coal particles within the bed. But if it is so high they entrained out of the reactor so it should be adjusted well. It is also important that the temperatures within the bed are less than the initial ash fusion temperature of the coal to avoid particle agglomeration (Phillips, 2006).

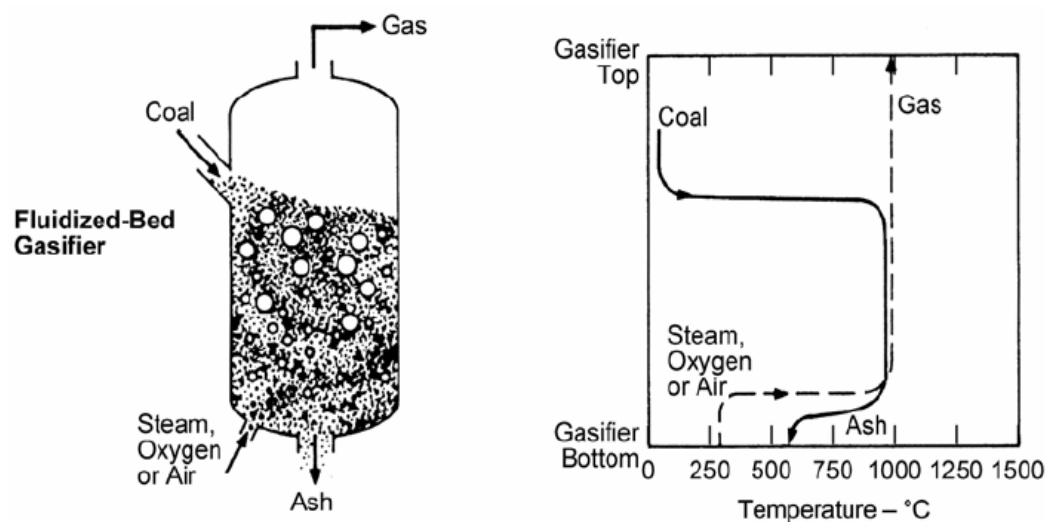


Figure 2.6: Diagram of a generic fluidized bed gasifier (Phillips, 2006)

Typically a cyclone downstream of the gasifier will capture the larger particles that are entrained out and these particles are recycled back to the bed. Overall, the residence time of coal particles in a fluidized bed gasifier is shorter than that of a moving bed gasifier (Phillips, 2006).

Generic characteristics of fluidized bed gasifiers include:

- Extensive solids recycling;
- Uniform and moderate temperature; and
- Moderate oxygen and steam requirements (Phillips, 2006).

Winkler's process, which is the first developed fluid bed technology, operated in a fluidization regime, where a clear distinction exists between the dense phase or bed and the freeboard where the solid particles disengage from the gas. Over the years gasification processes have been developed using three regimes, each process exploiting the particular characteristics of a regime to the application targeted by the process development. These differences are portrayed in Figure 2.7 (Higman and Van Der Burgt, 2003).

In the modern gasification processes oxygen/steam mixtures are used as blast. However when the gas is to be used for power generation, gasification with air may be applied and in the case of biomass gasification, it often is (Higman and Van Der Burgt, 2003).

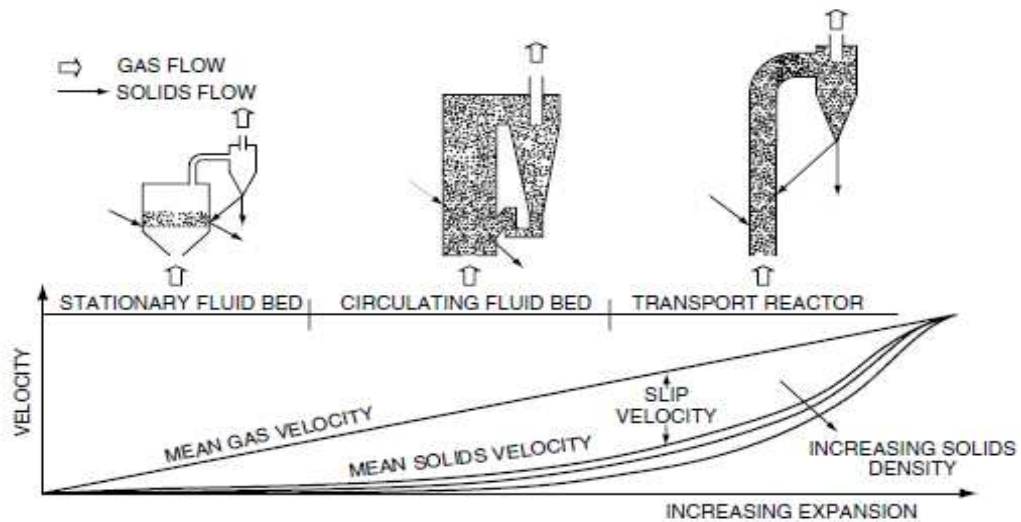


Figure 2.7: Fluid bed regimes (Higman and Van Der Burgt, 2003)

2.2.3 Entrained flow processes

The majority of the most successful coal gasification processes that have been developed after 1950 are entrained flow slagging gasifiers operating at pressures of 20–70 bar and at high temperatures of at least 1400°C. Entrained flow gasifiers have become the preferred gasifier for hard coals and have been selected for the majority of commercial sized IGCC applications (Higman and Van Der Burgt, 2003).

A diagram of a generic entrained flow gasifier is shown in Figure 2.8. Finely ground coal is injected in cocurrent flow with the oxidant. The coal rapidly heats up and

reacts with the oxidant. The residence time of an entrained flow gasifier is on the order of seconds or tens of seconds. Because of the short residence time, entrained flow gasifiers must operate at high temperatures to achieve high carbon conversion. Consequently, most entrained flow gasifiers use oxygen rather than air and operate above the slagging temperature of the coal (Phillips, 2006).

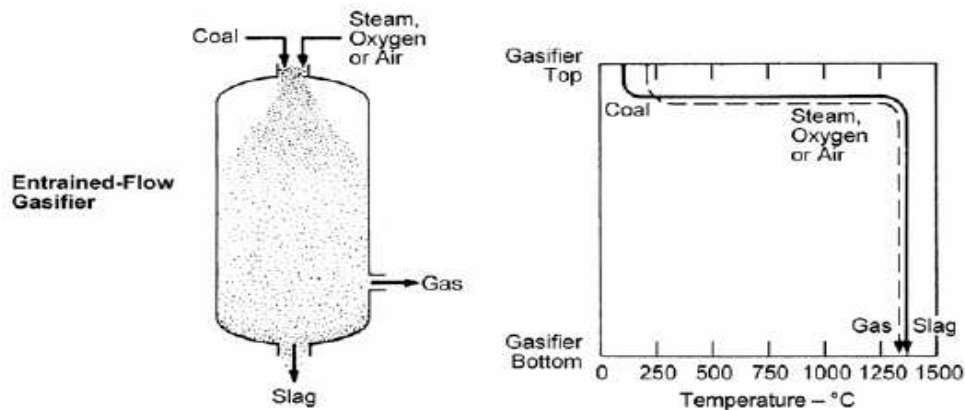


Figure 2.8: Diagram of a generic entrained flow gasifier (Phillips, 2006)

In entrained flow gasifiers the fine coal particles react with the concurrently flowing steam and oxygen. Entrained flow gasifiers produce the highest quality synthesis gas because of the low methane content. Entrained flow gasifiers have relatively high oxygen requirements, and the raw gas has a high sensible heat content. The various designs of entrained flow gasifiers differ in their feed systems (dry coal feed in a high density fluidized state or coal water slurries), vessel containment for the hot conditions (refractory or membrane wall), configurations for introducing the reactants, and the ways in which sensible heat is recovered from the raw gas. Some gasifiers use two stages to improve thermal efficiency and to reduce the sensible heat in the raw gas and to lower the oxygen requirements. In the present coal-water slurry-feed gasifiers, a substantial part of the reactor space is used to evaporate the water of the slurry. This is reflected in the temperature profile of this gasifier (Higman and Van Der Burgt, 2003).

Generic characteristics of entrained flow gasifiers include:

- High-temperature slagging operation;
- Entrainment of some molten slag in the raw syngas;

- Relatively large oxidant requirements;
- Large amount of sensible heat in the raw syngas; and
- Ability to gasify all coal regardless of rank, caking characteristics or amount of fines (Phillips, 2006).

2.3 Synthetic Fuels

For transportation and upgrading reasons there is often a need for converting one fuel into another fuel. On the one hand this may concern the conversion of coal or remote natural gas into a liquid fuel, and on the other hand the conversion of coal into substitute or synthetic natural gas (SNG) (Higman and Van Der Burgt, 2003).

Virtually all modern coal gasification processes were originally developed for the production of synthesis gas for the subsequent production of chemical feedstocks or hydrocarbon liquids via Fischer-Tropsch synthesis. The only place in the world where the process sequence of coal gasification to Fischer-Tropsch is currently practiced is at the Sasol complex in South Africa (Higman and Van Der Burgt, 2003).

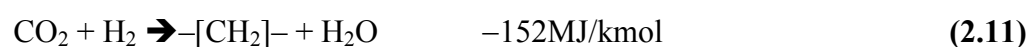
2.3.1 Coal to liquids

FTS is one of the most important processes for the conversion of syngas, a mixture of hydrogen and carbon monoxide, to hydrocarbons and other chemicals. FTS mechanism is generally given as Rxn 2.10.



The product can be very complex. It includes light hydrocarbons, gasoline, diesel, wax, and oxygenates (Jianguo et al., 2009)

The basic Fischer-Tropsch process produces a mixture of straight chain hydrocarbons from hydrogen and carbon monoxide is given in Rxn. 2.11 (Higman and Van Der Burgt, 2003).



where $-\text{[CH}_2\text{]}-$ is the basic building block of the hydrocarbon molecules. The product mixture depends on the catalyst, the process conditions (pressure and temperature), and the synthesis gas composition (Higman and Van Der Burgt, 2003).

Different FT syntheses require different H_2/CO ratios in the syngas and additional hydrogen is often required for product work-up. These differences demand an individual approach to syngas generation for each project, depending on the synthesis process selected, the desired product slate, and the product work up scheme (Higman and Van Der Burgt, 2003).

Table 2.2: Specification for Fischer-Tropsch Synthesis Gas (Higman and Van Der Burgt, 2003).

Gas Component	Max. Allowable Concentration
$\text{H}_2\text{S} + \text{COS} + \text{CS}_2$	<1ppmv
$\text{NH}_3 + \text{HCN}$	<1ppmv
$\text{HCl} + \text{HBr} + \text{HF}$	<10ppbv
Alkaline metals	<10ppbv
Solids (soot, dust, ash)	essentially nil
Tars including BTX	below dewpoint
Phenols and similar	<1 ppmv

A typical specification for Fischer-Tropsch syngas is shown in Table 2.2. From this we can see that the gas must be sulfur-free, since sulfur is a catalyst poison. Whereas with catalytic reforming processes the desulfurization must be performed upstream of gas generation to protect the reforming catalyst, with partial oxidation one also has the option of desulfurizing in the syngas. In fact, syngas desulfurization has a number of advantages over natural gas desulfurization. First, organic sulfur species in the natural gas are converted to H_2S (and traces of COS) in the partial oxidation reactor, thus obviating the need for an upstream hydrogenation stage complete with hydrogen recycle. Second, the syngas from a typical partial oxidation unit has a very high CO partial pressure and high Boudouard equilibrium temperature (about 1050°C), which makes it an extremely aggressive metal dusting agent. Syngas desulfurization leaves the sulfur in the syngas while it is in the dangerous temperature range. The sulfur is therefore able to act as an effective corrosion inhibitor. And third, sulfur-free synthesis gas can be subject to spontaneous methanation at temperatures above about 400°C , given the right conditions. Against these benefits is the fact that the volume of the synthesis gas to be treated is about three times that of the natural gas feed. The

level of desulfurization is therefore less, and equipment will tend to be larger (Higman and Van Der Burgt, 2003).

2.3.2 SNG from coal

Clean transportation fuels can be made from coal via four sequential steps. These steps include coal gasification, syngas cleanup, FT (Fischer-Tropsch) synthesis, and FT product workup. These fuels are known as CTL (coal to liquids) fuels. Schematic representation of CTL process is given in Figure 2.9 (Shen et al., 2007).

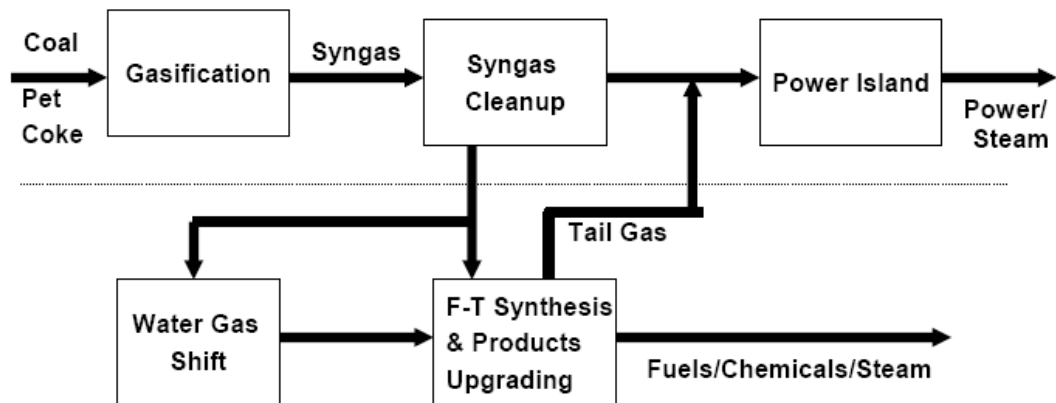
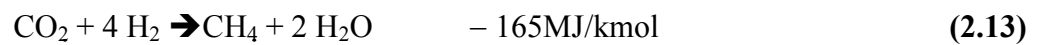
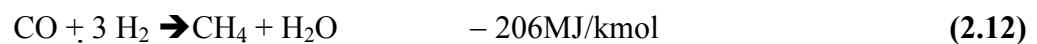


Figure 2.9: CTL (coal-to-liquids) fuels production via coal gasification (Shen et al., 2007).

SNG consists primarily of methane, which is synthesized by the reaction of carbon oxides with hydrogen over a nickel catalyst according to the equations 2.12 and 2.13.



Specifications for SNG require a maximum hydrogen content of 10% and, depending on the heating-value requirement, a limitation on CO_2 . Typically, this results in a requirement on the stoichiometry of the synthesis gas such that the stoichiometric number ($\text{SN} = \text{H}_2 / (3 \text{CO} + 4 \text{CO}_2)$) has a value between 0.98 and 1.03 (Higman and Van Der Burgt, 2003).

In Figure 2.10 the block flow diagram of SNG production from coal is given.

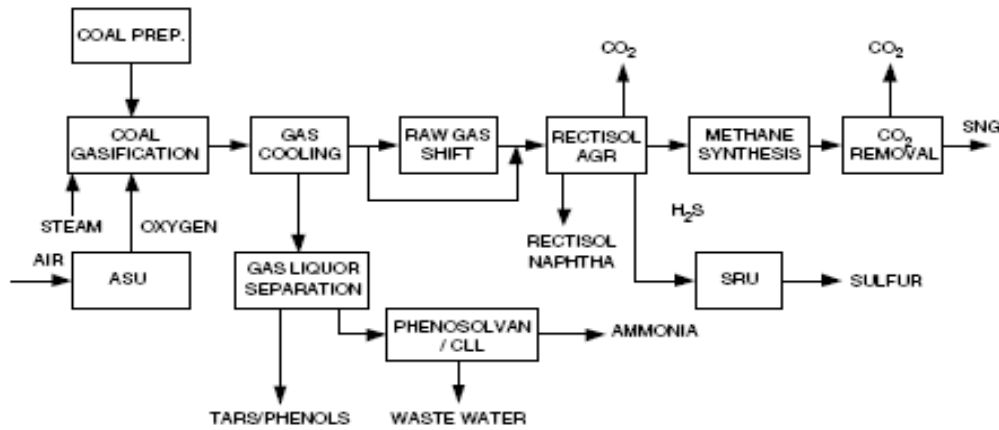


Figure 2.10: Block flow diagram of SNG manufacture from coal (Higman and Van Der Burgt, 2003)

The raw gas contains more CO than that required by the methane synthesis, so a partial stream is shifted on a raw gas shift catalyst. In the downstream acid-gas removal, the residual hydrocarbons, sulfur and nitrogen compounds (NH_3 and HCN), must be removed. To achieve the correct stoichiometry, a partial CO_2 removal is also required. The sulfur specification for the nickel catalyst is maximum 100 ppbv or even lower. In order to achieve the low CO_2 specification of the SNG, CO_2 may be removed in a final Rectisol stage, which also provides the necessary drying function (Higman and Van Der Burgt, 2003).

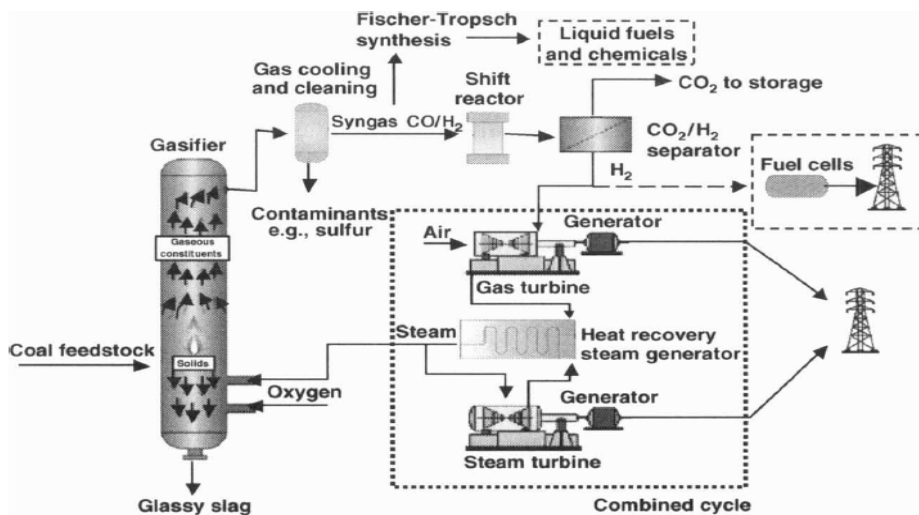


Figure 2.11: Concept of a poly generation plant based on the IGCC process (Clark et al., 2004)

In Figure 2.11 flow chart of a poly generation plant based on IGCC process is given

3. GAS CLEAN UP AND PROCESSING

The products of coal gasification are varied insofar as the gas composition varies with the system employed and the predetermined follow-up to the production of products. It is emphasized that the gas product must be first freed from any pollutants such as particulate matter and sulfur compounds before further use, particularly when the intended use is a water gas shift or methanation (Speight, 2008).

If coal is heated in an inert atmosphere, this intricate molecular structure breaks down and volatile matter, including hydrogen, water, methane, and higher boiling tar is produced (Speight, 2008).

Because the necessary gases are carbon monoxide, hydrogen and methane, the reaction conditions must be carefully controlled by controlling the amount of oxygen in the combustion chamber so that other reactions can occur. Hence, coal gasifiers are designed to favor the reactions that produce energy-rich gases, such as the coal-oxygen reaction to form carbon monoxide reactions and the coal steam reaction to produce synthesis gas (a mixture of carbon monoxide and hydrogen) (Speight, 2008).

Sulfur in the coal will also react with oxygen or hydrogen to release energy and to form either sulfur oxides or hydrogen sulfide. Nitrogen present in the air of the combustion chamber may also form nitrogen oxides (Speight, 2008).

Depending on the type of coal being processed and the analysis of the gas product desired, pressure also plays a role in product definition. In fact, some (or all) of the following processing steps will be required:

1. pretreatment of the coal;
2. primary gasification of the coal;

3. secondary gasification of the carbonaceous residue from the primary gasifier;
4. removal of carbon dioxide, hydrogen sulfide, and other acid gases;
5. shift conversion for adjustment of the CO/H₂ mole ratio to the desired ratio; and (f) catalytic methanation of the CO/H₂ mixture to form methane.

If high heat-content (high-Btu) gas is desired, all of these processing steps are required since coal gasifiers do not yield methane in the concentrations required (Speight, 2008).

In this part we will emphasize the hydrogen sulfide removal, tar removal and shift conversion which have the strong effect on the FT synthesis and the fuel quality.

3.1 Hydrogen Sulfur Removal

Hydrogen sulfur is a colourless compound. It has a very typical smell of rotten eggs and can be smelled at concentrations as low as 0.5 ppb. However, at 100 ppm, it can no longer be smelled. Breathing H₂S at a concentration higher than 500 ppm can be fatal after a few breaths, due to its broad spectrum toxicity (Busca and Pistarino, 2003).

In the gasification of coal or blends with other alternative fuels, sulphur is mainly present in the gas as hydrogen sulphide. This sulphur compound must be removed to avoid damage to the turbines. In the chemical industry, the presence of H₂S leads to larger corrosion problems (pipes, compressors, etc.) and also problems with some catalysts. The scrubbing of sulphur from the gas stream has been widely studied using different agents (Alvarez and Clemente, 2008).

For the removal of H₂S at high temperatures diverse metal compounds are used. Sorbent regeneration without significant degradation during a certain number of cycles is extremely important. The main problem is the sufficient duration of cycles without degradation (Alvarez and Clemente, 2008).

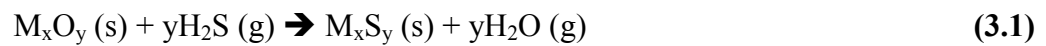
3.1.1 Criteria for selecting sulfur sorption materials

Criteria that the sorbent material must satisfy, for syngas desulfurization to be both economical and operational, are:

1. High adsorption capacity for H₂S. So the sorbent quantity and process equipment size will be reduced.
2. Fast adsorption kinetics.
3. Mechanical properties: low attrition rate and able to tolerate high temperature.
4. Chemical properties: stable in reducing environment containing steam and hydrocarbon.
5. Regenerable through a suitable pathway while maintaining efficient sulfur sorption capacity during repeated sulfidation-regeneration cycles (Cheah et al., 2009)

3.1.2 Basic sulfidation reactions

Much of the research conducted to date uses metal based sorbent materials that are presumed to remove H₂S according to the general reaction:



where M denotes a suitable metal. This metal may be zinc, manganese, copper, iron, rare earth or calcium. Reaction 3.1 describes a solid-gas reaction. This reaction is distinct from, and preceded by, a surface reaction that occurs when the time scale for sulfidation is short (Cheah et al., 2009).

In addition to thermodynamic properties, kinetics of desulfurization (or sulfidation of the solid sorbents) is critical to establishing sorbent performance. Several studies indicated the intrinsic reaction kinetics of the sulfidation of ZnO, MnO, CaO, Fe, and Cu on ceria to have first-order dependence in H₂S (Cheah et al., 2009).

3.1.3 Zinc-based materials

Zinc-based sorbents were one of the first materials to be studied extensively for coal syngas desulfurization. Sulfate formation is a factor that needs to be carefully addressed when zinc-based sorbent is used (Jianguo et al., 2009). The addition of an inert solid in the ZnO sorbent is, in fact, expected to stabilize the metal oxide against its reduction to the metal form and/or volatilization (Rosso et al., 2003).

Among the different tested oxides, zinc oxide has the highest equilibrium constant for sulfidation, yielding H₂S removal down to even fractions of 1 ppm. Its principal limitation is that in the highly reducing atmosphere of synthesis gas it is partially reduced to elemental zinc, volatile above 600 °C, with consequent sorbent loss; for this reason the addition of TiO₂, which has a stabilizing effect, is recommended for high temperature applications. In contrast, if the operating temperature is low, pure zinc oxide has been singled out as the sorbent of choice for desulfurization of coal gas. (Rosso et al., 2003).

The reaction takes place between the gas-phase reactant and the solid phase surface:



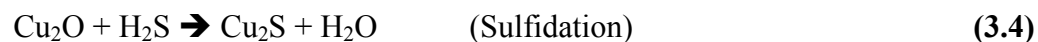
As the reaction proceeds, the solid particle storage capacity is progressively consumed and the unreacted core of the particle shrinks, thus increasing the difficulty of the H₂S molecules to reach the fresh sorbent material (Rosso et al., 2003).

3.1.4 Copper-based materials

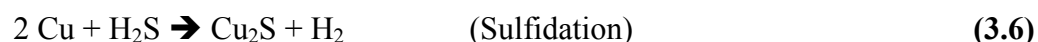
Copper oxide is able to achieve low levels of H₂S in the clean fuel gas provided the sorbent is not reduced to elemental copper. This is because copper oxide readily reduces in high temperature reducing atmospheres, and elemental copper is an order of magnitude less active for sulfidation than Cu₂O and CuO (Cheah et al., 2009).

Copper-based sorbents do not suffer from metal volatility problems, hence, they could be used at elevated temperature without loss of reactivity and capacity associated with metal vaporization. Bulk copper oxide, however, suffers from thermodynamic limitations and has not been considered as a practical sorbent. In

contact with a reducing gas containing H₂S and H₂ (or CO) the following reactions take place (Franklin et al., 1995).



or



Combining these reactions will result in the overall sulfidation reaction:



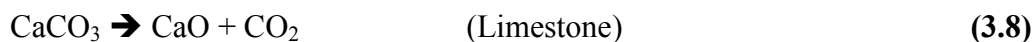
In view of the large H₂/H₂S ratio and the ease of reduction in Reaction 3.3 and 3.5, sulfidation will be governed by the equilibrium of Reaction 3.6 which usually results in an insufficient level of desulfurization. Moreover, agglomeration of the metallic copper produced by reduction would result in a material of low surface area and poor kinetics. However, the sorbent performance can be improved by combining copper oxide with other oxides to improve the sorbent stability in reducing atmosphere (Franklin et al., 1995).

3.1.5 Calcium-based materials

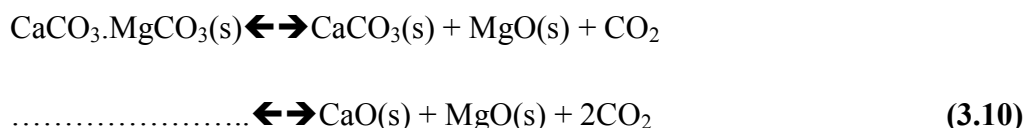
Calcium-based sorbents such as limestone (CaCO₃) or dolomite (CaCO₃·3MgCO₃) are relatively low cost and can be used in both reducing and oxidizing conditions. Equilibrium calculations and experiments by several research groups have shown that calcium is most active for H₂S removal near 880 °C, the temperature at which CaCO₃ decomposes to CaO (lime) and CO₂. This property makes it suitable for systems operating at higher temperatures and thus attractive from a thermal efficiency standpoint. However, other research suggested that H₂S removal by limestone was restricted to conditions far away from the calcination equilibrium and that the simultaneous presence of CO₂ and H₂S would inhibit both calcination and sulfidation reactions. Due to thermodynamic constraints, H₂S removal efficiencies

with calcium based materials are only on the order of 90% under typical gasification conditions and this results with residual H₂S levels of 100 ppm or greater. This limits the sorbent's usefulness to bulk H₂S removal (Cheah et al., 2009).

Limestones and dolomites are the most common sources of calcium oxide. The thermal decomposition of the calcium carbonate and the sulfidation of the produced calcium oxide can be described by the overall reactions (Evangelos et al., 1992):



Dolomite (CaCO₃.MgCO₃) is the other Ca based sorbent which is used for sulfur removal. Depending on the CO₂ partial pressure and the temperature, the sorbents may decompose to the respective oxides (Patrik et al., 1996).



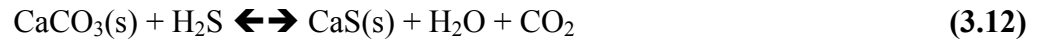
In fluidized-bed gasifiers, used in Integrated Gasification Combined Cycles (IGCC) concepts, the conditions are such that MgCO₃ always calcines to MgO. However, the stability of CaCO₃ is dependent on the CO₂ partial pressure and the temperature (Patrik et al., 1996).

Depending on the conditions, the sulfur absorbents present in the gasifier are referred to as follows:

- CaCO₃, uncalcined limestone;
- CaO, calcined limestone;
- CaCO₃.MgCO₃, uncalcined dolomite;
- CaCO₃ + MgO, halfcalcined dolomite;

- CaO + MgO, fully calcined dolomite.

Thus, the two sulfidation reactions considered are (Patrik et al., 1996):



If dolomite is used as an absorbent, the MgO will not react with sulfur compounds, because MgS is an unstable compound under gasification conditions (Patrik et al., 1996).

Reactions 3.12 and 3.13 are both limited by thermodynamic equilibrium, and not all H₂S can be captured with Ca based sorbents in a gasification reactor. Depending on the conditions, there will remain a H₂S equilibrium concentration of 100-500 ppm. Due to this, in practical implementations a secondary desulfurization step may be needed (Patrik et al., 1996).

Hartman et al. (2002) measured the sulfidation rates of different limestone calcines as weight gain in a differential, fixed-bed flow through reactor at ambient pressure and high temperatures of up to 800 °C. As the sulfidation of limestone calcines proceeds both the porosity of solids and the reaction rate decrease appreciably. A simple relationship was proposed and verified between the porosity of the reacted solid and the conversion of calcium oxide to calcium sulfide. An important feature of the sulfidation lies in the fact that the reacting particles remain significantly porous (~20%) even when the complete conversion of CaO to CaS is attained. Although the rate of reaction decreases in the course of sulfidation, high conversions can be reached under the practical conditions. The rate of the sulfidation conversion is favorably influenced by increasing the temperature and gas-phase H₂S partial pressure. On the other hand, it is adversely affected by increasing the particle size and conversion. There is a marked variation in H₂S reactivity among calcines originating from different naturally occurring rocks. The petrographic grain (crystallite) size and the overall genesis of parent carbonates play important roles in developing the calcine reactivity. The calcines prepared from very fine-grained carbonate rocks achieve a high sorption efficiency.

Abad et al. (2004) analyzed the performance of a pressurized moving bed on the hot coal-gas desulfurization for the countercurrent and cocurrent configurations, and used different calcium-based sorbents. Two more-important design and operating variables which are the bed height and the Ca/S molar ratio were used to determine the H₂S concentration at the gas outlet and the sorbent utilization, and both affected the longitudinal profiles of concentration and solid conversion in the bed. It was found that it was possible to reach a full coal gas desulfurization with calcium-based sorbents, limited only by the thermodynamic equilibrium, in a pressurized moving bed (1 MPa) working at high temperatures (in the range of 1073-1273 K) both in countercurrent and cocurrent configuration. The limestones were only effective for desulfurization under calcining conditions, whereas the dolomites could be used both under calcining and noncalcining conditions. Under these conditions, the effective conversion of the sorbents used was ~85%. The sulfidation at higher conversions was extremely slow, and it was not effective during the operation in a moving-bed reactor. The countercurrent configuration was more effective in the H₂S removal. The optimum sorbent utilization was obtained at Ca/S molar ratio of 1.

Rodriguez and Clemente (2008) chose dolomite for their research due to its properties and low cost in reducing the presence of H₂S in coal gasification. A mixture of gasification gas was simulated and sent to the dolomite bed. Gas velocity, bed length, grain size, gas temperature, and gas composition were investigated. Lower gas velocities, lower inlet H₂S concentrations and higher bed lengths result in lower H₂S content in outlet gases. A temperature between 850 °C and 950 °C has very little influence on the breakthrough curves and only a slight influence on the initiation of the curves. Lower steam and CO₂ concentrations in the inlet gas lead to significant reductions in the amount of H₂S present in the outlet gas in the initial adsorption stage of H₂S. To reach an upper threshold (e.g., 400 ppm) of H₂S at the outlet, dolomite conversion with a bed length of 17 cm is approximately 68% with 2% H₂S, 6% CO₂, 18% H₂ and 10% steam at the inlet and approximately 2.6% CO₂, 14.6% H₂ and 15.4% water at the outlet. COS present shows the same trend as H₂S in its breakthrough curves. Temperature (850 °C or 950 °C) has very little influence on the resulting COS. The amount of COS present in the outlet gases is highly

dependent on the composition of the gas, especially the content of H_2S , H_2 , CO and steam. Sulphidised dolomite acts as a catalyst for the reverse water shift reaction.

Meng et al. (2010) investigated the methods for both in situ and downstream sulphur capture. In situ sulphur capture is mainly done by using calcium-based sorbents such as limestone and dolomite, whereas downstream sulphur capture is mainly focused on the use of regenerable single, mixed, and supported metal oxides. A good solution should be either the use of calcium acetate salts of pelletized sorbents (e.g. SG-sorbent) depending upon the gas quality and optimal cost. Zinc oxide sorbent exhibits the most favorable thermodynamic property of H_2S but due to vaporization, zinc migration and agglomeration problem at high temperature, the utilization of pure ZnO as sulphur sorbent is limited to a temperature of around 600°C . Copper oxide can reduce H_2S from several thousand ppmv to sub-ppmv levels. However, CuO is easily reduced to metallic copper by the H_2 and CO , which lowers the desulphurization efficiency. Manganese oxides combine the advantages of high sulphur capacity and high reactivity in the moderate temperature range. However, manganese oxide sorbents are easily prone to sulphate formation and need to be regenerated at very high temperature. Iron oxide desulphurization potential is somewhat lower. However, iron sulphide formed during the sulphidation or absorption step can be most conveniently regenerated by oxidizing it with air or N_2 -diluted air at considerably lower temperatures than other metal oxides. In addition, the product of sulphidation, FeS_x , is known to react with SO_2 to form Fe_3O_4 and elemental sulphur, which is the most preferred route for SO_2 fixation from the regeneration product gas. In order to overcome these problems, additives, such as Ti , Al , Si , Zr , Co , Ni , and Fe , and promoters (Co , Ni , and Fe) were added to different metal oxide based sorbents to improve their sulphur capture capacity.

Nakazato et al. (2003) used a powder particle fluidized bed as the reactor for their desulfurization study. In this process coarse particles of several hundred micrometers are fluidized via hot gas consisting of H_2S , H_2 , and N_2 while fine limestone particles are fed continuously into the bed. Micrometer-size particles of limestone were used as a feasible sorbent in the high-temperature, dry H_2S removal process using a powder-particle fluidized bed. A gaseous mixture consisting of 2000 ppm H_2S and

5% H_2 , and the balance of which was N_2 , was used as a reference feed gas. Desulfurization experiments using 5- μm limestone at atmospheric pressure revealed that over 90% H_2S removal could be achieved at 1073 K and $\text{Ca/S} = 2$, even under very short residence time of gas in the bed of, for example, $\tau = 0.3$ s. Higher specific surface area of CaO yielded a higher H_2S removal efficiency. At 1123 and 1173 K, less reactive pores of less than 60 Å in diameter were generated after desulfurization, whereas pores of 80-200 Å in diameter were plugged by CaS formation.

Garcia et al. (2004) analysed the effect of pressure on sulfidation of calcined dolomite. They studied on sulfidation process for two calcined limestones and a fully calcined dolomite under pressurized conditions (up to 1.0 MPa), at temperatures of 723-1173 K, and with sorbent particle sizes of 0.25-2.0 mm. It was observed that the sulfidation rate of the sorbents increased with total pressure when the volume fraction of H_2S was constant. However, the sulfidation rate decreased with total pressure when the partial pressure of H_2S was constant. A reaction order on H_2S of 1 was obtained at the different total pressures that were analyzed. In addition, the rate of H_2S retention decreased as the sorbent particle size increased.

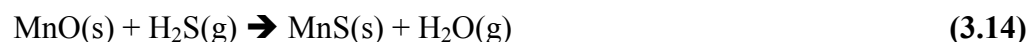
Adanez et al. (2001) performed studies on the regeneration of sulfided dolomite by steam and carbon dioxide and analysed the samples in a thermogravimetric system at temperatures between 475 and 650 °C. Different gas concentrations from 5 to 40% and different $\text{H}_2\text{O}/\text{CO}_2$ ratios were used to isolate the effect of the different gases on the regeneration process. It was observed that dolomite particles of 0.4-0.63 mm can be completely regenerated in 100 minutes at 650 °C with an equimolar gas concentration $\text{H}_2\text{O}/\text{CO}_2$ of 15%. The kinetic parameters of the dolomite regeneration was found to be of first order with respect to the H_2O and CO_2 concentrations.

3.1.6 Manganese-based materials

In a reducing gas environment, manganese oxides of higher oxidation states are likely reduced to MnO. The thermodynamics of MnO sulfidation is not as favorable as some other metal oxides such as zinc oxide and copper oxide. However, MnO does not decompose to elemental manganese readily in reducing gas environment. Thus, manganese-based materials offer the advantage of stability at high

temperatures, which better matches biomass gasification and tar reforming process temperatures. The potential disadvantage is that manganese-based sorbents are prone to sulfate formation and have to be regenerated at very high temperature (Cheah et al., 2009).

The general sulfidation reaction for the Mn based sorbents is (Ben-Slimane and Hepworths, 1995):



3.1.7 Iron-based materials

Iron-based and iron-modified materials are relatively low cost and have considerable sulfidation efficiency even when reduced (Cheah et al., 2009).

Iron oxides have high sulfur sorption capacity and are highly reactive with H_2S . A high temperature (700 °C) detrimentally affects the reaction of H_2S removal due to the reduction of Fe_3O_4 to FeO or Fe in a reduction atmosphere. The FeO has been shown to be an unfavorable sorbent for H_2S . This phenomenon also can be explained through thermodynamic properties. The sulfidation reactions of Fe_3O_4 and FeO are expressed as Rxn. 3.15 and follows:



The sulfidation equilibriums of Fe_3O_4 are vastly superior to that of FeO (Torres et al., 2007).

3.2 Tar Removal

“Tars” are a complex mixture of secondary and tertiary products (mostly aromatics) from thermal decomposition or partial-oxidation of any organic material. The primary products of organic decomposition during biomass gasification or pyrolysis are oxygen rich compounds such as alcohols, aldehydes, ketones, carboxylic acids, phenols and furans. At temperatures above 500°C, the primary products further decompose into secondary products that comprise aromatics of one ring (benzene, toluene, phenols, and benzaldehydes), two rings (naphthalenes, benzofurans) and

three rings (phenanthrenes) with very small concentrations of compounds with more than three rings. Gasification in the range of 700–900°C produces polyaromatic compounds with 4 rings (pyrene, fluoranthene) and traces of five ring compounds (perylene). Figure 5.1 shows the evolution of tar species produced upon gasification of sawdust with steam and oxygen as a function of process temperature (Torres et al., 2007).

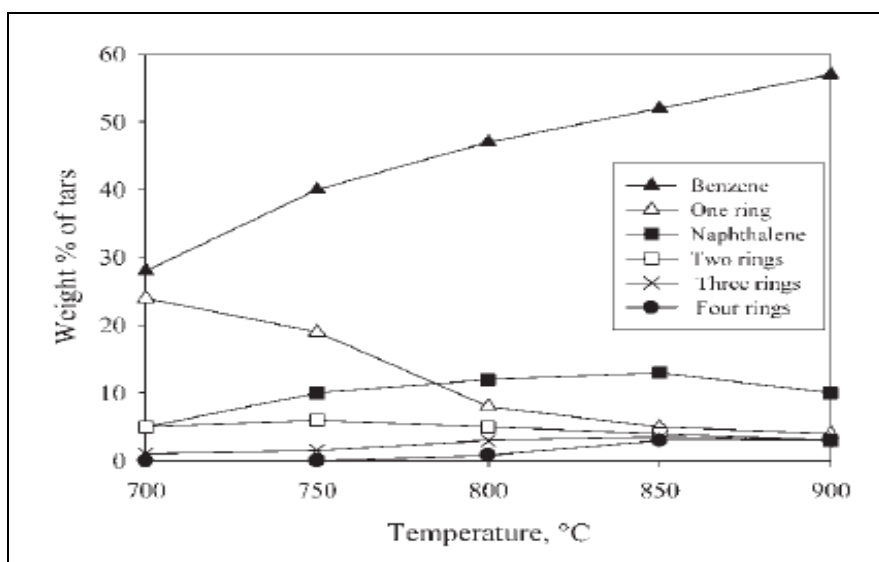


Figure 3.1: Evolution of the tar species upon gasification of sawdust with steam and oxygen (Torres et al., 2007).

The complex composition of biomass tars makes it difficult to understand the reaction mechanisms. Therefore, most studies used model tar compounds such as benzene, toluene, phenol, and naphthalene in the research. The properties of these model compounds are shown in Table 3.1 (Xu et al., 2010).

Table 3.1: Characteristics of the common model tar compounds (Xu et al., 2010).

Compound	Characteristics
Benzene	A stable aromatic structure in tars formed with high temperature processes
Toluene	A stable aromatic structure apparent in tars formed with high temperature processes. With toluene, catalyst deactivation due to charring can be less severe and the hydrocarbon conversion to gases is much higher in comparison with real tar
Phenol	The major tar compound from processes at temperatures lower than 800 °C
Naphthalene	The major single compound in tars. The thermal reactivity follows the order of toluene > naphthalene > benzene

Catalysts for tar removal reactions have been used in the gasifier and in secondary catalytic reactors in which tars react with some of the permanent gases in the flue gas at temperatures close to that of the gasification reactor. Sometimes, additional oxidant (O₂ or H₂O) is injected into the secondary catalytic bed. Tars can be cracked or hydrocracked into light hydrocarbons or converted into CO and H₂ through the so-called steam and dry reforming reactions (Torres et al., 2007).

Reactions that result in the gasification of tars in the presence of components of the gasifier gas are represented by Rxn. 3.16 through 3.20 using toluene as an example of “tars” (Torres et al., 2007).

Steam reforming reactions



Dry reforming reactions



Hydrocracking



Hydrocracking the “tar” all the way to methane (Rxn. 3.20) can be either desirable or undesirable depending on the end use of the biomass gas. If the gas is to be used for energetic purposes, then conversion into methane will increase the “heating” value of the gas. If the gas is to be used for synthesis of methanol or ammonia, then methane is undesirable. A common byproduct in all these catalytic processes is carbonaceous materials deposited on the catalyst as per Rxn. 3.21 and Rxn. 3.22 given below. The water gas shift reaction (Rxn. 3.23) can also occur, increasing the concentration of H₂ at the expense of CO (Torres et al., 2007).

Cracking



Boudouard reaction



Water gas shift



The spectrum of studied catalytic materials covers acidic solids for cracking, basic solids for “reforming” reactions, and metal oxides with both acidic and metal sites for cracking and hydrocracking reactions (Torres et al., 2007).

Generally the mechanism of tar cracking (assuming toluene as the model compound) may be illustrated as follows in Figure 3.2. The tar molecule adsorbs on the surface of the catalyst, and forms radicals or other intermediate compounds (active or inert species). CO_2 , O_2 and H_2O in the fuel gas absorb on the surface of catalyst, and dissociate into CO (desorbing into the gas phase) and free radicals of O, OH and H, followed by desorption of the free radicals. Reactions of free radicals form CH_4 , CO_2 and H_2 as well as a small amount of benzene (Xu et al., 2010).

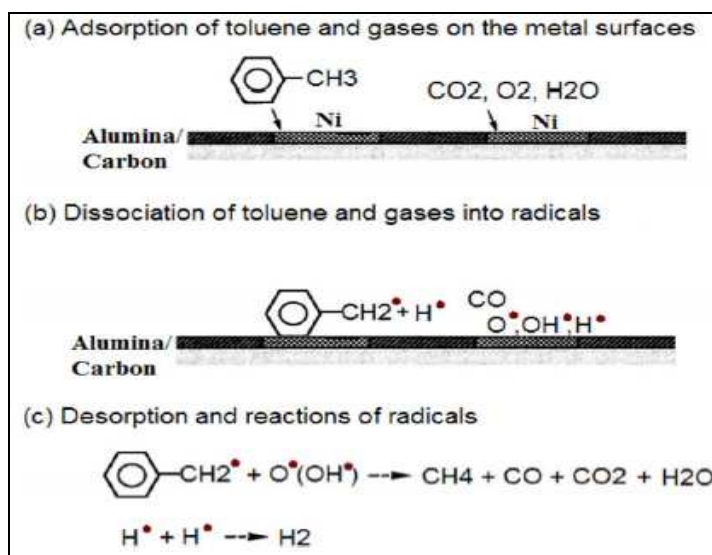


Figure 3.2: Mechanism of tar cracking over a catalyst (e.g., Ni supported) (Xu et al., 2010).

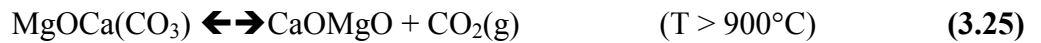
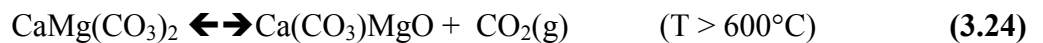
Desirable properties of a good catalyst for any of these reactions are:

1. capability to efficiently convert “tars” into useful gas products in an environment containing high concentrations of H₂, CO, CO₂, and H₂O at temperatures between 600 and 800°C at ambient pressure;
2. resistance to deactivation and poisoning by species in the gas, such as sulfur containing compounds;
3. resistance to attrition. It is also desirable to carry out the tar conversion process in such a way as to keep the accumulation of carbonaceous materials on the catalyst surface under control (Torres et al., 2007).

3.2.1 Catalysis for tar removal

Generally the catalysts which are used for tar removal are acid catalysts (acidic zeolites), basic catalysts, iron catalysts and nickel base catalysts. Acidic catalysts have a high tolerance for sulfur compounds.

The most common basic catalysts are CaO and MgO. Activity of CaO is much higher than MgO but the mixture of this two has the highest activity. The natural mixture of these compounds are obtained by the calcination of dolomite. At higher temperatures dolomite lose CO₂ and produces “half calcined” and “fully calcined” forms according to the reactions below:



The catalytic activities of calcined dolomites are very sensitive to the content of CO₂. In order for these materials to retain high catalytic activity, the CO₂ partial pressure in the reactor cannot be greater than the equilibrium decomposition pressure of dolomite (Cheah et al., 2009). When the gasifier downstream are sent to the dolomite bed H₂ and the H₂/CO ratio are increases but concentration of CO₂ and CH₄ don not change. These results evidence the balance between the reactions of tars and light hydrocarbons with steam and CO₂, and the water gas shift reaction. Phenols and

oxygenate compounds decompose readily on the dolomite bed but the polycyclic aromatic hydrocarbons (PAHs) remain in the flue gas (Torres et al., 2007).

The catalytic activity of iron species is related to their oxidation state. Metallic iron (Fe^0) is thought to be the active catalytic species in the hydrogenation of aromatics and in coal gasification reactions with steam. In Table 3.2 performance of iron catalysts for the decomposition of tar was shown. Olivine is a iron containing compound which belongs to a crystalline series of silicates of magnesium and iron ($\text{Mg}_2(\text{SiO}_4) \text{Fe}_2(\text{SiO}_4)$). Because of its hardness, olivine offers the advantage of attrition resistance (Torres et al., 2007).

Table 3.2: Performance of iron catalysts for the decomposition of tars (Torres et al., 2007).

Catalyst	Dry gas composition, v%					Tar, (g/Nm ³)
	H ₂	CO	CO ₂	CH ₄	C ₂ 's	
Gasifier output						
-	18.5	22.0	11.5	2.4	0.4	42
Output of catalytic reactor at 900°C (residence time 0.2–0.3 s)						
Ankerite	31.5	22.4	11.9	1.0	0	< 0.1
Sintered iron	29.0	21.0	13.0	3.2	0.1	3.6
Iron pellets	26.6	19.2	14.0	3.1	0	5.8

Commercial nickel catalysts, commonly used for steam reforming of methane/naphtha and hydrogenation reactions, have been widely tested as secondary catalysts for the removal of tars from gasifiers. When placed in a secondary reactor, nickel catalysts require a hot filter to retain particulates. Problems arise when the hot filter gets plugged with carbon deposits. An alternative to the filter + nickel catalytic bed combination is the use of nickel-coated monoliths. This way a reasonable external surface area, short diffusion distances and low pressure drop are obtained. The honeycomb structure of these monoliths allows for the catalyst to operate with gases containing particulates. With secondary nickel catalysts, the levels of tars have been reduced to about 1 g tar/Nm³. Reduction of tar levels to the scale of mg/Nm³ has been achieved by using two catalysts, one in the gasifier reactor (typically, calcined dolomites) and a nickel catalyst in a secondary reactor. In an alternative configuration, the dolomite catalyst was placed in a guard bed between the gasifier and the nickel bed. The nickel bed affects the flue gas composition, typically by consuming water, increasing the H₂-to-CO concentration ratio and decreasing the

concentration of methane and C₂ hydrocarbons. Deactivation of the catalyst is signaled by a decrease in the rates of tar and methane removal and coke accumulation. The time for the beginning of catalyst deactivation varies from a few hours to tens of hours (Torres et al., 2007).

3.2.5 Controlling carbon accumulation and sulfur poisoning

In catalytic tar clean-up units, the loss of catalytic activity has been associated with chemical and physical variables, such as the formation of carbon-rich solids, poisoning by sulfur, chlorine, basic nitrogen compounds in the flue gas, volatilization, phase transformation, and sintering. The issues of carbon accumulation and sulfur poisoning have been addressed more frequently (Torres et al., 2007).

3.2.5.1 Carbon accumulation

Carbonaceous solids may form through addition of benzyl or aryl radical intermediates (formed by pyrolysis in the gas phase) to surface bound aromatics, or they may form as a result of surface reactions involving adsorbed monocarbon species (C, CO, CH_x).

When high temperatures are used for the catalytic tar removal process accumulation of carbon decreases. For nickel and calcined dolomites, removal of any carbonaceous deposits is done by gasifying the solid with hydrogen, steam or air at temperatures above 600°C. The problem is that repeated use and recycling of catalysts at such high temperatures leads to permanent catalyst deactivation by sintering and phase transformations. Therefore, strategies to prevent catalyst deactivation by carbon accumulation are always important.

In the context of steam reforming reactions, several approaches to control the selectivity of the reaction to favor steam reforming over carbon accumulation have been proposed. One approach is the use of catalytic promoters and supports that help gasify carbonaceous deposits (e.g. the use of alkali and alkaline earth oxides for nickel catalysts). Another approach is the doping of the catalyst with a species that

prevents carbide formation on the surface. An example of this has been the use of a Ni/MgAl₂O₄ catalyst doped with Cr₂O₃ and La₂O₃.

A third approach for coke minimization in steam reforming reactions, called “ensemble size control,” requires the controlled addition of a strong adsorbate (e.g. sulfur) to slow both the hydrocarbon gasification and coke production rates. However, the impact on coke production rates should be more pronounced because the number of surface sites needed for the formation of coke is higher than that required for the gasification of hydrocarbons. This is not practical (Torres et al., 2007).

3.2.5.2 Sulfur poisoning

The raw gas from biomass gasification may contain up to a few hundred ppm of sulfur. The major sulfur containing species is H₂S with minor fractions of COS and heterocyclic compounds. Among sulfur compounds, H₂S is particularly poisonous to metal catalysts. Exposure of a nickel surface to gas streams containing as low as 1 ppm H₂S results in surface Ni_xS_y phases characterized by heats of adsorption that decrease with surface coverage (Torres et al., 2007).



Sulfur reconstructs the nickel surface preventing or modifying further adsorption of reactant molecules (Torres et al., 2007).

Metallic catalysts that have been poisoned by sulfur can be regenerated by steam, H₂ and CO at temperatures around 900°C, for example, through the sequence of Rxn. 3.27 through Rxn. 3.29 (Torres et al., 2007).



As the levels of sulfur compounds in the biomass gasification gas are relatively low, and as nickel catalysts are considered by a number of experts in biomass gasification

as the best for catalytic tar treatment, one trend is to try to improve the resistance of the nickel catalyst by promoting it with oxides of Li, K, Ca, and Mg. For example, Figure 3.3 shows the results for the gasification of naphthalene on Ni/Al₂O₃ catalysts doped with MgO in the presence of a synthetic fuel gas. In an H₂S-free fuel gas, 100% conversion of naphthalene was obtained at all temperatures. Addition of H₂S to the fuel gas resulted in catalytic deactivation but a residual activity for hydrocarbon gasification remained. In experiments at 750°C, the naphthalene conversion decreased below 30% as the concentration of H₂S increased to 200 ppm (Torres et al., 2007).

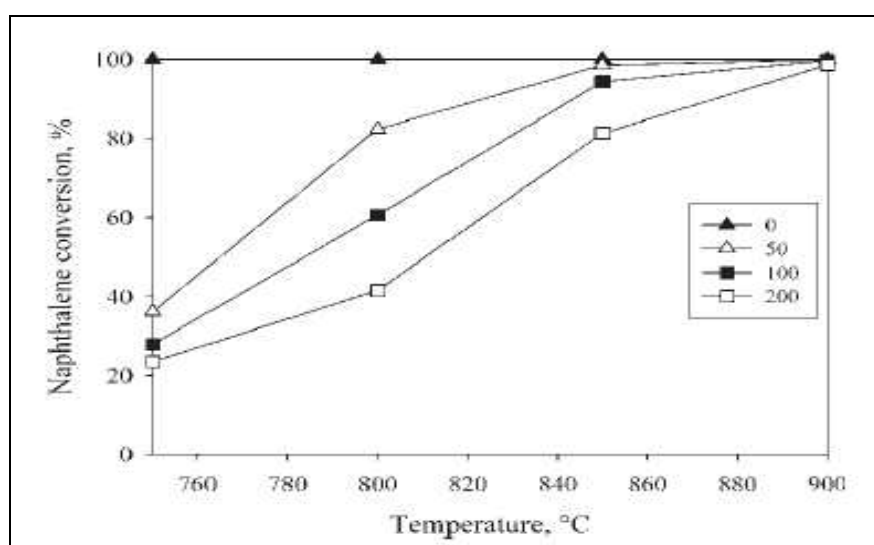


Figure 3.3 : Initial removal of naphthalene from a syngas on Ni/Al₂O₃ catalyst (Torres et al., 2007)

Gusta et al. (2009) carried out catalytic gasification of wood biomass by using a double-bed microreactor in a two-stage process. In the first bed biomass was gasified at 200-850 °C. In the second bed which contains various dolomites catalytic decomposition and gasification of volatile compounds was analysed. Dolomites from Canada, Australia, and Japan were examined for their effects on tar decomposition. A total of 74% of biomass carbon was emitted as volatile matter during tar gasification (200-500°C biomass bed temperature). Dolomites improved tar conversion to gaseous products by an average of 21% over noncatalytic results at a 750 °C temperature using 1.6 cm³ dolomite/g of biomass. The iron content in dolomite was found to promote tar conversion and the water-gas shift reaction, but the effectiveness reached a plateau at 0.9 % w Fe in Canadian dolomites. The

maximum tar conversion of 66% was achieved at 750 °C using Canadian dolomite. Carbon conversion to gaseous products increased to 97% using 3.2 cm³ dolomite/g of biomass at the same temperature. Operating at 800 °C using 1.6 cm³/g of biomass, Canada 1 seemed stable after 3 repeated runs, equivalent to 15 h of cyclic use.

Li et al. (2009) developed mayenite ($\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ or $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$) and applied this as Ni support for biomass tar steam reforming in the absence and presence of H_2S because of its high oxygen restoring property in the structure. Toluene was chosen as tar model compound. The influence of the catalyst preparation, reaction temperature, $\text{H}_2\text{O}/\text{C}$ ratio and space time on catalyst activity and products selectivity were analysed. A long-time evaluation (more than 76 h) exhibited excellent resistance to coking. These results were compared to these obtained by commercial-like catalysts: It was observed that Ni/mayenite exhibited excellent property for biomass tar reforming, with higher H_2 yield than commercial catalyst and higher CO selectivity than that of NiO/mayenite. The Ni/mayenite catalyst is effective and relative cheap.

Sato and Fujimoto (2007) examined the gasification of tar by catalytic steam reforming in the gasification process of biomass. They investigated tar reforming characteristics of the newly-developed Ni/MgO–CaO (based on dolomite) catalyst which was doped with WO_3 as a sulfur-resistant promoter. A simulation gas which was containing naphthalene as tar was used. Developed catalyst was showed a high naphthalene reforming activity. It was stable even in gas containing hydrogen sulfide. The catalyst also exhibited superior resistance to coking as well as sulfur poisoning compared to several commercial steam-reforming catalysts. The new catalyst exhibited higher activity at low temperature. The developed catalyst performed constant tar reforming to better than 90% in the presence of H_2S at 800–850 °C. It also accomplished a 100-h steady tar-reforming operation in the presence of H_2S .

Zamboni et al. (2011) prepared different Fe/CaO sorbents by using CaO , CaCO_3 and $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ and two iron salts, $\text{Fe}(\text{CH}_3\text{COO})_2$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in CO_2 capture and tar removal study. The most appropriated calcination temperature to get CaO phase was obtained as 750 °C. Iron(II) acetate promotes the formation of Fe_2O_3 phase and iron (III) nitrate leads to the formation of $\text{Ca}_2\text{Fe}_2\text{O}_5$. The mechanical

mixture leads to the formation of Fe_2O_3 while sol–gel and impregnation methods promote the formation of $\text{Ca}_2\text{Fe}_2\text{O}_5$. Finally the preparation from mechanical mixture of calcium and iron(II) acetates will be the best compromise between a high CO_2 absorption capacity and the presence of Fe^0 efficient for the tars reforming.

3.3 Synthesis Gas Conditioning

The usefulness of syngas to produce diesel is directly linked to the heating value of the gas. Various gasification agents can give rise to differing heating values of the product gas, as shown in Table 3.4. For efficient use of carbon in FT synthesis, minimization of CH_4 formation during gasification and to convert all carbon in the coal or biomass to CO and CO_2 is important (Url-2).

Table 3.4: Heating value of syngas using various gasification agents (Url-2).

Gasification agent	Heating value of gas	Remark
Air and air/steam	4 - 6 MJ/Mm ³	Low heating value
O ₂ and steam	12 - 18 MJ/Mm ³	Medium heating value
H ₂	40 MJ/Mm ³	High heating value

The syngas contains CO and H₂. The H₂/CO mole ratio in the syngas from air gasification is ≤ 1 , which is not well suited for synthesis of FT diesel. On the other hand, steam gasification of biomass provides an H₂/CO mole ratio of >1 , which is suitable for synthesis of liquid hydrocarbons. One can tune the ratio by using a mixture of gasifying agent and a water-gas shift reaction. Ideally a good mole ratio is 2:1 (Url-2).

3.3.1 Fisher-Tropsch synthesis

There are four main steps to producing FT products: syngas generation, gas purification, FT synthesis and product upgrading. Figure 3.4 depicts a generic process flow diagram. When using natural gas as feedstock it is recommended that autothermal reforming or autothermal reforming in combination with steam reforming as the best option for syngas generation. If the feedstock is coal the syngas is produced via high temperature gasification in the presence of oxygen and steam. Depending on the types and quantity of FT products desired, either low (200 – 240°C) or high temperature (300 – 350°C) synthesis is used with either iron or cobalt

catalyst. FTS temperatures are usually kept below 400°C to minimize CH₄ production. Generally, cobalt catalysts are only used at low temperatures. Because at higher temperatures, a significant amount of methane is produced. Low temperatures yield high molecular mass linear waxes while high temperatures produce gasoline and low molecular weight olefins. If maximizing the gasoline product fraction, it is best to use an iron catalyst at a high temperature in a fixed fluid bed reactor. If maximizing the diesel product fraction, a slurry reactor with a cobalt catalyst is the best choice (Url-3).

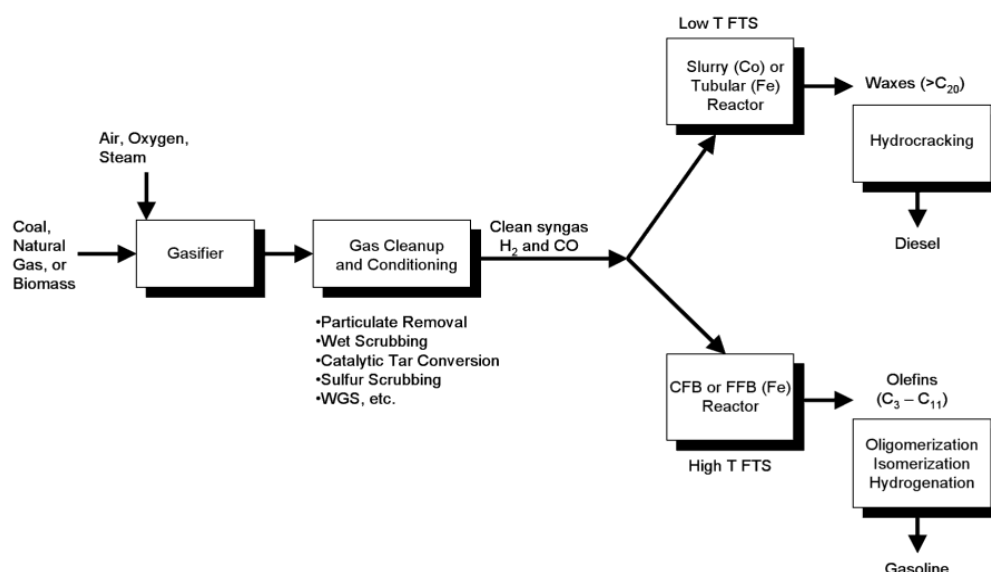
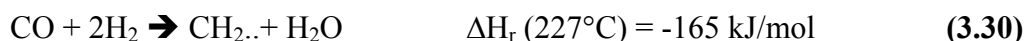


Figure 3.4: FTS General Process Flow Diagram (Url-3)

The following is the FTS reaction:

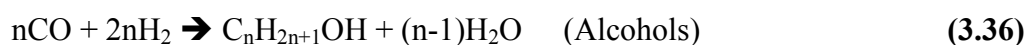


The water-gas shift (WGS) reaction is the second reaction that readily occurs when Fe catalysts are used. Combining the reaction 3.30 with reaction 3.31 gives the net reaction for Fe catalyzed FTS (Rxn. 3.32)



The required H₂ to CO ratio for cobalt catalyst is 2.15 but since the iron catalyst performs WGS in addition to the FT reaction, the H₂ to CO ratio can be slightly lower for the iron catalyst, 1.7 (Url-3).

Specific FTS products are synthesized according to the following reactions.



Another competing reaction that becomes important in FTS is the Boudouard reaction:



Carbon deposition on the catalyst surface causes catalyst deactivation (Url-3).

Group VIII transition metal oxides are generally regarded as good CO hydrogenation catalysts. The earliest catalysts used for FTS were Fe and Co. In decreasing order of activity Ru > Fe > Ni > Co > Rh > Pd > Pt. Ni is basically a methanation catalyst and does not have the broad selectivity of other FT catalysts (Url-3).

The three key properties of FT catalysts are lifetime, activity and product selectivity. Optimizing these properties for desired commercial application has been focus of FT catalyst research and development since the processes were first discovered. Each one of these properties can be affected by a variety of strategies including (Url-3);

- use of promoters (chemical and structural)
- catalyst preparation and formulation
- pretreatment and reduction
- selective poisoning
- shape selectivity with zeolites

Osa et al. (2011) studied on catalyst pretreatment and reaction conditions (reaction temperature, $\text{H}_2\text{O}/\text{CO}$ molar ratio and space velocity) for the Water Gas Shift reaction in a bench scale set-up. A commercial catalyst and an industrial coal-derived syngas feed was used. The activity of commercial catalyst was deeply affected by the reaction conditions. Catalytic activity was influenced by the reaction temperature and space velocity but seemed not to be influenced by $\text{H}_2\text{O}/\text{CO}$ molar ratio. An increase in reaction temperature improved CO conversion. It was also observed that a decrease in space velocity led to the highest CO conversion. Also for a higher CO conversion temperature which is higher than 350°C is necessary. Reduction with H_2 resulted in lower conversion values compared with sulfiding pretreatment at the same activation conditions. The maximum level of H_2S (recommended by commercial specifications) provided the best catalytic results. Selectivity to CO_2 was close to 100% in all the experiments.

Haryantoa et al. (2009) discussed the thermodynamic limits of the synthesis gas upgrading process. The method used in this process is minimization of Gibbs free energy function. The analysis is performed for temperature ranges between 400 and 1300 K, pressure of 1–10 atm and different carbon to steam ratios. The study concludes that to get optimum H_2 yields, with negligible CH_4 and coke formation, upgrading syngas is best practiced at a temperature range of 900–1100 K. At these temperatures, H_2 could be possibly increased by 43–124% of its generally observed values at the gasifier exit. The analysis revealed that increasing steam resulted in a positive effect. Also increasing pressure from 1 to 3 atm can be applied at a temperature >1000 K to further increase H_2 yields.

Hla Shwe et al. (2009) investigated the effects of H_2S concentrations on the performance of an iron/chromium based high temperature water gas shift catalyst by using simulated dry-feed coal-derived syngas. It was found that small concentrations of H_2S (≤ 50 ppm) have a minor effect on the activity of HTC2. But if the H_2S concentration in the feed gas has risen to around 250 ppm, the catalyst has lost approximately half of its original activity. Concentrations of H_2S in excess of 700 ppm do not seem to cause any further significant deterioration in the performance of the catalyst. When H_2S is removed from the syngas the initial activity of HTC2 is

completely restored. The reaction orders with respect to H_2S concentration in the feed gas were calculated to be -0.24 ± 0.09 for a lower range of H_2S concentration (17–70 ppm) and -0.55 ± 0.05 for a higher range of H_2S concentration (120–1100 ppm).

Lima et al. (2009) prepared platinum on ceria-zirconia (CZO) catalysts for the water–gas shift (WGS) reaction with various platinum loadings. In addition, the activity of Pt/CZO catalysts was tested at a gas hourly space velocity (GHSV) of 5000 h^{-1} . Activity tests were also conducted at GHSV of $200,000 \text{ h}^{-1}$ with limited conversions, and activation energies and pre-exponential factors for rate equations were obtained by fitting the data. In this study synthesized Pt/CZO catalysts were showed a high level of WGS activity. The results show that a substantial portion of Pt can be lowered without any significant loss of activity.

Chen and Syu (2010) constructed a novel device of RPB (rotating packed bed) for triggering WGSR and producing hydrogen in a high gravity environment. The effects of the rotor speed, reaction temperature and steam/CO ratio on the CO conversion of the WGSR have been analysed. First, a dimensionless parameter, the G number has been developed to account for the ratio between the centrifugal force and the gravitational force. It was found that the centrifugal force acting on the WGSR can be as high as 234 g on average when the rotor speed is 1800 rpm. The experiments indicated that the CO conversion in the WGSR can be enhanced in a high gravity environment. The enhancement of centrifugal force on hydrogen production in the regime of relatively low G number is more significant than that in the regime of high G number. A higher reaction temperature or a lower steam/CO ratio disadvantages WGSR, the improvement of the RPB on CO conversion tends to become more noticeable. The CO conversion can be improved up to 70% in this study.

4. EXPERIMENTAL

4.1 Materials And Methods

In this study for sulfur and tar removal studies dolomite, which was supplied from Eskişehir region, was used. For gas conditioning studies four different commercial catalyst were tried. One of these catalyst (Catalyst I) was also investigated for tar removal.

4.1.1 Dolomite

Dolomite used in the experimental studies was supplied from Eskişehir region, Turkey. The chemical analysis and ignition loss of dolomite are given in Table 4.1. The original, the calcined and the used dolomite samples were characterized by wet chemical, nitrogen adsorption and thermogravimetric analysis methods. The surface area and pore volume of dolomite were determined by a Quantachrome Instruments Autosorb-IQ-Chemi model gas sorption system and thermogravimetric analysis of the samples were carried out by TA Q600 SDT model TGA. The results of adsorption measurement are given in Table 4.1 and Table 4.2 and that of thermogravimetric analyses are presented in Figure 4.1, Figure 4.2, Figure 4.3 and Figure 4.4.

Table 4.1: Chemical analysis of dolomite .

Moisture (%)	Ignition loss (%)	CaO (%)	MgO (%)	SiO ₂ (%)	Fe ₂ O ₃ (%)	AlO ₃ (%)	MnO ₄ (%)	Na ₂ O (%)
0.010	45.980	36.930	16.880	0.081	0.098	0.125	0.003	0.050

Table 4.2: Physical analysis of the original, calcined and used dolomite.

Sample	BET Surface Area (m ² /g)	Total Pore Volume (cm ³ /g)	Average Pore Diameter (Å)
Original Dolomite	0.0069	1.489 x 10 ⁻³	8.605 x 10 ⁺²
Calcined Dolomite	11.3	2.513 x 10 ⁻¹	8.895 x 10 ⁺²
Used Dolomite	2.548	4.679 x 10 ⁻²	7.346 x 10 ⁺²

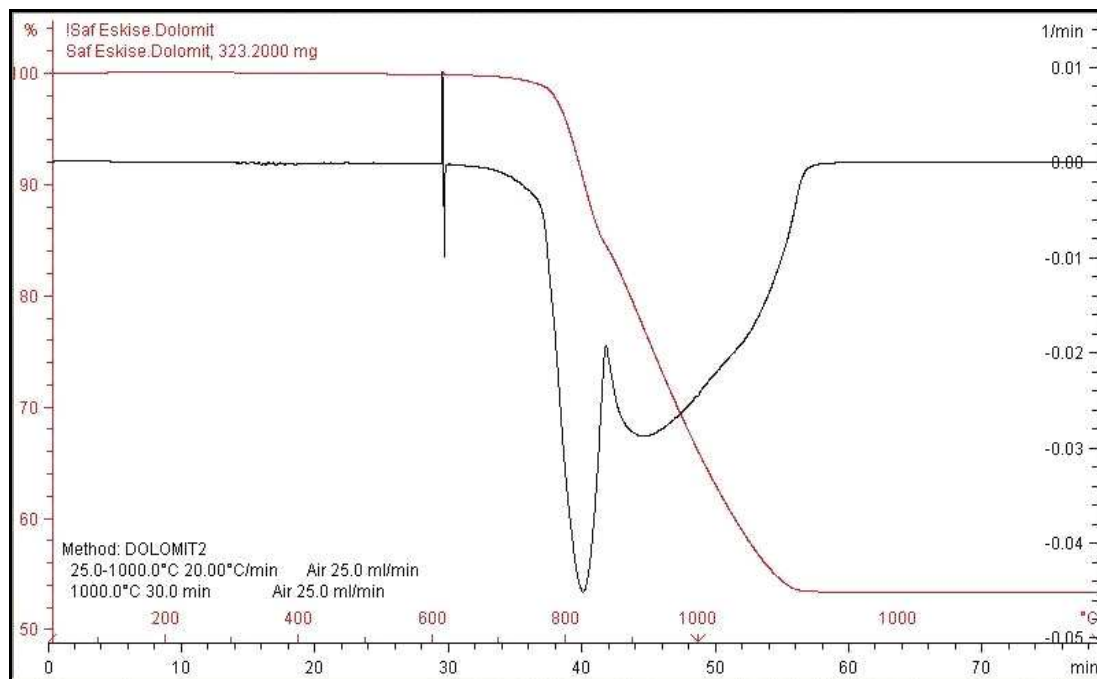


Figure 4.1: Thermogravimetric analysis of original dolomite

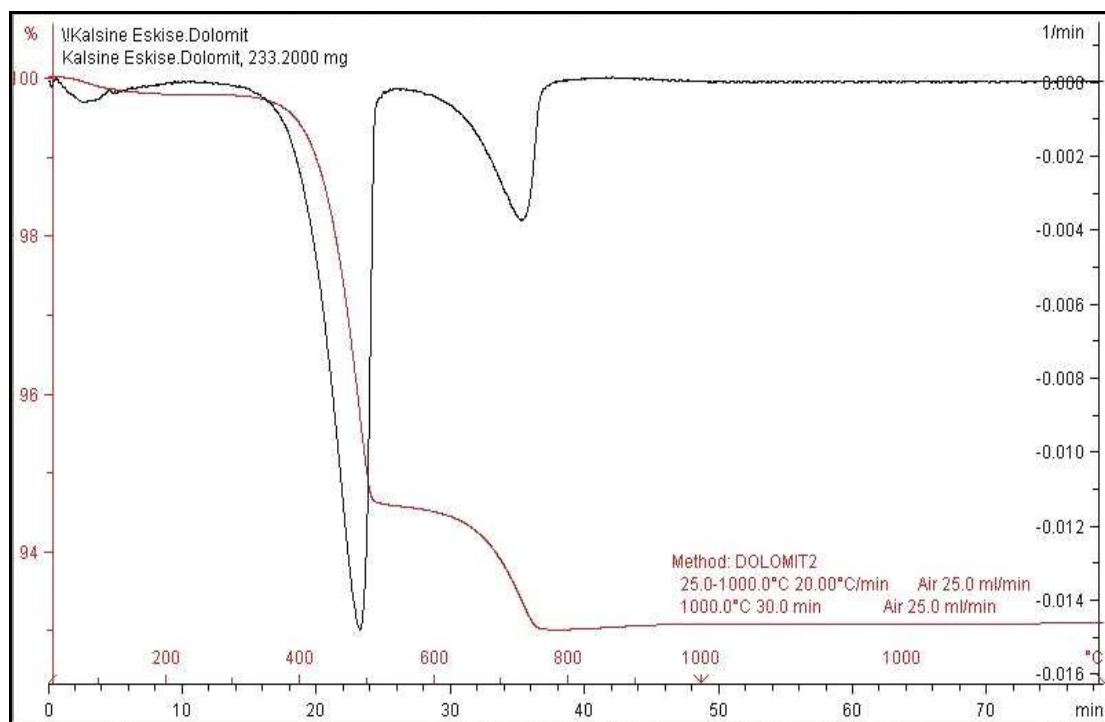


Figure 4.2: Thermogravimetric analysis of calcined dolomite

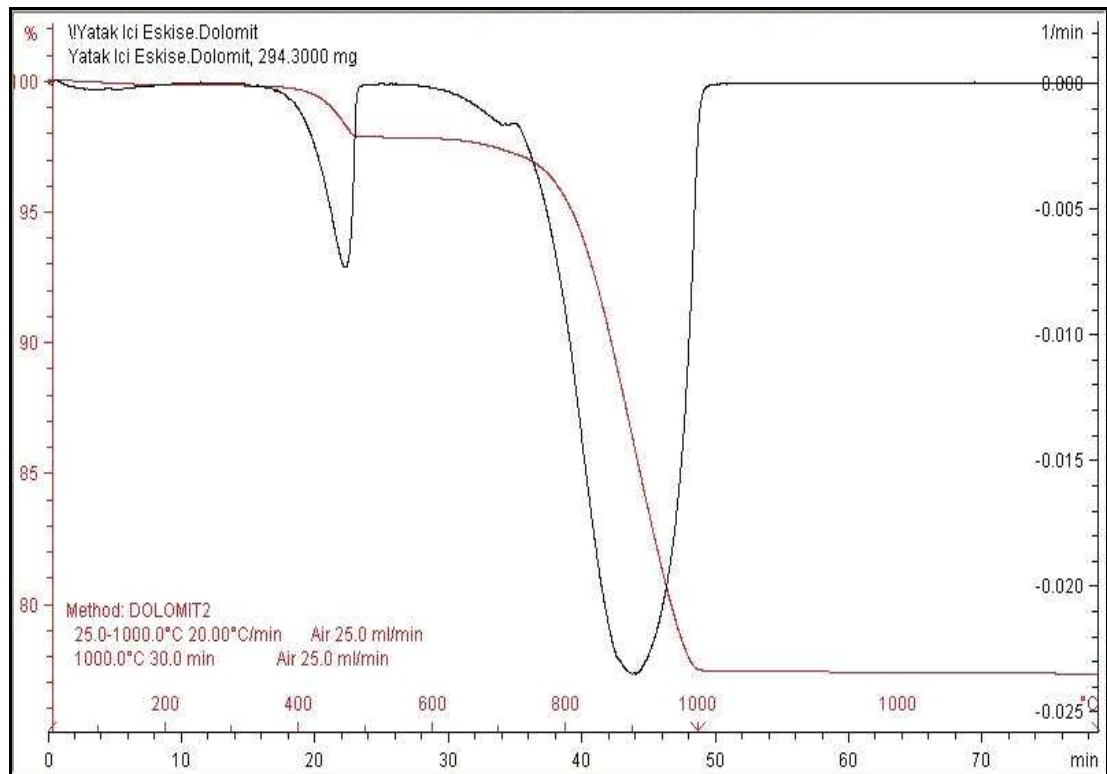


Figure 4.3: Thermogravimetric analysis of used dolomite

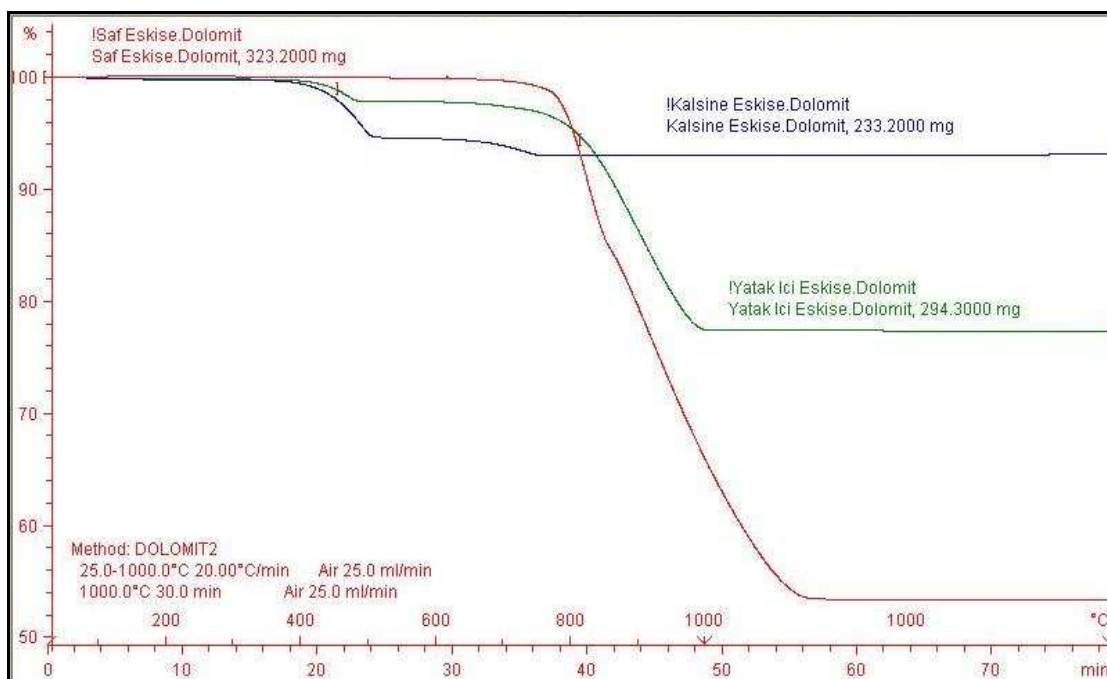
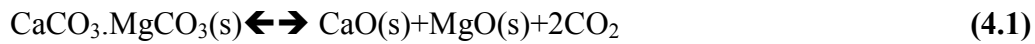


Figure 4.4: Comparison of TGA curves of the original, the calcined and the used dolomite

In Figure 4.1, Figure 4.2 and Figure 4.3 thermogravimetric analyses of original, calcine and used dolomite are given respectively. And in Figure 4.4 the derivative of the thermogravimetric analyses original, calcined and used dolomites are shown in the same graphic and these were compared with each other. As seen from this Figure 4.1 the weight loss of original dolomite is the biggest one and it starts at about 850-1000°C. The main reason of the weight loss is the CO₂ loss of dolomite according to reaction 4.1. This means that at this temperature dolomite start to being calcined and at 1100 °C it is fully calcined. Also as seen in Figure 4.3 there is weight loss for the used dolomite. The reason of this weight loss is the loss of sulfur which was adsorbed in according to reaction 4.2. Another reason of the weight loss is that after the calcination CaCO₃ turns to CaO but when CO₂ was sent to the dolomite bed in the simulation gas mixture this CaO compound reacts with CO₂ and turns to CaCO₃ again. And when it is heated in the TGA it give off CO₂. Also the TGA analysis of calcined dolomited which was calcined for 18 hours at 850 °C temperature was performed. For uncalcined dolomite weight loss for calcination is approximately 45%. In figure 4.2 it can be seen that the weight loss of calcined dolomite is 7% and this means that 18 hours calcination time is enough for 233.2 mg dolomite.



For the laboratory studies, dolomite sample was calcinated at 850°C under air atmosphere until CO₂ exit from the reactor was not observed before experiments.

4.1.2 Gases

In our experiments various gases were used. Some of them were used for the preparation of the simulation gas mixture. The others are necessary for the gas chromatographs as mobile phase, flammable gas or flame formation. The name, property and the purpose of the usage of these gases are given in Table 4.3.

Table 4.3: Gases which were used in the laboratory studies.

Gases	Properties	Intended Use
H ₂ S-N ₂		For preparation of experimental gas mixture
H ₂		For preparation of experimental gas mixture Flammable gas for GC
N ₂	Purity ≥	For preparation of experimental gas mixture Mobile phase for GC
CO ₂	%99.5	For preparation of experimental gas mixture
CH ₄		For preparation of experimental gas mixture
CO		For preparation of experimental gas mixture
He		Mobile phase for GC
Dry Air		For flame formation in GC

4.1.3 Catalysts for tar removal and gas conditioning studies

In the tar removal and gas conditioning studies four types of commercial catalyst were used. Name and properties of these catalysts are given in table 4.4.

Table 4.4: Properties Of Used Commercial Catalysts.

Catalyst Name	Catalyst Type	Diameter (mm)	Length (mm)
Catalyst I	Precious metal based catalyst	25.4	20
Catalyst II	Precious metal based catalyst	25.4	20
Catalyst III	HTS Monolith	20.0	66
Catalyst IV	LTS Monolith	20.0	66

4.1.4 Experimental set up

A fixed bed reactor system was used in the experimental studies. The experimental system is schematically shown in Figure 4.5. Also a photograph of the experimental set up is given Figure 5.6. It consists of the following units:

1. Gas feeding system
2. Steam and tar vapor feeding systems
3. Reactor -oven
4. Cooling system
5. Gas analysers

Gas feeding system consists of six MFCs and relevant control unit. Gases from gas cylinders were controlled, measured via MFC and were mixed in mixer according to the required gas composition.

Steam and tar vapor feeding systems consist of a controlled evaporator and mixer (CEM) and two mass flow control valves. During the experimental studies H₂ gas was sent to the CEM by MFC and then heated. Water and tar is stored in a vessel and by pressurizing these vessels these liquids are fed to the liquid mass flow controller valves in the specified pressures (3-4 bar). The flow rates of the water and tar were arranged with the liquid MFC and then sprayed into the hot H₂ gas. So the flash evaporation was performed. The evaporated water or tar and H₂ was sent to the reaction medium.

Reactor was a fixed bed type and made of stainless steel with of 42.5 mm inner diameter and 800 mm length. It was inserted into a furnace with temperature controlling units. The temperatures were measured at inlet and outlet of the reactor using K-type thermocouples. Temperatures were continuously measured by a digital read out unit attached to the thermocouples.

Cooling system was used for cooling the reactor outlet gas to the ambient temperature. Coil cooling reservoir was kept in water bath which was at a temperature of 5°C. Then the dry gas mixture which is separated from the water and tar was fed to the gas chromatography equipments. For tar analyses the gas flow which consists tar was sent to the tar analyser with a heated by-pass line before entering to the cooling system.

Gas analysers include three HP Agilent 6890 model gas chromatography (GC) equipments. Sulfur gas analyses performed by the GC which consists of Pulsed Flame Photometric Detector (PFPD), Flame Photometric Detector (FPD) and DB-1 (105 m x 530 µm x 5 µm nominal) and GS-GASPRO (60 m x 320 µm x 0 µm) columns. The permanent gas (H₂, CO, CO₂, CH₄, etc.) analysis are performed by the GC which includes Thermal Conductivity Detector and HP PLOTQ (30 m x 530 µm x 40 µm), HP PLOTQ (15 m x 530 µm x 40 µm) and HP MOLSIEVE (30 m x 530 µm x 50 µm) columns. The hydrocarbon analyses (benzene, toluene, xylene)

were performed in the GC which includes Flame Ionization Dedector (FID) and DB-VRX (60 m x 250 μm x 1.4 μm nominal) and GS-GASPRO(60 m x 320 μm x 0 μm) columns.

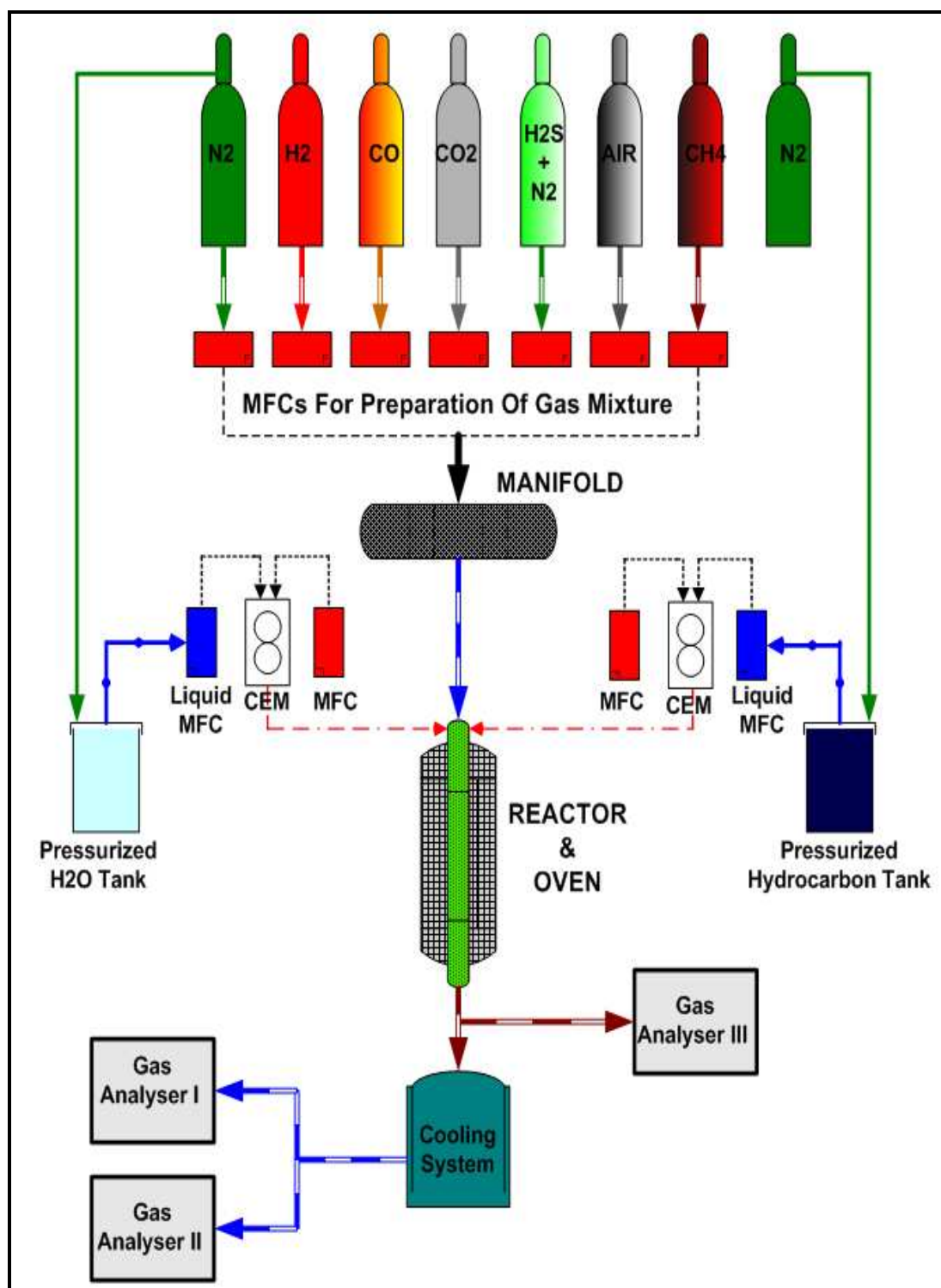


Figure 4.5: The schematic of experimental setup



Figure 4.6: Photograph of the experimental setup

5. RESULTS AND DISCUSSION

5.1 Sulfur Removal Studied With Dolomite

Hot gas cleanup experiments by dolomite were carried out first using a $\text{H}_2\text{S}-\text{N}_2$ mixture and the effect of operating temperature on the sulfur removal performance of the dolomite was investigated. Approximately 180 g of calcined dolomite sample was loaded to the reactor. The diameter and the bed height of the dolomite bed is 42 mm and 84 mm respectively and the L/D ration (bed height/bed diameter) is 2. Dolomite particle size was 0.8 – 2 mm.

5.1.1 H_2S removal in N_2 atmosphere

After the calcination was completed the sulfur removal capacity of dolomite was analysed for different gas compositions. A nitrogen stream initially containing 500 ppmv H_2S ($C_{\text{H}_2\text{S},i} = 500 \text{ ppmv}$) was fed to the reactor. The reactor temperature varied between 200 and 800 °C. Gas hourly space velocity (GHSV) was kept constant at 5600 h^{-1} . Results are presented in Figure 5.1. As seen in the figure, dolomite was very active in reducing H_2S to trace levels in nitrogen atmosphere. Adsorption of H_2S slightly started at 200°C and accelerated considerably at 400 °C. The degree of H_2S adsorption on dolomite reached its maximum level at 500 °C. The H_2S levels of lower than 1 ppm were detected in the reactor outlet gas stream in the temperatures between 500 and 800 °C.

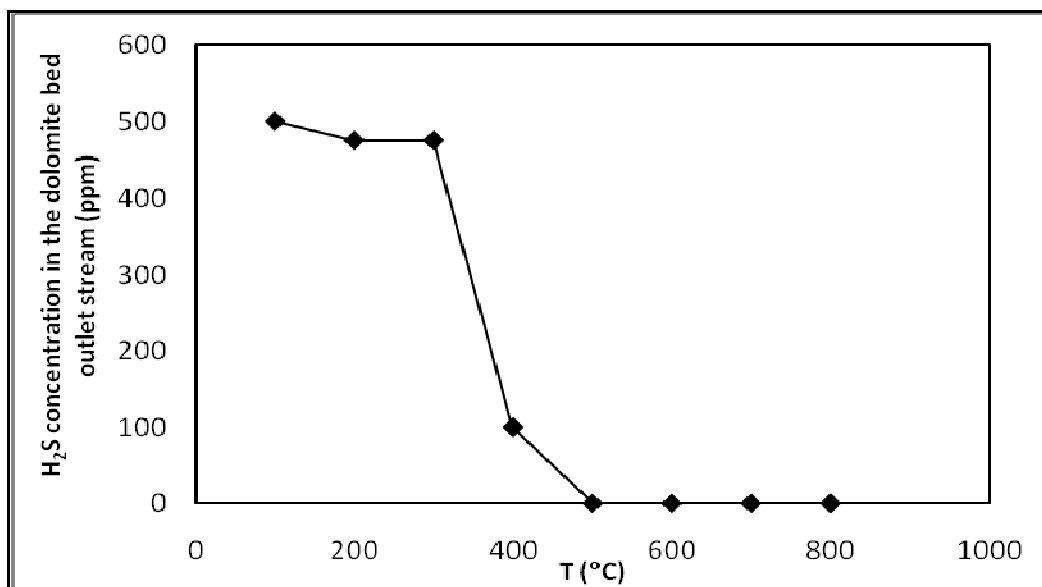


Figure 5.1: Change of H₂S concentration in the reactor outlet gas stream with temperature. Gas mixture: H₂S-N₂, C_{H₂S,i}=500 ppmv, GHSV=5600 h⁻¹

5.1.2 H₂S Studies with binary gas mixtures

In order to investigate the effect of the gas composition on the H₂S removal performance of dolomite, a series of experiments were carried out with binary gas mixture which composed of two gases and contained H₂S at ppm levels. In the experiments H₂-N₂-H₂S, CO-N₂-H₂S and CO₂-N₂-H₂S mixtures were tested. Experiment were performed at 750°C with GHSV=5600 h⁻¹. The used gas composition and obtained results are compiled in Table 5.1.

As seen from Table 5.1, all H₂S has successfully been captured by dolomite in the presence of 27% H₂-73% N₂ gas mixture at 750°C. The H₂ concentration of the inlet and outlet gas did not change. H₂ seemed to behave like an inert gas and gave similar results as that obtained with H₂S removal in pure nitrogen atmosphere.

The sorption experiments carried out with 10% CO₂ and balance nitrogen indicated that dolomite has a very high activity towards H₂S and can reduce its level substantially in this atmosphere. The inlet H₂S concentration was 1800 ppm but only 2-3 ppmv H₂S has been detected in the reactor outlet stream. It seems from the outlet gas composition that no other reaction occurred in the reactor in this case either.

A set of experiments was carried out with 10% CO and balance nitrogen containing 1800 ppm H₂S. As seen from Table 5.1, CO₂ was detected in the reactor outlet stream indicating chemical reaction of some type took place between gas and dolomite in addition to H₂S sorption. CO percentage decreased from 10% to 8.7% and a 1.8% CO₂ was detected in outlet stream. In addition, also a trace amount of COS formed while during the sorption but no H₂S has been detected. The formation of CO₂ showed that Boudouard reaction took place in the CO atmosphere according to the following reaction;



Table 5.1: Removal of H₂S from binary gas mixture by dolomite (dry basis), GHSV=5600 h⁻¹, T=750°C.

Feed stream gas composition, (v %)	Inlet H ₂ S concentration (ppm)	Outlet gas composition, (v %)	Outlet contaminant concentration (ppm)
27 H ₂ , 73 N ₂	1460	27 H ₂ , 73 N ₂	~0
10 CO ₂ , 90 N ₂	1800	10 CO ₂ , 90 N ₂	2-3
10 CO, 90 N ₂	1800	1.8 CO ₂ , 89.5 N ₂ , 8.7 CO	~0 H ₂ S; 1 COS

5.1.3 H₂S Studies with tertiary gas mixtures

A series of experiment were carried out with tertiary gas mixtures to investigate the effect of feed gas composition on the removal of H₂S by dolomite. A gas composed of 10% CO₂, 26% H₂ and 64% N₂ were introduced to the dolomite bed. The inlet H₂S concentration ranged from 1280 ppm to 1700 ppm. All experiments were performed at 700°C and GHSV of 5600 h⁻¹. As seen from Table 5.2, significant changes in the outlet gas composition has been observed. CO and H₂ percentages have been decreased from 10% to 7% and 26% to 15%, respectively, whereas 6% CO formed. The formation of CO indicated that the reverse water gas shift reaction take place on dolomite surface:



Under these conditions, the H₂S removal efficiency of dolomite was lower in comparioson than that obtained with binary gas mixtures, but the level of H₂S in the inlet gas can be still substantially reduced. About 90% of H₂S removal was achieved.

More COS (about 11 ppmv) has been detected in the outlet stream compared to the experiment done with feed gases containing 10% CO. In both cases CO and CO₂ were presented in the outlet stream. This indicated that COS can form in gas atmosphere containing CO and CO₂ simultaneously.

Table 5.2: The results of H₂S removal from tertiary gas mixtures with dolomite (dry basis), GHSV=5600 h⁻¹, T=750 °C.

Feed stream gas composition, (v %)	Inlet H ₂ S concentration (ppm)	Outlet gas composition, (v %)	Outlet contaminant concentration (ppm)
10 CO ₂ , 26 H ₂ , 64 N ₂	1280	7 CO ₂ , 26 H ₂ , 6 CO, 64 N ₂	128 H ₂ S 11 COS
10.2 CO, 11.7 H ₂ O, 78.2 N ₂	1564	5.7 CO ₂ , 3.5 CO, 8.4 H ₂ , 82.4 N ₂	157 H ₂ S 9 COS
10 CO ₂ , 5 NG, 85 N ₂	1700	9.8 CO ₂ , 83.6 N ₂ , 5.4 CH ₄ , 1.2 CO	70 H ₂ S 7 COS 0.05 EtMr
7.9 NG, 20.9 H ₂ O, 71.2 N ₂	1424	2.35 CO ₂ , 84.2 N ₂ , 10.65 CH ₄ , 2.8 H ₂	190 H ₂ S EtMr

To investigate the possibility of water gas shift reaction, 10.2% CO has been fed to the dolomite bed together with 11.7% H₂O in N₂ atmosphere. Gas composition has changed remarkably due to the water gas shift reaction occurred in the dolomite bed. At the outlet stream, CO percentage decreased drastically from 10.2% to 3.5%, whereas 5.7% CO₂ has formed. 90% H₂S removal efficiency has been obtained. Due to the coexistence of CO and CO₂ in the reaction media, a few ppmv of COS has been detected. The water gas shift and the reverse water gas shift reactions may occur depending upon gas composition, possibly due to the presence of iron in the dolomite composition.

The possibility of other reactions such as dry reforming (reaction 5.3) and steam reforming was investigated as well. For dry reforming, 10% CO₂ and 5% natural gas (90% of natural gas is methane) has been introduced to the reaction bed. Under these

conditions, more than 95% of H₂S was captured by dolomite. 7 ppmv COS formed with trace amount of ethyl mercaptane. At the outlet, 1.2% CO has been detected with increased amount of methane. Hydrogen was not observed in the outlet stream. The absence of hydrogen prohibited the occurrence of dry reforming reaction. H₂, if it is not an intermediate product, is consumed immediately in other possible reactions such as hydrogenation of carbon on the dolomite surface.



CO in the outlet stream likely formed due to Boudouard reaction, defined by the following reaction,



Carbon that required for this reaction could come from the partial decomposition of natural gas components in the feed gas in the dolomite bed.

To explore possibility if steam methane reforming to occur, gas mixture composed of 7.9% natural gas and 20.9% steam (steam/C was 2.6) was fed to the dolomite bed. 86% of H₂S was adsorbed onto the dolomite. COS did not form. This shows that the formation of COS requires simultaneous presence of CO and CO₂ in the gas. In the presence of natural gas, trace amount of ethyl mercaptane formed. 2.8% hydrogen and 2.35% CO₂ were detected in the outlet stream. Interestingly, methane content of the gas stream increased from 7.1% (since 90% of natural gas is methane) to 10.65%. Methane might form by the hydrogenation of carbon, which likely formed via Boudouard reaction, on surface of the dolomite. Hydrogen and CO₂ may be released due to the steam reforming of heavier fraction (ethane, propane and butane) of natural gas, via reaction seen below:



5.1.4 H₂S studies with real gasifier outlet gas mixtures

In order to investigate the effect inlet concentration of H₂S on the H₂S removal performance of dolomite experiments were carried out with two highly different H₂S concentration, namely 200 ppmv and 1260 ppmv. For the former case, gasifier outlet was simulated as 16.1% CO, 3.5% CO₂, 64.3% H₂, 6% CH₄ and 10% N₂ on dry basis. The gas composition is given in Table 5.4 on the wet basis. In the experiment performed at temperature 750°C and with GHSV of 5600 h⁻¹, a H₂S removal efficiency of 30% was obtained. Again, the simultaneous presence of CO and CO₂ results in COS formation as previously verified. Gas composition changed due to water gas shift and Boudouard reactions. CH₄ was not detected in outlet stream, possibly due to adsorption of it on the surface of dolomite at the initial phase of the reaction. After this initial period methane was detected in the outlet gas stream. In another experiment, a gas mixture composed of 7% CO₂, 27% H₂, 3% NG in balance nitrogen with 1260 ppmv H₂S was fed to the dolomite bed at 750°C with GHSV of 5600 h⁻¹ and 85% of total H₂S was removed successfully. This phenomena shows that dolomite can be an effective sorbent for bulk H₂S removal from synthesis gases. For polishing purposes to reduce sulfur concentration below 10 ppmv, a ZnO bed or a scrubber may be incorporated into the process. Due to the reverse water gas shift reaction, outlet gas composition of 4.2% CO₂, 20% H₂, 5.8% CO and 1-2% methane in balance N₂ was produced during the sulfur removal process. Results obtained for different gas compositions are given in Table 5.3.

Table 5.3: The results of H₂S removal by dolomite under simulated gasifier outlet gas composition, GHSV=5600 h⁻¹, T=750 °C.

Feed stream gas composition, (v %)	Inlet H ₂ S concentration (ppm)	Outlet gas composition, (v %)	Outlet contaminant concentration (ppm)
16.1 CO, 3.5 CO ₂ , 64.3 H ₂ , 6.0 CH ₄ , 10.0 N ₂ (dry)	200	10.1 CO, 4.5 CO ₂ , 78.0 H ₂ , 0.0 CH ₄ , 7.4 N ₂	140 H ₂ S 11 COS
13.7 CO, 3.0 CO ₂ , 54.6 H ₂ , 5.1 CH ₄ , 8.5 N ₂ , 15.1 H ₂ O (wet)			
7 CO ₂ , 27 H ₂ , 3 NG, 63 N ₂	1260	4.2 CO ₂ , 20 H ₂ , 1-2 CH ₄ , 5.8 CO, 69 N ₂	189 H ₂ S 11 COS

5.2 Tar Removal Studies

Tar, which is composed of wide-range heavy hydrocarbon components, is one of the most common and problematic impurities in synthetic gases from gasifier. It can condense and accumulate on the heat transfer surfaces, impeding heat transfer, blocking gas flow and harmfully affecting downstream catalysts.

5.2.1 Tar removal studies with dolomite

Tar removal performance of Turkish dolomite has also been investigated by using the surrogated compounds of tar, namely benzene, toluene and xylene. A gas mixture composed of 28.5% CO, 25% CO₂, 31.4 H₂, 3.2% CH₄ and 11.9% N₂ with GHSV of 5600 h⁻¹ was fed to the catalyst bed at 750°C. The results are presented in Table 5.4. As seen from the table, xylene mostly and toluene partly were converted into benzene, as apparent from the increased value of benzene in the outlet stream. It could be the result of thermally broken methyl groups in xylene and toluene producing benzene and methane. The increase in methane percentage from 3.2% to 4.0% supported this suggestion. As discussed above, the reverse water gas shift reaction is the major reason for change in the gas composition in favor of CO and H₂O.

Table 5.4: Tar removal by dolomite under simulated gasifier outlet gas composition, GHSV = 5600 h⁻¹, T=750°C.

Feed stream composition, (v %)	Contaminants in the inlet stream (dry)	Outlet gas composition, (v %, dry)	Contaminants in the outlet stream (dry)
28.5 CO, 25.0 CO ₂ , 31.4 H ₂ , 3.2 CH ₄ , 11.9 N ₂ (dry)	240 ppmv H ₂ S 1710 mg/h Benzene 1710 mg/h Toluene 2280 mg/h Xylene	35 CO, 22.0 CO ₂ , 25 H ₂ , 4.0 CH ₄ , 14.0 N ₂	216 ppmv H ₂ S trace COS 3000 mg/h Benzene 1500 mg/h Toluene 250 mg/h Xylene
24.2 CO, 21.3 CO ₂ , 26.7 H ₂ , 2.7 CH ₄ , 10.1 N ₂ , 15 H ₂ O (wet)			

5.2.2 Tar removal studies with Catalyst I

Commercial precious metal based steam reforming Catalyst I has been tried to investigate its tar reforming activity at changing tar loads and temperatures. The diameter and length of the metallic monoliths were 25.4 mm and 20 mm, respectively. Xylene was chosen as the surrogated tar compound. In the first set of experiments, xylene in equal amount of 60 870 mg C/Nm³ was fed to the reactor together with steam in N₂ atmosphere. Total gas flow rate was adjusted to give a GHSV of 90 000 h⁻¹. Steam to C and steam to xylene ratios were 0.26 and 2.1, respectively. To investigate the effect of temperature on possible tar reforming reactions, experiments were performed in the 30-773°C temperature range by stepwise increase heating of the reactor. The gas products, formed during the reforming reactions, were monitored by gas chromatograph. Results obtained at constant steam/C ratio are given in Table 5.5.

Table 5.5: Tar reforming by Catalyst I under nitrogen atmosphere at constant Steam/C ratio, GHSV=90 000 h⁻¹, Steam/C=0.26, Steam/Xylene=2.1.

Feed gas composition	Temperature (°C)	Inlet xylene amount, (mgC/ Nm ³ , dry)	Outlet gas composition, (mol %,dry)	Outlet contaminant amount, (mgC/ Nm ³ , dry)
100% N ₂ , 15.45 g/h Xylene 5.5 g/h H ₂ O	365	60 870	Only N ₂	Benzene 16 494 Toluene 9 818 Xylene 35 558
100% N ₂ , 15.45 g/h Xylene 5.5 g/h H ₂ O	563	60 870	0.3 CO ₂ 0.007 CO 0.055 H ₂ 0.06 CH ₄ 0.007 C ₂ H ₆ Balance N ₂	Benzene 25 823 Toluene 11 990 Xylene 23 056
100% N ₂ , 15.45 g/h Xylene 5.5 g/h H ₂ O	775	60 870	0.3 CO ₂ 0.007 CO 0.055 H ₂ 0.06 CH ₄ Balance N ₂	Benzene 308 Toluene 679 Xylene 724

After the experiment which were conducted at constant steam/C ratio, steam/C ratio was increased and the observed results are given in Table 5.6.

Table 5.6: Tar reforming by CatalystI under nitrogen atmosphere, GHSV=90000 h⁻¹.

Feed gas composition	Temperature (°C) Steam/C	Inlet xylene amount, mgC/ Nm ³ (dry)	Outlet gas composition, (mol %, dry)	Outlet contaminant amount, (mgC/ Nm ³ , dry)
100% N ₂ , 7 g/h Xylene 6.8 g/h H ₂ O	T=775 °C Steam/C=0.71 Steam/Xylene=5.73	27 620	0.25 CO ₂ 0.18 H ₂ 0.03 CH ₄ 0.007 C ₂ H ₆ Balance N ₂	Benzene 227 Toluene 972 Xylene 552
100% N ₂ , 0.5 g/h Xylene 6.8 g/h H ₂ O	T=775 °C Steam/C=10 Steam/Xylene=80	1973	0.01 H ₂ 0.05 CH ₄ 0.002 C ₂ H ₆ Balance N ₂	Benzene 470 Toluene 232 Xylene 707
100% N ₂ , 0.5 g/h Xylene 6.8 g/h H ₂ O	T=665 °C Steam/C=10 Steam/Xylene=80	1973	H ₂ trace CH ₄ Balance N ₂	Benzene 290 Toluene 325 Xylene 345
100% N ₂ , 7.5 g/h Xylene 72 g/h H ₂ O	T=850°C Steam/C=7.1 Steam/Xylene=57	29 588	0.7 CO ₂ 0.33 H ₂ trace CH ₄ Balance N ₂	Benzene 115 Toluene 85 Xylene 600

After the tar reforming studies methane reforming activity of the same catalyst, Catalyst I was tested. For this reason 3 l/min N₂ and 1 l/min Natural Gas (NG) was sent to the catalyst bed at different Steam/C ratios and different temperatures. Obtained results are given in Table 5.7

Table 5.7: Methane reforming on Catalyst I without contaminant, GHSV =90000 h⁻¹.

Feed gas composition	Temperature (°C)	Steam/C	Outlet gas composition, (v %, dry)
75% N ₂ 25% NG 120 g/h H ₂ O	770	2.50	5.25 CO ₂ 1.1 CO 15.2 H ₂ 17.5 CH ₄ Balance N ₂
75% N ₂ 25% NG 55 g/h H ₂ O	770	1.14	4.5 CO ₂ 1.8 CO 15.0 H ₂ 15.5 CH ₄ Balance N ₂
75% N ₂ 25% NG 55 g/h H ₂ O	665	1.14	5.0 CO ₂ 0.98 CO 14.8 H ₂ 18.5 CH ₄ Balance N ₂
75% N ₂ 25% NG 120 g/h H ₂ O	665	2.50	6.3 CO ₂ 0.6 CO 18.3 H ₂ 15.5 CH ₄ Balance N ₂

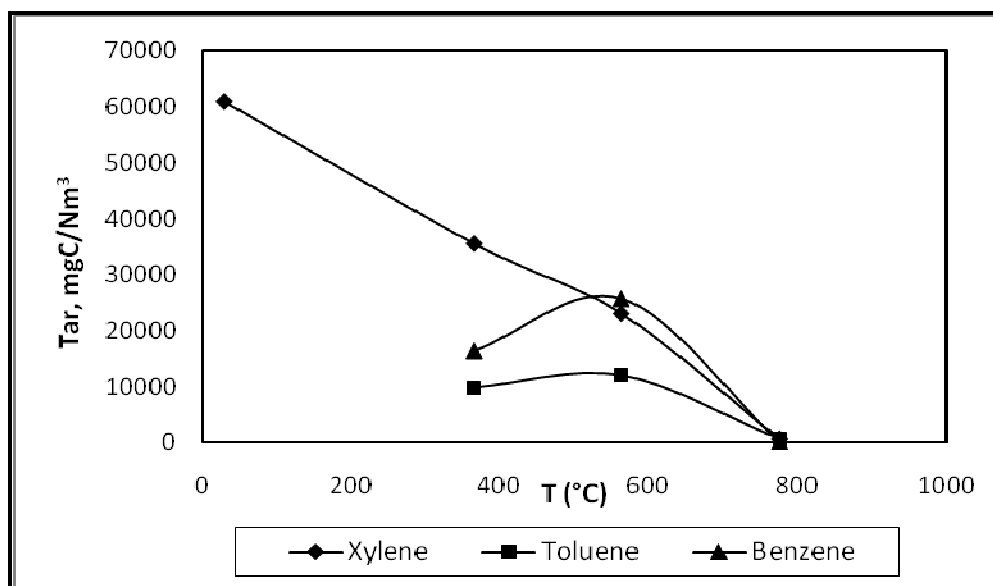
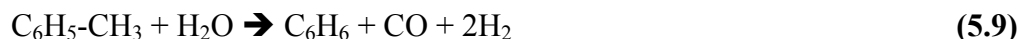


Figure 5.2: Changing in tar reforming extension via Catalyst I with temperature under nitrogen atmosphere

Figure 5.2 indicates that xylene was converted into benzene and toluene at temperature above 365 °C. This shows that selective steam reforming and steam dealkylation reactions were the dominant reactions in steam reforming process for high tar loads at around 60 000 mgC/Nm³ according to the reaction mechanisms below;



The degree of dealkylation of xylene and selective steam reforming increased with temperature in the temperature range considered. During the reforming of tar at 563°C and 775°C the gaseous products presented in Table 5.8, showing the presence of selective steam reforming reactions onto the catalyst.

Table 5.8: Gasoues products formed during tar reforming on Catalyst I.

Gases (v %, dry)	Temperature (°C)	
	563	775
CO ₂	30	25
CO	0,7	1,7
H ₂	5,5	25
CH ₄	6	0,1
C ₂ H ₆	0,7	-
Hexane	Trace	-
N ₂	Balance	Balance

In Figure 5.3 toluene to xylene and benzene to xylene ratios were plotted against temperature. It shows that toluene to xylene ratio increased with temperature whereas benzene to xylene ratio was first increased and then decreased. At 775°C where benzene to xylene ratio decreased, more CO and H₂ were released as seen in Table 5.8 compared to the temperature of 563°C. This may be attributed to the ring opening reaction (degradation) of benzene into CO and H₂ at 775°C.

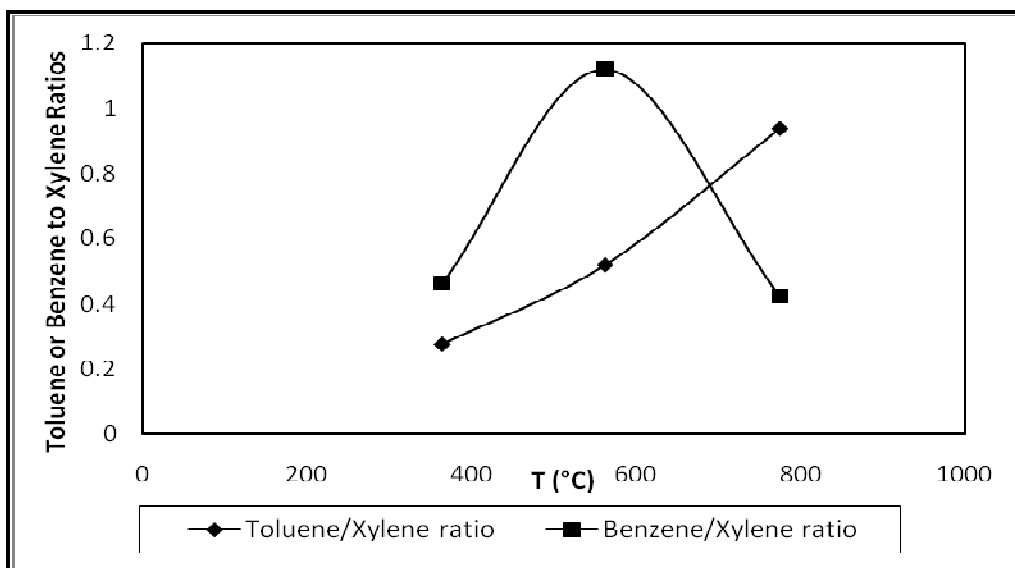


Figure 5.3: Changing toluene/xylene and benzene/xylene ratios with temperatures in the Catalyst I reactor under nitrogen atmosphere

To investigate the effect of inlet tar load on the activity of the catalyst, experiment were performed with varying inlet tar load ranging from 1 973 mg C/Nm³ to 60 870 mg C/Nm³. Steam to C ratios was increased at the same time from 0.26 to 10. As seen from Figure 5.4 that xylene conversion increased with increasing inlet tar load. This shows that xylene conversion is dependent on inlet tar load, or in other words partial pressure of xylene. After a certain amount of inlet tar load, namely 27 620 mg C/Nm³, rate order of selective steam reforming of xylene went to the zero and reaction rate became independent of xylene partial pressure.

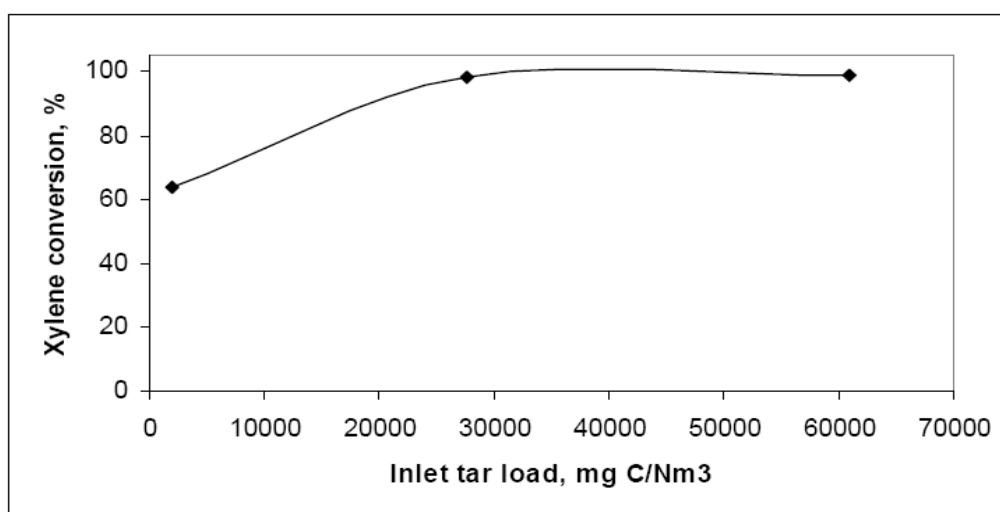


Figure 5.4: Changing of xylene conversion with inlet tar load on a Catalyst I under nitrogen atmosphere

After the experiments ended, the catalyst in the reactor removed and inspected for the carbon deposition. Carbon deposition was observed on the surface of the catalysts by naked eyes. The photographs of fresh and used catalysts and glass wool, which was used as the support bottom, are shown in Figure 5.5. Figure clearly indicates the both catalyst and bottom wool were covered by the carbon formed during the tar conversion process.

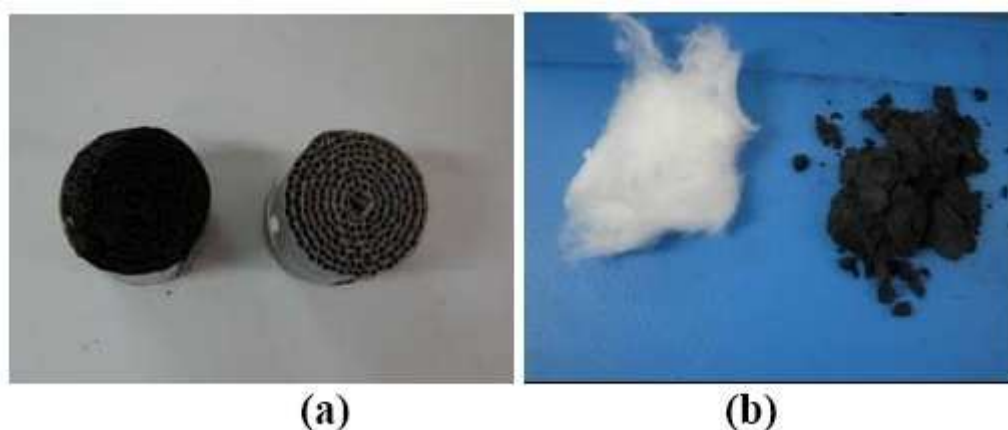


Figure 5.5: The pictures of catalyst I and bottom wool before and after tar removing process a) Catalyst, b) Bottom wool.

5.3 Gas Conditioning Studies

After the gas clean up studies which include sulfur and tar removal gas conditioning studies were performed. In accordance with this purpose four different commercial catalyst and three different gas composition was tested.

5.3.1 Steam reforming of methane

In the steam reforming of methane experiments Catalyst I which was used in the tar removal studies was tried for the methane reforming activity. For steam methane reforming, 25% natural gas in nitrogen was fed to the reactor of fresh catalyst with steam/CH₄ ratios of 1.1 and 2.5 and the performance of the catalyst was tested. The catalyst showed a lower catalytic activity for this reaction (~ 30-40% conversion) at GHSV of 38 000 h⁻¹ (25°C and 1 atm) and at lower methane partial pressure as seen Table 5.9. Lower conversions were considered to be due to the lower methane partial pressure in the reaction atmosphere. When methane concentration is decreased from

25% to 5%, same amount of conversion has been achieved, showing the independence of methane partial pressure at least to some extent.

Table 5.9: Methane reforming over Catalyst I under nitrogen atmosphere, GHSV=38000 h⁻¹.

Feed gas composition, (v %, dry)	Temperature, (°C)	Steam/C	Inlet amount of H ₂ O (g/h)	Outlet gas composition, (% v, dry)
75 N ₂ 25 Natural Gas (NG)	770	2,5	120	5.25 CO ₂ 1.1 CO 15.2 H ₂ 17.5 CH ₄ Balance N ₂
95 N ₂ 5 Natural Gas (NG)	850	3,11	30	0.85 CO 6.0 H ₂ 3.5 CH ₄ Balance N ₂

After the first experiment with Catalyst I, it was seen that the activity of the catalyst was not satisfactorily high. So, a second precious metal based catalyst (Catalyst II) was tested. 25% methane was fed with 75% nitrogen under steam/CH₄ ratios of 2.5. The test results are given in Figure 5.6 and Figure 5.7.

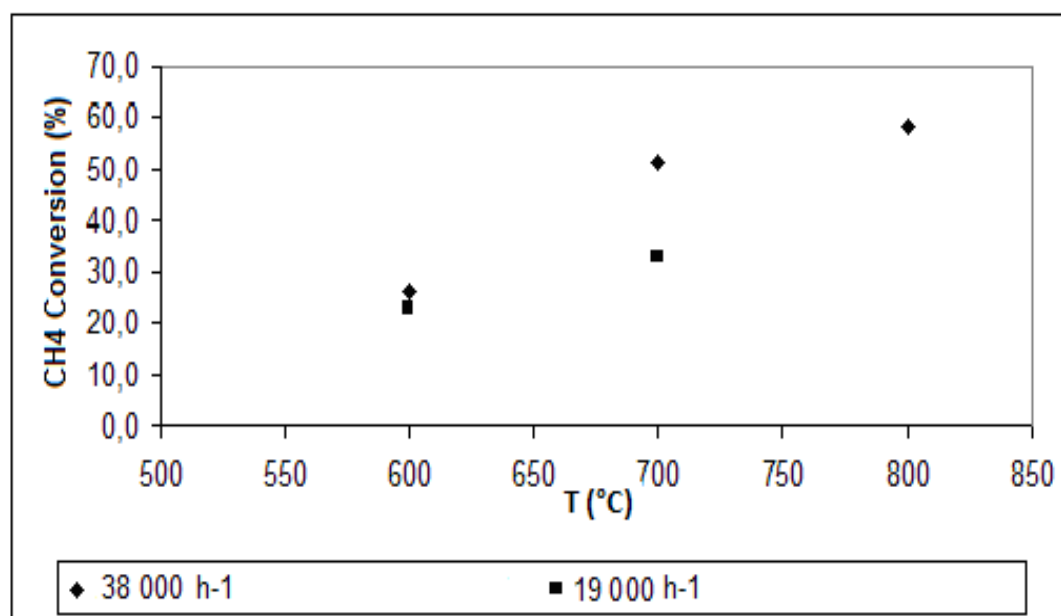


Figure 5.6: Methane conversion with temperature using Catalyst II (at 25°C and 1 atm ♦GHSV= 38 000 h⁻¹ ■GHSV= 19 000 h⁻¹)

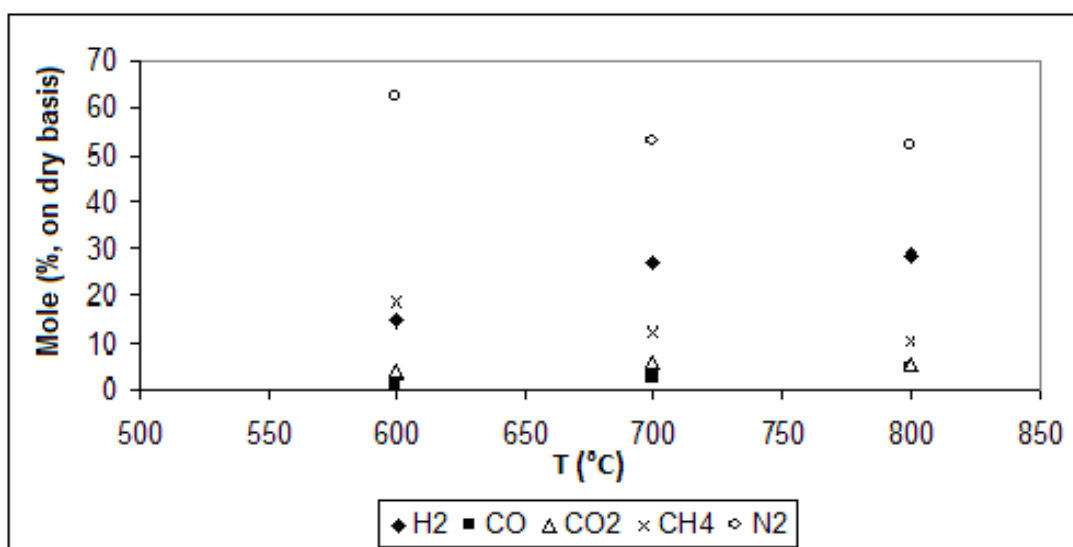


Figure 5.7: Changes in the product composition with temperature during methane reforming over Catalyst II, GHSV = 38000 h⁻¹

As seen from Figure 5.6, methane conversion has increased with GHSV. At 600°C and with GHSV = 38 000 h⁻¹, a methane conversion of 26% has been reached while conversion at 700°C and 800°C were 51% and 58% respectively. For GHSV=19 000 h⁻¹, methane conversions decreased to 23% and 33% at 600°C and 700°C respectively. At GHSV=38 000 h⁻¹, hydrogen formation has been favored. While 14.6% hydrogen has been released on dry basis at the product side at 600°C, 700°C and 800°C, hydrogen percentages on dry molar basis have been increased to 27.1% and 28.8%, respectively. CO formation has also been promoted with temperature and a highest CO value of 4.2% has been reached. These results showed that the rate of steam reforming reaction could be accelerated with increase in temperature and GHSV. When comparing the commercial catalyst I and II under the same conditions, Catalyst I mostly gave 30-40% methane conversions but commercial Catalyst II gave 60% methane conversion values.

5.3.2 High temperature shift (HTS) studies

After the gas clean up unit gas composition should be arranged for the Fischer Tropsch (FT) synthesis. H₂/CO ratio should be about 1.5-1.8 for FT unit. For this reason in gas conditioning unit a second set of catalyst which has water gas shift (WGS) reaction activity should be used. (Rxn. 5.13)



High temperature shift reaction was conducted for two different gas compositions. In these experiments a commercial HTS catalyst (Catalyst III) was used.

5.3.2.1 Simulated gas composition I

To investigate the effect of H₂ and CO₂ on water gas shift (WGS) gas mixture composed of 29 % CO, 18 % CO₂, 33 % H₂, 3 % N₂ and 17 % H₂O was prepared and used.

The effect of reaction temperature, Steam/CO ratio and gas hour space velocity (GHSV) on the CO conversion, selectivity and H₂/CO ratio was investigated. The conversion and selectivity were calculated using the following equations:

$$\text{CO conversion (\%)} = \frac{[\text{CO}\%]_{\text{in}} - [\text{CO}\%]_{\text{out}}}{[\text{CO}\%]_{\text{in}}} \times 100 \quad (5.12)$$

$$\text{Selectivity} = \frac{([\text{CO}_2\%]_{\text{in}} - [\text{CO}_2\%]_{\text{out}}) + ([\text{H}_2\%]_{\text{in}} - [\text{H}_2\%]_{\text{out}})}{([\text{CO}_2\%]_{\text{in}} - [\text{CO}_2\%]_{\text{out}})} \quad (5.13)$$

In Figure 5.8, Figure 5.9 and 5.10 CO conversion, selectivity and H₂/CO ratio respectively, are plotted as a function of temperature for Steam/CO=0.6 and GHSV=25000 h⁻¹. As seen from the Figure 5.8 at 250°C CO conversion was at very low, but a drastic increase was observed in conversion when temperature increased from 250 °C to 300 °C. At temperature higher than 300°C, conversion did not change considerably and attained a steady value around 35-40%.



At low temperatures (250 – 300°C) and especially at low Steam/CO ratios Boudouard reaction (5.14) dominates the process and therefore carbonization occurs to some extent on the catalyst surface. It is clear from Figure 5.9 and Figure 5.10 that under the same conditions at temperature higher than 300°C, both of selectivity and H₂/CO ratio was increased. This is because water shift reaction is much more effective than the Boudouard reaction at high temperature.

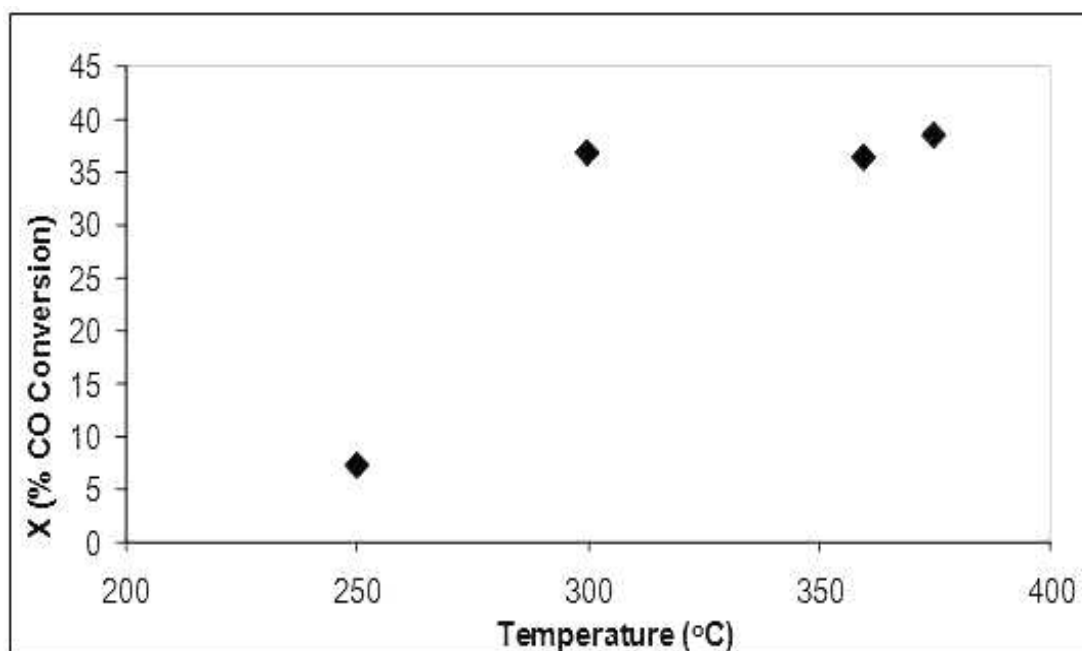


Figure 5.8: The change in CO conversion with temperature, Steam/CO = 0.6, GHSV = 25000 h⁻¹, Catalyst: Catalyst III

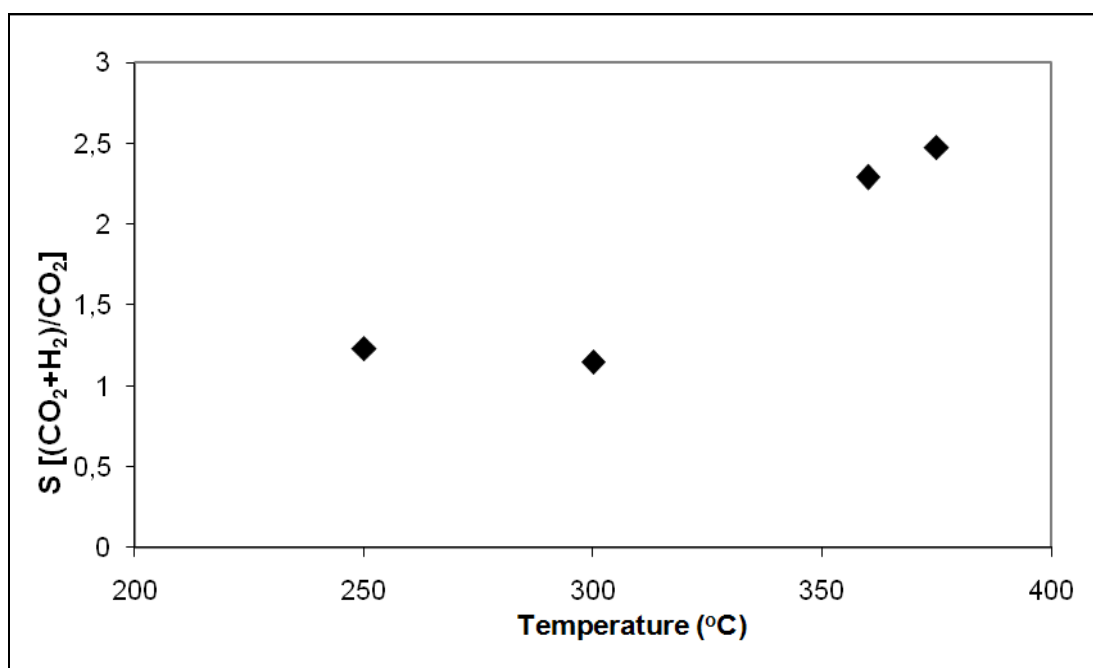


Figure 5.9: The change in selectivity with temperature, Steam/CO = 0.6, GHSV=25000 h⁻¹, Catalyst: Catalyst III

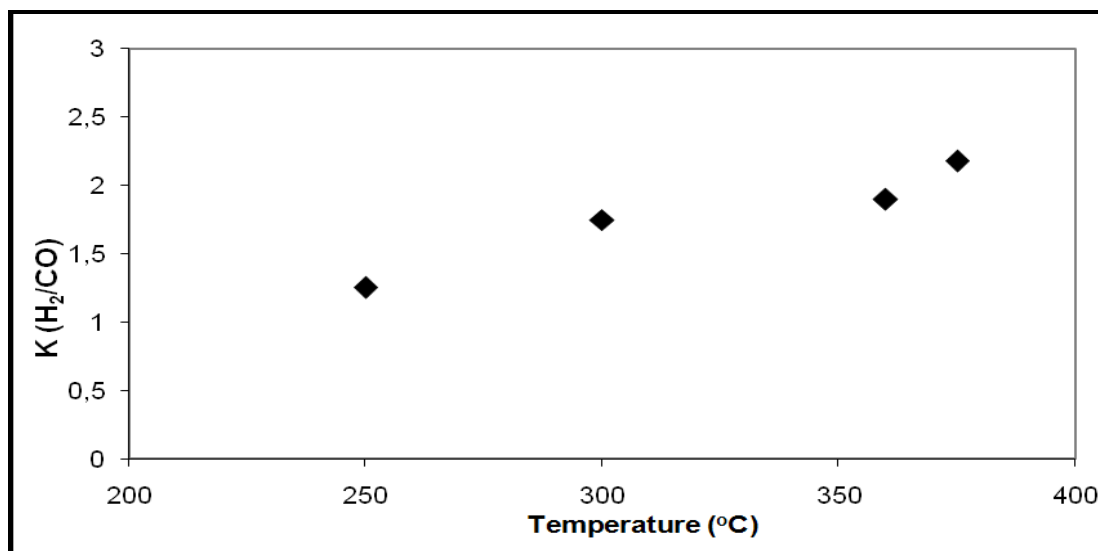


Figure 5.10: Change in the H₂/CO ratio with temperature, Steam/CO=0,6, GHSV=25000h⁻¹, Catalyst: Catalyst III

A series of experiments were performed to investigate the Steam/CO ratio on the conversion, selectivity and H₂/CO ratio in the HTS process. Results are given in Figure 5.11, Figure 5.12 and Figure 5.13. As seen in Figure 5.11, at process temperature $T = 300^{\circ}\text{C}$, Steam/CO ratio seemed not affect the CO conversion. At $T = 360^{\circ}\text{C}$, however, CO conversion gradually improved with increase in Steam/CO ratio. This indicates that, steam can enhance the conversion when a proper process temperature is attained in the water gas shift process catalyzed via Catalyst III.

The relation between selectivity and Steam/CO ratio looks opposite to that which was observed between CO conversion and Stream/CO ratio, Figure 5.12. At $T = 300^{\circ}\text{C}$, selectivity increased from around 1% for Steam/CO = 0.5 to higher than 2% for Steam/CO = 2. At $T = 360^{\circ}\text{C}$, in the same Steam/CO ratio range, selectivity was higher and changed slightly between 2.0% and 2.3%.

Figure 5.13 clearly indicates that, H₂/CO ratio in the outlet gas stream leaving HTS reactor of Catalyst III was significantly affected by Steam/CO ratio. Concentration of the H₂ steadily increased with increase in the amount of steam fed to the reactor. This might be due the reaction between carbon formed through Boudouard reaction and steam which produces H₂ according the following reaction:



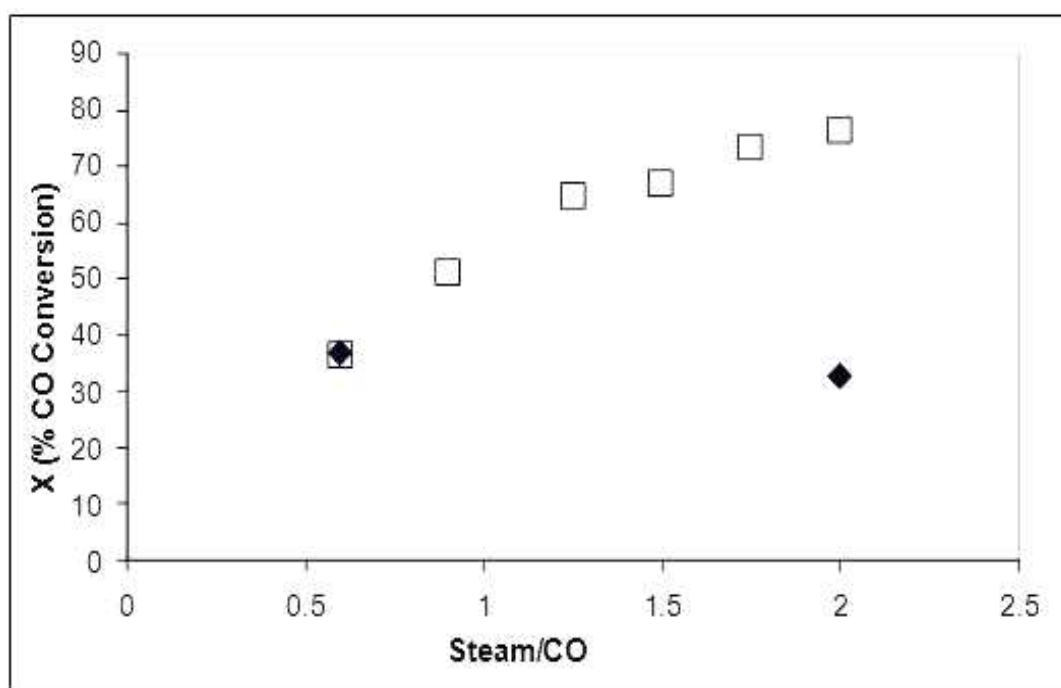


Figure 5.11: The change in CO conversion as a function of inlet Steam/CO, GHSV=25000 h⁻¹, Catalyst: Catalyst III, ◆ T=300°C, □ T=360°C

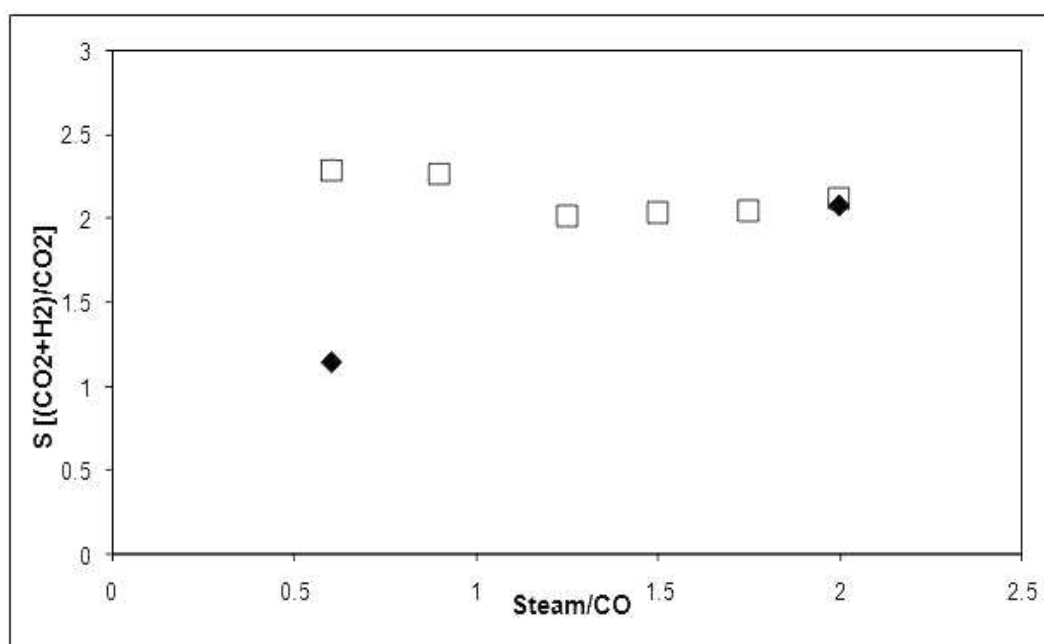


Figure 5.12: Selectivity as a function of inlet Steam/CO, GHSV=25000 h⁻¹, Catalyst: Catalyst III, ◆ T=300°C, □ T=360°C

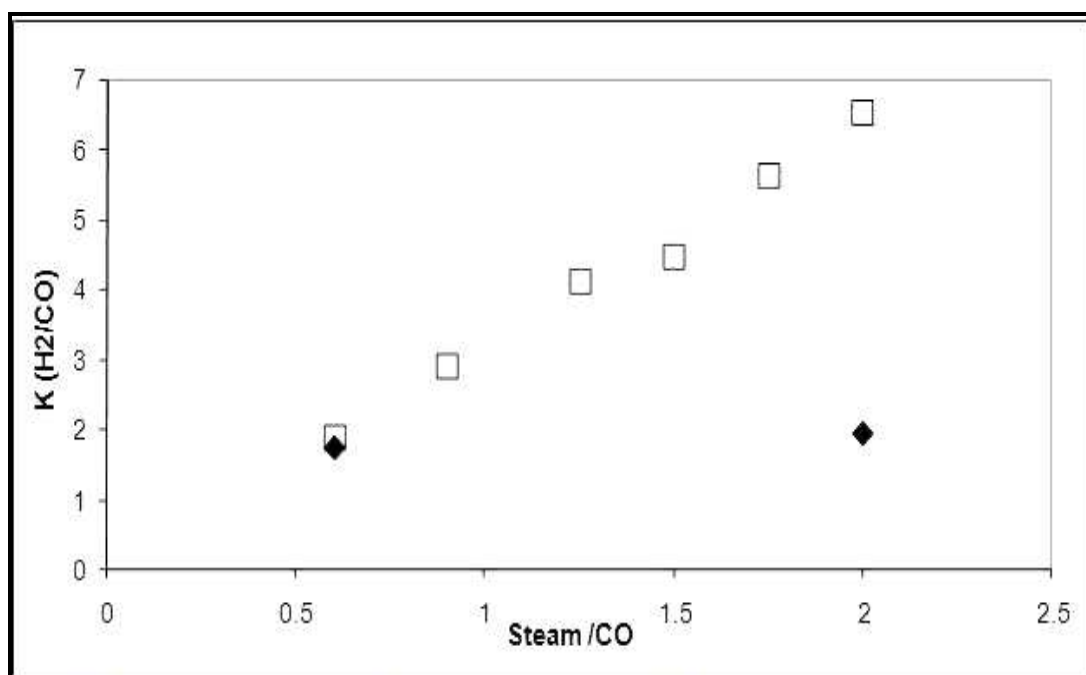


Figure 5.13: The change of H₂/CO ratio with inlet Steam/CO, GHSV=25000 h⁻¹, Catalyst: Catalyst III, ♦ T=300°C, □ T=360°C

For analysing the effect of gas hour space velocity (GHSV) on the HTS reaction, experiments were carried out with GHSV ranging from 25000h⁻¹ to 70000 h⁻¹. The temperature and Steam/CO ratio were kept at 375°C and 2, respectively. Results are presented in Figure 5.14, Figure 5.15 and Figure 5.16. Increase in GHSV leads shorter contact time between gas mixture and catalyst. As consequence of this, CO conversion decrease as GHSV increased, Figure 5.14. This decrease was more significant above GHSV = 50000 h⁻¹ and the CO conversion was decreased from %70 to %55. In addition to this at 375°C and Steam/CO = 2 water gas shift reaction was more dominant than Boudouard reaction. Therefore insipite of increasing GHSV, no significant changes observed in the selectivity. It remained almost constant at about 2 as seen in Figure 5.15. As previously discussed, increase in GHSV decreases CO conversion which and therefore, results in a decrease in H₂/CO ratio according to the Boudouard reaction, Figure 5.16.

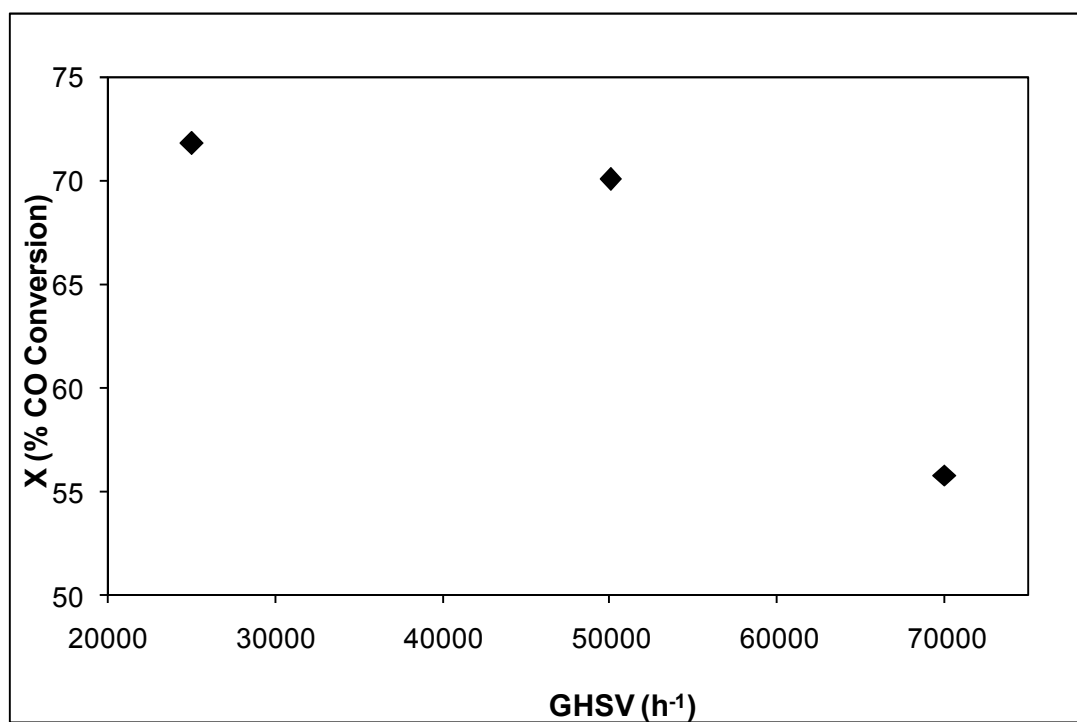


Figure 5.14: The change in CO conversion with GHSV, T=375°C, Steam/CO=2, Catalyst: Catalyst III

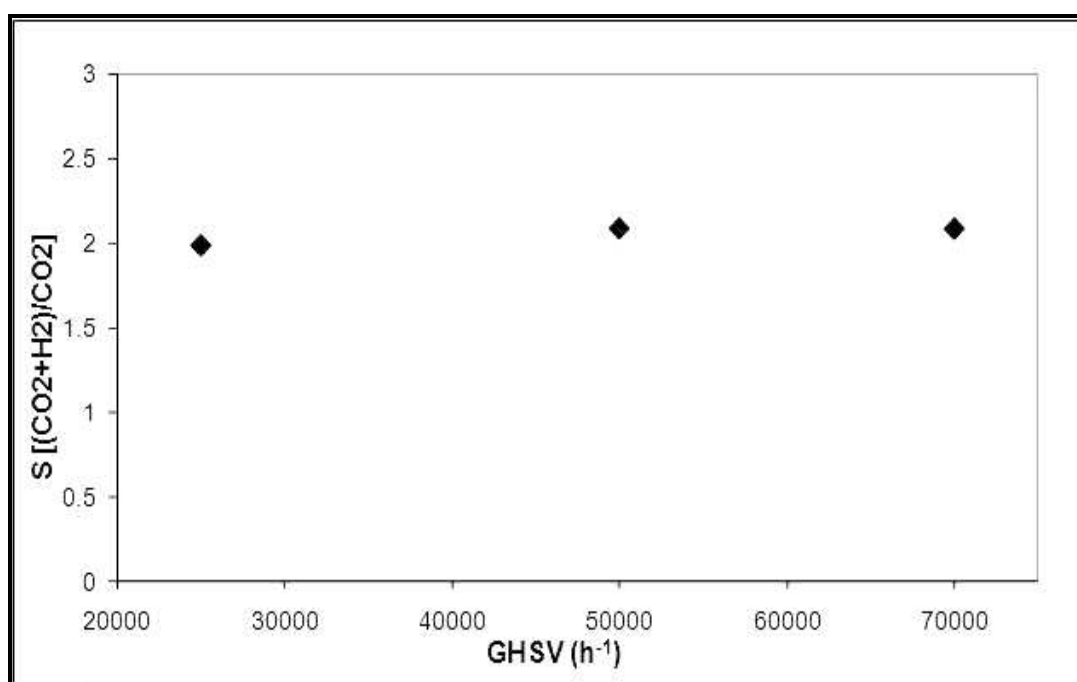


Figure 5.15: The change in selectivity with GHSV, T=375°C, Steam/CO=2, Catalyst: Catalyst III

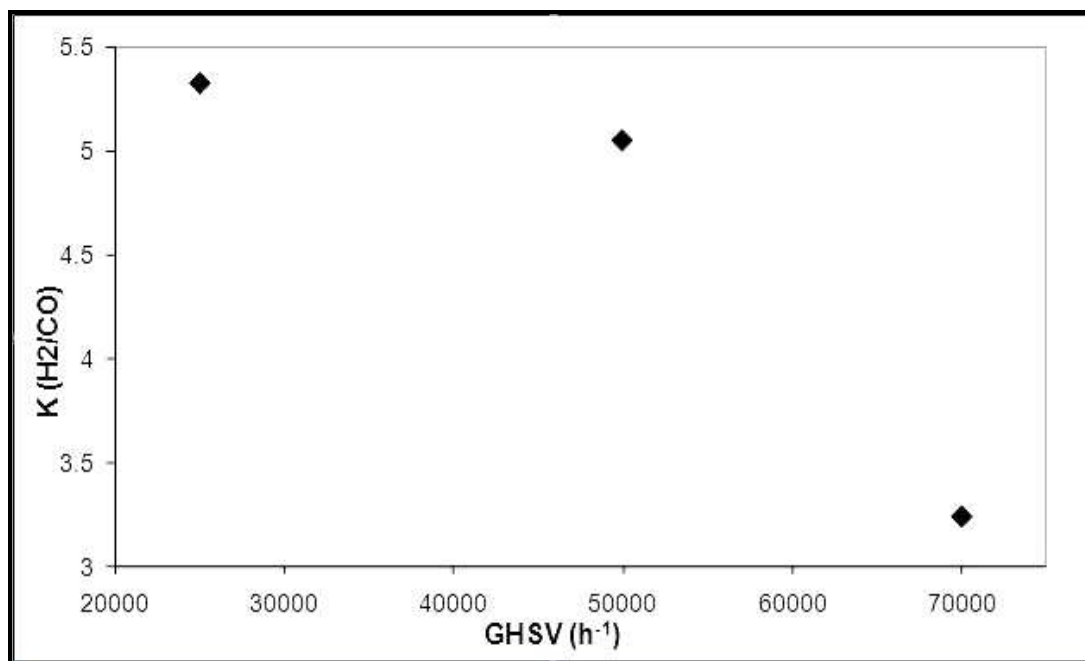


Figure 5.16: The change in H₂/CO ratio with GHSV, T=375°C, Steam/CO=2, Catalyst: Catalyst III

In Figure 5.17, Figure 5.18 and Figure 5.19 CO conversion, selectivity and H₂/CO ratio respectively, are plotted as a function of temperature for Steam/CO = 2 and GHSV = 50000 h⁻¹. As seen from Figure 5.17 and Figure 5.19 below the 350°C CO conversion and H₂/CO ratio is low because of the low water gas shift reaction activity. But CO conversion and H₂/CO ratio increase suddenly at 350°C and higher temperatures because of the effectivity of water gas shift reaction. At higher temperatures (400-500°C) a decrease was observed in CO conversion and H₂/CO ratio. This is because higher temperatures could cause the activity loss of the catalyst by the agglomeration on the catalyst surface, the studies at higher temperatures are not appropriate.

As seen from Figure 5.18 the selectivity value is constant at 2 at higher temperatures which the water gas shift reaction is more effective than Boudouard and CO conversion is high.

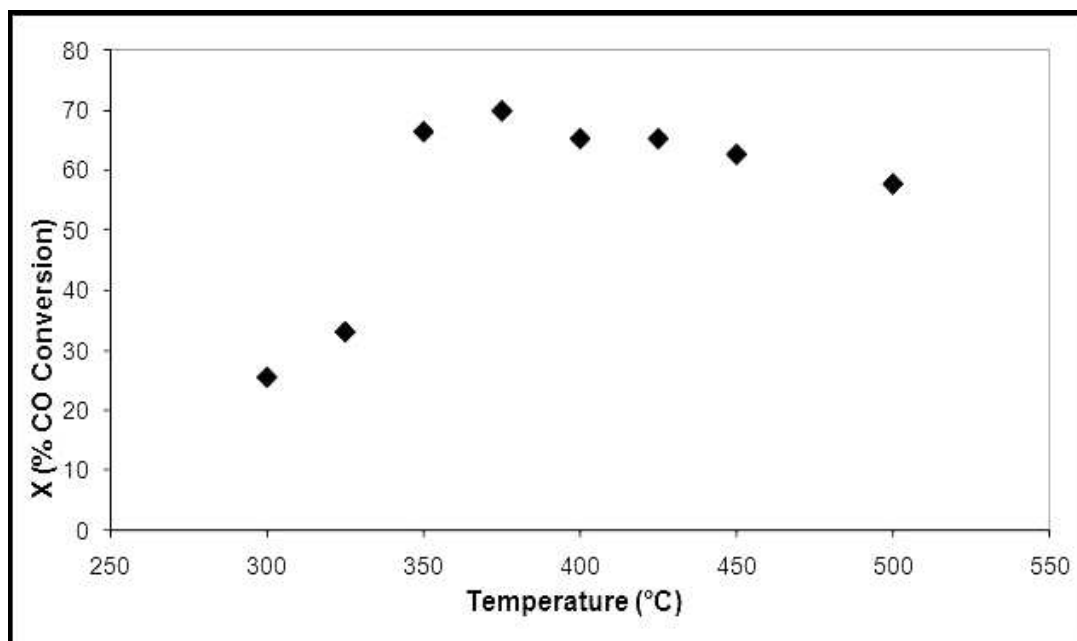


Figure 5.17: The change in CO conversion with temperature, GHSV=50000 h⁻¹, Steam/CO ratio=2, Catalyst: Catalyst III

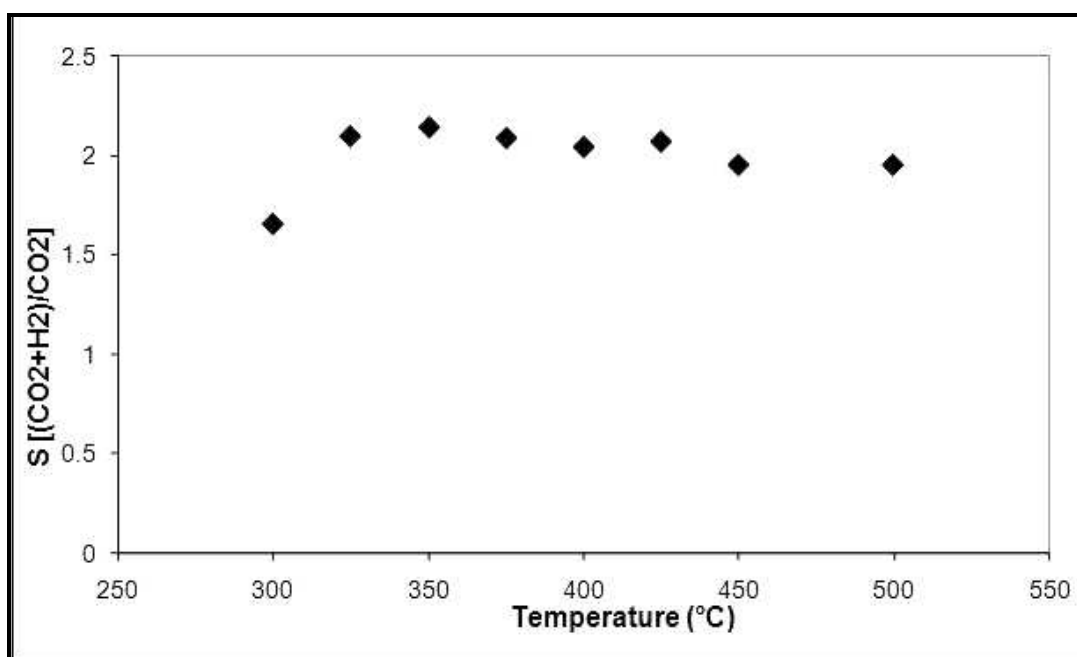


Figure 5.18: The change in selectivity with temperature, GHSV=50000 h⁻¹, Steam/CO ratio=2, Catalyst: Catalyst III

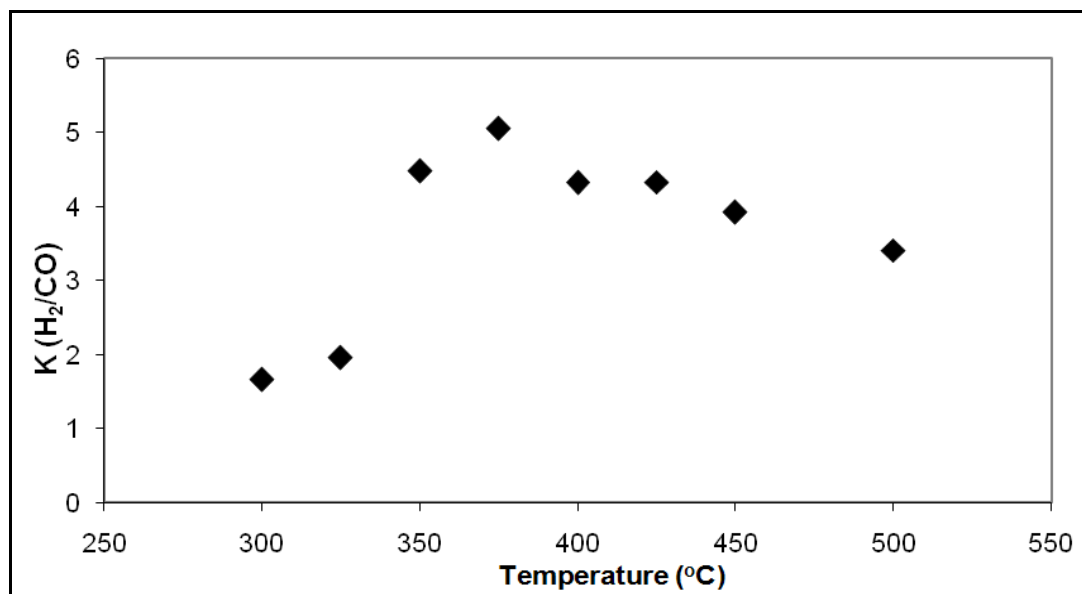


Figure 5.19: The change in H₂/CO ratio with temperature, GHSV=50000 h⁻¹, Steam/CO ratio=2

5.3.2.2 Simulated gas composition II

To investigate the gas composition on the water gas shift (WGS) reaction a different gas mixture composed of 19.2% CO, 13.7% CO₂ and 67.1% H₂ was prepared and used.

The reaction was preceded at 400°C and GHSV of 50000 h⁻¹ by using Catalyst III. The catalyst bed outlet gas composition is given in Table 5.10.

Table 5.10: Outlet gas composition (v %, dry basis), T=400°C, GHSV=50000 h⁻¹, Catalyst: Catalyst III.

Inlet Steam/CO	CO	CO ₂	H ₂	CH ₄
1.5	10.5	18.5	70.75	0.15
1.93	8.2	19.9	71.5	0.13
2.48	7.0	20.6	72.1	0.085

In Figure 5.20, Figure 5.21 and Figure 5.22 CO conversion, selectivity and H₂/CO ratio respectively, are plotted as a function of Steam/CO ratio for T=400°C and GHSV=50000 h⁻¹. As seen in Figure 5.20 when Steam/CO ratio is increased from 1 to 1.75 CO conversion increases from 60% to 85%. But CO conversion remain at 85% for Steam/CO ratio higher than 1.75. It is seen from Figure 5.21 that selectivity value of 2 was obtained showing the presence of water gas shift reaction at choosen

reaction conditions. This ratio showed that WGS has been realized under coke free conditions.

Figure 5.22 shows that H_2/CO ratio in the outlet stream leaving HTS reactor was significantly affected by Steam/CO ratio. H_2/CO conversion increased with increase in the amount of steam fed to the reactor. But above the Steam/CO ratio of 1.75 H_2/CO ratio remain at the same value. As seen in the Figure 5.22 after a certain Steam/CO ratio, around 1.75 - 2, H_2/CO value reached its maximum level.

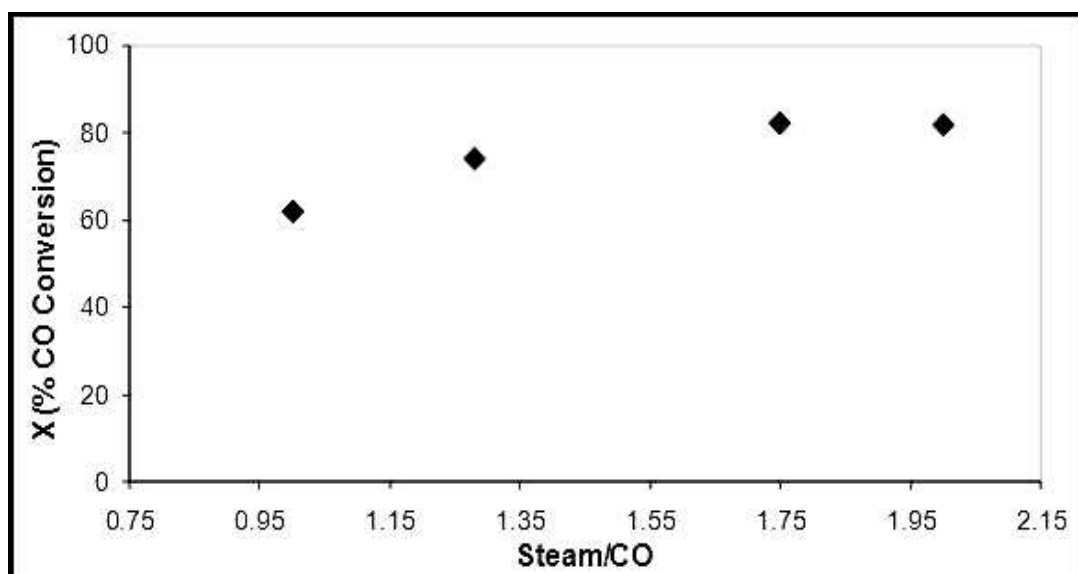


Figure 5.20: The change in CO conversion with Steam/CO ratio, GHSV=50000 h^{-1} , $T=400^{\circ}C$, Catalyst: Catalyst III

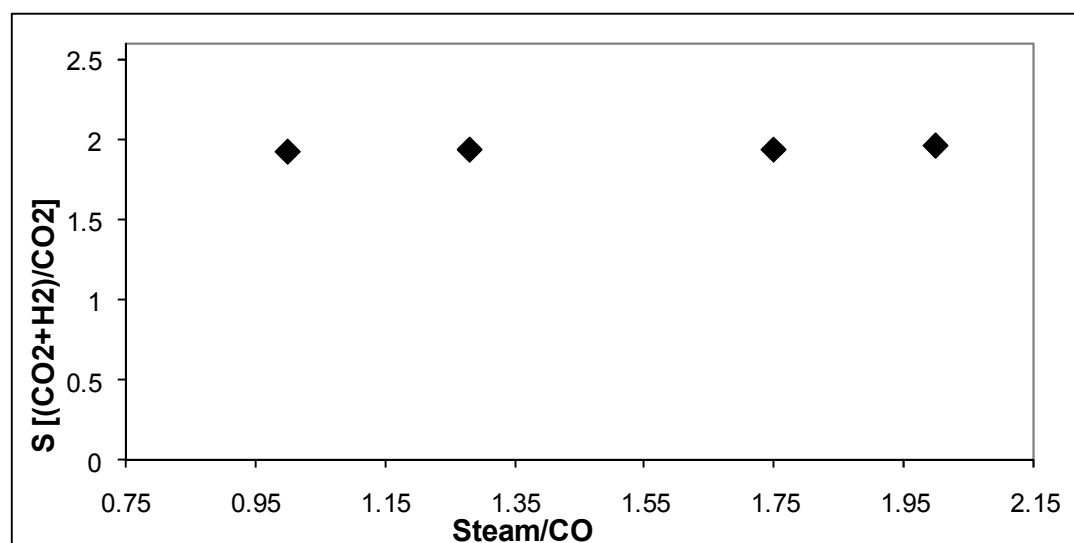


Figure 5.21: The change in selectivity with Steam/CO ratio, GHSV=50000 h^{-1} , $T=400^{\circ}C$, Catalyst: Catalyst III

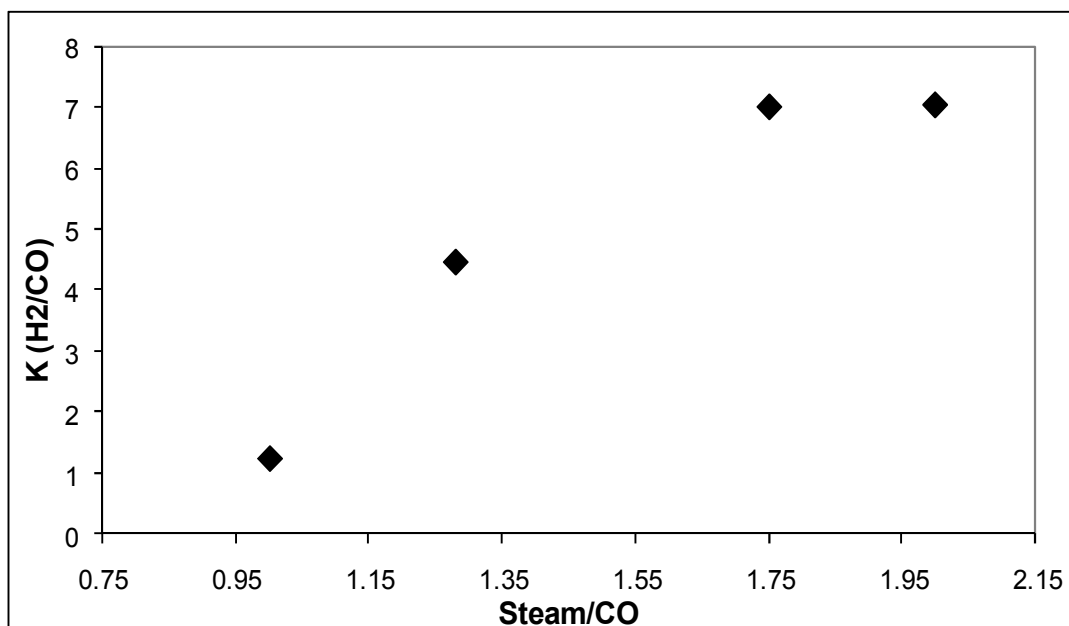


Figure 5.22: The change in H₂/CO ratio with Steam/CO ratio, GHSV=50000 h⁻¹, T=400°C, Catalyst: Catalyst III

5.3.2.3 Simulated gas composition III

For the investigation of the gas composition on water gas shift reaction a third gas composition which includes 10% CO, 5% H₂ and 85% N₂ was used.

In Table 5.11 the obtained results at GHSV of 50000 h⁻¹, 400°C temperature and at different Steam/CO ratios are given. As seen from this table amount of H₂ and CO₂ increased with the increase in the amount of steam fed to the reactor. This result shows that the water gas shift reaction occurs.

Table 5.11: Outlet gas composition on dry basis as volume %, GHSV=50000 h⁻¹, T=400°C.

Inlet Steam/CO	CO	CO ₂	H ₂
1.0	3.78	6.2	10.75
1.28	2.6	7.1	11.6
1.75	1.76	7.79	12.3
2.0	1.79	7.9	12.6

In Figure 5.23 and Figure 5.24 CO conversion and H₂/CO ratio respectively, are plotted as a function of GHSV (h⁻¹) for T=400°C and Steam/CO ratio=1.28. In this study Catalyst III was used.

CO conversions slightly decreased with GHSVs for the ranges between 25000 h⁻¹ and 70000 h⁻¹ because increase in GHSV leads shorter contact time between gas mixture and catalyst. As consequence of this, H₂/CO ratio decrease as GHSV increased, Figure 5.24. Hence, GHSV value of 50000 h⁻¹ was taken as the optimum point for the selected gas composition.

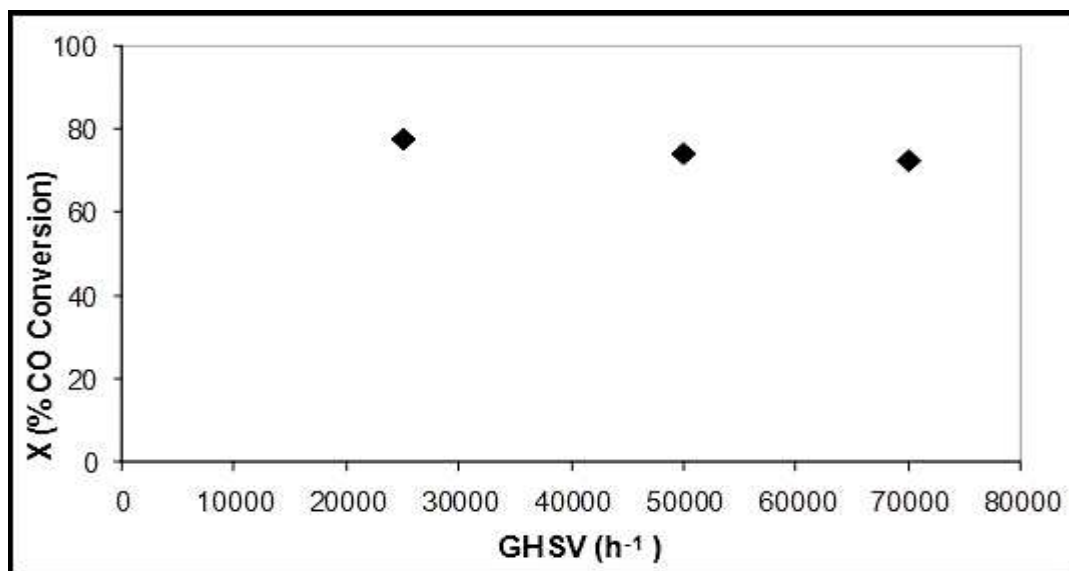


Figure 5.23: The change of CO conversion with GHSV h⁻¹, T=400°C, Steam/CO=1.28, Catalyst: Catalyst III

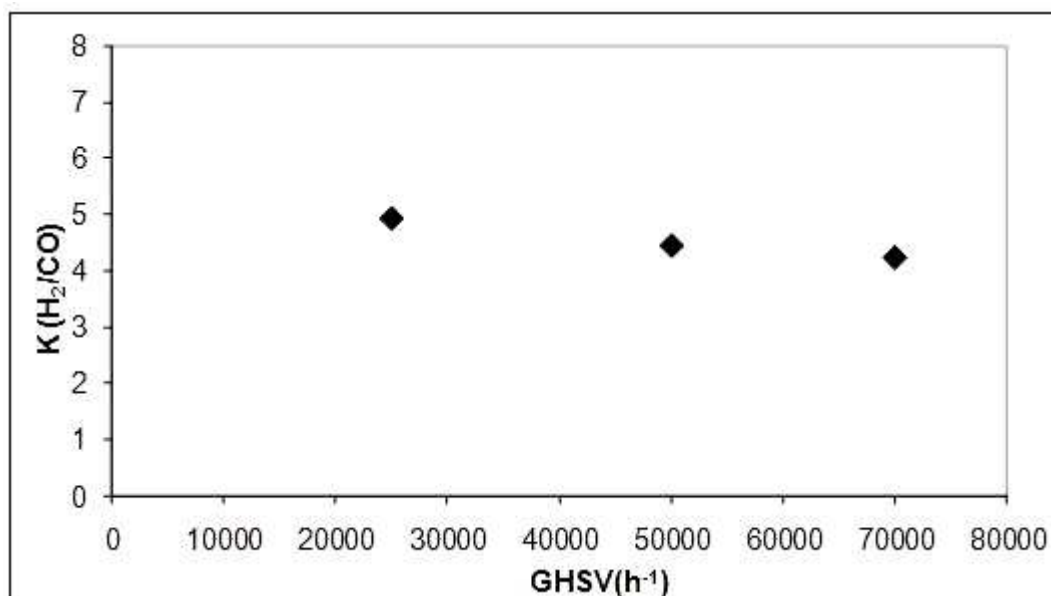


Figure 5.24: The change of H₂/CO ratio with GHSV h⁻¹, Steam/CO=1.28, T=400°C, Catalyst: Catalyst III

5.3.3 Low temperature shift (LTS) study

For determination of the LTS studies the HTS outlet composition of the Gas Composition II was used as a based. As seen in Table 5.10 the HTS catalyst bed outlet gas composition is 7% CO, 20.6% CO₂ and 72.1% H₂ at Steam/CO ratio of 2.48. The simulated inlet and outlet gas compositions are given below. In these experiments a commercial LTS (Catalyst IV) was used.

Table 5.17: Outlet gas composition (v%, dry) for different GHSV and Steam/CO ratios at 275 °C, Catalyst: Catalyst IV.

Inlet Steam/CO	GHSV	CO	CO ₂	H ₂
2.5	50 000	6.80	21.3	71.7
2.5	20 000	5.40	22.0	72.4
4.5	20 000	5.40	23.1	71.5
5.0	10 000	3.70	23.5	72.8
7.5	10 000	3.00	24.0	72.8
5.0	5 000	2.80	24.5	72.8
7.5	5 000	2.00	25.3	72.9
2.5	5 000	5.15	22.6	72.2

As seen from the experimental results, high steam to CO ratios and low gas hourly space velocities are required to obtain the acceptable low temperature shift reaction activities. An inlet steam to CO ratio between 5 and 7.5 and GHSV value of 5000 h⁻¹ were found the optimal operating conditions for the given inlet LTS gas composition.

6. CONCLUSION

In the present study, the performance of Turkish dolomite has been tested for high temperature sulfur removal. In this process water gas shift and reverse water gas shift reactions may occur depending upon gas composition, possibly due to the presence of iron in the dolomite composition. Sulfur removal efficiency seems to be highly dependent on sulfur concentration. At low sulfur concentrations, namely below 200 ppmv, 20% - 30% of sulfur was captured by dolomite. In case of high inlet H₂S concentrations of around 1500-2000 ppmv, dolomite seems to be able to remove 90% of sulfur from hot gases.

Simultaneous presence of CO and CO₂ in the feed gas results in COS formation up to 8-10 ppm in sulfur soption process by dolomite. In addition, natural gas, trace amount of ethyl mercaptane were detected in the reactor outlet gas stream.

The best sulfur adsorption performance of dolomite seem to be achieved at 750°C – 800°C and with GHSV=5000 h⁻¹.

Tar removal activity of Turkish dolomite has also been investigated. Benzene, toluene and xylene were chosen as the surrogated compounds of tar. Xylene was converted mostly into benzene and partly into toluene at 750°C. Beside dolomite, a commercial precious metal based catalyst was also tried to investigate its tar reforming activity at changing tar loads and temperatures. It was seen that selective steam reforming and steam dealkylation reactions were the dominant reactions in relation to steam reforming reaction. The degree of dealkylation of xylene and selective steam reforming increased with temperature in the range of 350-750°C. Xylene conversion was seen to be dependent on inlet tar load. After a certain amount of inlet tar load, reaction rate becomes independent of xylene partial pressure.

In the gas condition studies commercial four different commercial catalysts were examined. The obtained results in these studies are shows that:

- Limited conversion values (around 40%) have been obtained within 250°C to 380°C. Boudouard reaction and hence coking has been observed at low temperatures, dominantly between 250°C and 300°C.
- CO conversion increases with increase in Steam/CO ratio. High steam presence may favor Boudouard reaction at low temperatures ($T < 300^{\circ}\text{C}$).
- CO conversion and H_2/CO ratio decreases with increase in GHSV value. Because when GHSV increase contact time with catalyst and the gas mixture decreases. So the 50000 h^{-1} was chosen as optimum GHSV value.
- When Steam/CO ratio and temperature increased water gas shift reaction has been observed as the dominant reaction in place of Boudouard reaction as apparent from obtained selectivity values of around 2.
- When temperature increased above 400°C catalyst loss activity and the CO conversion values decreases. Because higher temperature could cause agglomeration on the catalyst surface.
- At 400°C gas composition II and III were used and it was found that CO conversions slightly decreased with GHSVs for the ranges between 25000 h^{-1} and 70000 h^{-1} . Minor amounts of methane (0.33%) has been formed at GHSV value of 25000 h^{-1} . At other GHSV values, methanation did not occur.
- At a GHSV valu of 50000 h^{-1} Steam/CO ratio was changed between 1 and 2. Selectivity value of 2 was obtained which showing the presence of water gas shift reaction under coke free conitions.

- Also it was seen that H_2/CO ratio is a good measure of conversion for water gas shift reaction. At $400^{\circ}C$ and optimum GHSV value when Steam/ CO value is around 1.75-2 conversion values reached its maximum level.

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