**ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY**

# THE EFFECT OF SOME CATALYSTS ON THE GASIFICATION OF SUNFLOWER SEED SHELL

**M. SC. Thesis by**
**Elif ÇAGLAYAN, B.Sc.**

**Department :**
**CHEMICAL ENGINEERING**

**Programme: CHEMICAL ENGINEERING**

**JULY 2006**

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**Elif ÇAGLAYAN, B.Sc.**
**(506031027)**

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**Supervisor (Chairman):** Assoc. Prof. Dr. Serdar YAMAN
**Members of the Examining Committee** Prof.Dr. Sadriye KÜÇÜKBAYRAK (ITU)
Prof.Dr. Sibel ÖZDOGAN (M.U.)

**JULY 2006**

ISTANBUL TEKNIK ÜNIVERSITESI ★ FEN BILIMLERI ENSTITÜSÜ

# ÇESITLI KATALIZÖRLERIN AYÇIÇEGI ÇEKIRDEGI KABUGUNUN GAZLASTIRILMASINA ETKISI

**YÜKSEK LISANS TEZI**
**Kim. Müh. Elif ÇAGLAYAN**
**(506031027)**

**Tezin Enstitüye Verildigi Tarih : 8 Mayis 2006**
**Tezin Savunuldugu Tarih : 6 Temmuz 2006**

| | |
|---|---|
| **Tez Danismani :** | **Doç.Dr. Serdar YAMAN** |
| **Diger Jüri Üyeleri** | **Prof.Dr. Sadriye KÜÇÜKBAYRAK (ITÜ)** |
| | **Prof.Dr. Sibel ÖZDOGAN (M.Ü.)** |

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# ÇESITLI KATALIZÖRLERIN AYÇIÇEGI ÇEKIRDEGI KABUGUNUN GAZLASTIRMASINA ETKISI

## ÖZET

Dünyadaki enerji tüketimi son on yilda sabit bir oranda artmistir, beklentiler bu artisin gelecek on senede ivmelenecegi yönündedir. Fosil yakitlarin bugün oldugu gibi birincil yakit kaynagi olarak yeterli olmayacak olmasi, yenilenebilir enerji kaynaklarinin kullanimi konusunda yapilan çalismalari zorunlu kilmaktadir. Biyokütle insanligin kullandigi en eski yakit çesididir; ancak günümüzde amaç onu en verimli sekilde kullanabilmektir. Gazlastirma, içten yanmali motor, yakit pili gibi pek çok alanda kullanilabilecek temiz gaz ürünlerin üretilmesine olanak saglamasi nedeniyle iyi bir alternatif teknolojidir. Gazlastirmada bugün karsilasilan en önemli sorun yogusabilen hidrokarbon karisimlari olan katranin olusumudur. Gaz karisimi içerisinde bulunan katran, gaz türbinlerine zarar vermekte ve ömürlerini önemli ölçüde kisaltmaktadir. Gaz üründe katran olusumunun önlenebilmesi için uygulanabilecek bir yöntem katalitik maddelerin kullanimidir. Bu çalismada, çesitli katalitik maddelerin ayçiçegi çekirdegi kabugunun gazlastirilmasi üzerine etkileri incelenmistir. Seçilen biyokütle nümunesinin uçucu içerigi yüksek; buna karsin kül içerigi düsüktür. Kullanilan katalitik maddeler olivin, dolomit, zeolit, kireçtasi, $Na_2CO_3$ ve $K_2CO_3$'dür. Olivin, dolomit, kireçtasi ve zeolit gibi seçilen dogal katalizörler kullanilmadan kalsine edilmislerdir. $Na_2CO_3$ ve $K_2CO_3$'e herhangi bir ön islem uygulanmamistir. Biyokütle numunesi ve katalitik maddelerden olusan karisimlar termogravimetrik (TG) analiz cihazinda, azot atmosferi altinda ve 4 basamakli bir sicaklik programi uygulanarak gazlastirilmistir. Elde edilen DTG egrilerinden maksimum agirlik kaybinin gerçeklestigi sicakliklar tespit edilmis, kurulan piroliz deney düzenegindeki deneylerde ise bu sicakliklar (773 K) maksimum deney sicakligi olarak kullanilmistir. Deneyler yine azot atmosferinde (1lmin$^{-1}$) gerçeklesmistir ve deneylerde isitma hizi 20 Kmin$^{-1}$ olan adimli bir sicakli programi uygulanmistir. Katalizörlerin özellikle CO ve $CH_4$ konsantrasyonlarinda önemli artislar sagladigi gözlemlenmistir. En büyük CO konsantrasyon artisi kalsine edilmis zeolitin varliginda gerçeklesirken, en yüksek $CH_4$ konsantrasyonu $K_2CO_3$ varliginda elde edilmistir. Kati ürün miktari kullanilan isitma hizi ve düsük deney sicakliklarina bagli olarak artmistir.

## THE EFFECT OF SOME CATALYSTS ON THE GASIFICATION OF SUNFLOWER SEED SHELL

## SUMMARY

Global energy consumption which has been growing steadily for the last decade, is forseen to have an accelerated increase in the future. The fossil fuels will not be sufficient as the primary fuel source, therefore work has to be done on the utilization of renewable energy sources. Human beings has been using biomass as an energy source for centuries, but nowadays the aim is to use the most efficient way.Gasification is a promising technology to produce clean gaseous fuels which can be used in many applications such as internal combustion engines, fuel cells.One of the major problems encountered with gasification today is the formation of tars, mixtures of condensable hydrocarbons, which causes serious operational problems with turbines, etc. In order to eliminate the tars formed within the gaseous product catalytic materials are used. In this study the catalytic effects of the selected materials on the gasification of sunflower seed shell were investigated. The selected biomass sample had a high volatile and low ash content.The used catalytic materials were olivine, dolomite, zeolite, limestone, $Na_2CO_3$ and $K_2CO_3$. Natural catalysts such as dolomite, olivine, limestone and zeolite were calcined before the experiments. No pretreatment was applied to $Na_2CO_3$ and $K_2CO_3$.The blends consisting of the biomass sample and the catalytic materials were gasified in a thermogravimetric (TG) analyzer under nitrogen flow and a four step temperature program was applied. The temperature intervals (around 773 K) at which the maximum weight losses occured were the basis of the temperature program used in the pyrolysis experiments. The pyrolysis experiments were conducted under $N_2$ atmosphere ($1 l min^{-1}$) and had a stepped temperature program with a heating rate of $20 K min^{-1}$. The concentration of CO and $CH_4$ increased considerably in the presence of the catalysts. The highest CO concentration was achieved with the blend containing calcined zeolite whereas a maximum $CH_4$ yield was reached with $K_2CO_3$. The amount of solid product was higher than TGA due to the fact that lower operation temperatures were applied and the heating rate was $20 K min^{-1}$.

# 1. INTRODUCTION

Energy has a crucial place in today's civilization. It is needed almost in every part of daily life such as heating, lighting and cooking in households and for virtually every industrial, commercial and transport activity. Victor Hugo, in his masterpiece "Les Miserable", describes municipal wastes as an economically valuable source. He did not consider it as an energy source but today it has to be considered as one. The abundant sources in Hugo's days are getting scarcer. Consumption of energy had been growing steadily by around 2 % a year globally from 1990 to 2000 and this growth is forecasted to be more in the next two decades. Global consumption of fossil fuels are also increasing, it accounts for 79 % of the overall energy consumption. Fossil fuels have two main disadvantages; first, when they are burned they emit pollutants, including the greenhouse gases that are causing climate changes; second, countries without adequate reserves of fossil fuels are facing increasing risks to the security of their energy supplies [1].

The renewable energy sources provides 19 % of the total energy consumption worldwide, only in the US it has a portion of 11 %. European Union targeted an increase in the share of renewable energies from 6% to 12% of gross energy consumption, of green electricity from 14 % to 21 % of gross electricity production by 2010. The breakdown of energy consumption in EU in 2005 given in Figure 1.1 shows that biomass has the largest share (65 %) in renewables. Energy from biomass already accounts for nearly 4 % of the total EU energy supply. Biomass is the only available renewable energy source in today's technology that can produce competitively priced fuels for transport in larger quantities. Products from biomass that have similar properties to conventional fossil fuels make it possible to use the already existing structure and minimise the adaptation of end use technologies [1].

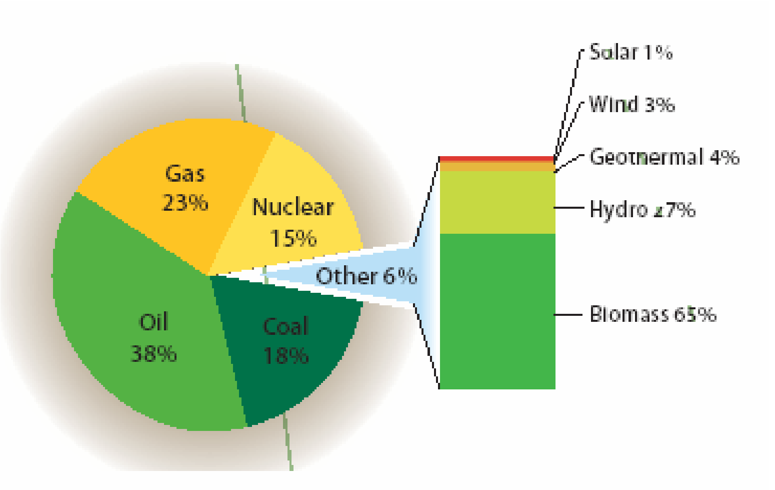


**Figure 1.1:** Breakdown of Energy Consumption in EU in 2005 [1]

Biomass gasification offers an alternative way to produce clean fuels; however, today 98 % of the energy obtained from biomass is by direct combustion. Large scale gasification plants ranging between 15-70 $MW_{th}$ are being developed in Europe that indicates that there is a clear drift from direct combustion to biomass conversion into syngas. In order to make gasification processes economically feasible, the gasifier should operate at lower temperatures than 750 $^0$C, which will reduce the energy cost, at the same time the formation of tar due to low operation temperatures has to be prevented. Gasification process requires temperatures around 750 $^0$C, in the presence of catalyst gasification temperature can be reduced up to 600 $^0$C. In the future; catalysts are reported to play a key role in gasification processes [1, 2].

The sustainable production and use of biomass as a fuel will have a very positive environmental impact due to the absorption of the emitted $CO_2$ by the new growth of biomass. In fact the net $CO_2$ emission resulting from the utilization of biomass as a fuel will be zero. Biomass usually has a lower sulphur content compared to coal, therefore when it is combusted small amounts of $SO_x$ are emitted [3].

## 2. BIOMASS

Biomass is generally defined as any organic material that is available on a renewable basis. It mainly consists of carbon, hydrogen, oxygen and nitrogen. The amounts of inorganic species within the biomass vary largely and the amount of occurring ash consequently. The sulphur content of biomass is considerably less than that of coal. The major organic components in biomass are; cellulose, hemicellulose and lignin. Their percentage in biomass, affect the gasification process, therefore it is very important. Cellulose is a polysaccharide with a generic formula of $(C_6H_{10}O_5)_n$ that has a skeletal structure and constitutes almost 50 % of the cell wall. It is insoluble in water. Hemicellulose is also a polysaccharide and cell wall material. It can be dissolved in dilute alkali solutions. The chemical structure of hemicellulose unlike cellulose is branched and has a general chemical formula of $(C_5H_8O_4)_n$. The third component lignin is highly branched and a mononuclear aromatic polymer. It can be found in the cell walls of some of biomass like woody species. They have a complex structure and are resistant to conversion. These three polymers contain relatively weak ether bonds (R-O-R) with bond energies of 380-420 $KJmol^{-1}$; therefore they are easily cracked at lower temperatures like 400-500 $^0C$. Whereas the immobile phase of coal has dense polycyclic aromatic hydrocarbons linked by C=C bonds. These bonds have bond energy of 1000 $KJmol^{-1}$. Agricultural residues are generally composed of 40-50 % cellulose, 20-30 % hemicellulose, 20-25 % lignin and 1-5 % ash. The chemical structures of cellulose, hemicellulose and lignin are given in Figure2.1 [4, 5, 6, 7, 8].

Biomass can be generally classified as forest residues, agricultural crops and wastes, wood and wood wastes, animal wastes, livestock operation residues, aquatic plants, industrial and municipal solid wastes. The utilization of agricultural, forestry or wood industry residues in energy production will help to resolve the environmental and disposal problems. Nowadays cultivation of energy crops such as poplar, willow, miscanthus, sugar cane, sweet sorghum, etc that are fast growing plants, are getting a worldwide attention. Biomass residues such as agricultural or forestry waste are used to generate energy directly or indirectly. The most appropriate commercially applied thermochemical methods are gasification and pyrolysis. When lignocellulosic materials are heated under an inert atmosphere, they decompose to char, tar and gases [5,6].

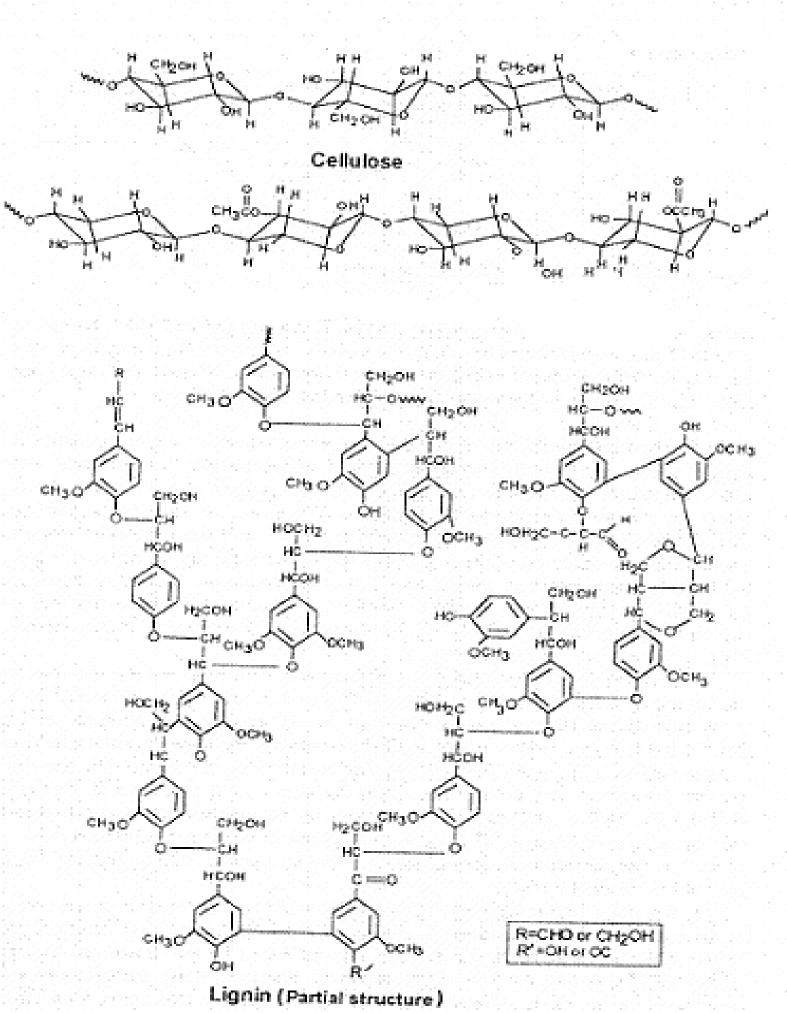


**Figure 2.1:** Chemical Structure of Cellulose [8]

Biomass residues are usually more reactive than coal due to their chemical and physical properties such as higher volatile content (in the range of 80-90 %) or hydrogen to carbon and oxygen to carbon ratios. For instance, rates 4-10 times greater than the ones achieved in lignite steam gasification are reached with biomass. Biomass charcoals, in particular wood charcoals have very high porosity in the range of 40-50% with pore sizes changing between 20-30 µm whereas the porosity of charcoal from coals changes between 2-18 % with pore sizes of 5Å. Therefore charcoal from biomass is considered as a new generation source of energy and industrial chemicals. Steam gasification of biomass is a very endothermic reaction that requires a considerable amount of heat, which can be supplied by partial combustion of the fuel. Catalyst can be used to reduce the amount of heat needed for the process by lowering the operating temperature and achieve favourable process rates. Although catalysts have many advantages, still most of the gasification processes are operated without catalysts. The cost of catalysts is still considerably high and regeneration of the catalyst is needed [8].

## 3. BIOMASS GASIFICATION

Gasification is a chemical, thermal or catalytic process that converts a feedstock to a valuable gaseous product. The product in the gas form obtained in gasification is easy to handle and combust with just a little excess of air and it leads to low contaminant levels. A general representation of the gasification process is given in Figure 3.1. Operational parameters such as temperature, pressure, heating rate, residence time, etc. affect the end product. For instance, at slow heating rates and low to intermediate temperatures after a long residence time, high charcoal yields are obtained. High reduction of solid yields and maximum gas or liquid production can be achieved at high heating rates. Temperatures above 647 $^0$C and residence times less than 1 s maximize the gas formation, however processes at temperatures between 347-647 $^0$C with lower residence times will result in high liquid yields [3, 5, 6, 10].

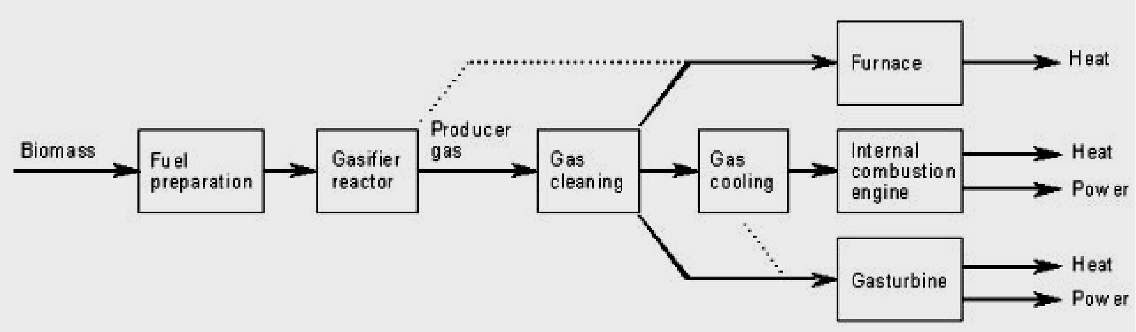


**Figure 3.1:** Possible Routes for Producing Power and/or Heat through Biomass Gasification [10]

Biomass gasification has a complex nature due to the large variety of fuels and possible reaction pathways. Therefore gasification process is hard to control and operate at the desired standards. Reactions taking place in the system have considerably high reaction rates. Three main gasification processes are; pyrolysis, partial oxidation and reforming. Pyrolysis, also known as destructive distillation, can be defined as thermal degradation in the absence of a reactive atmosphere. The pyrolysis of biomass, which is a nearly autothermal reaction, happens prior to or simultaneously with gasification reactions at 300-400 $^0$C. The main products are gases such as $CO$, $CO_2$, $H_2$, $H_2O$ and traces of $C_2$ to $C_5$, liquids including tars, and char. During partial oxidation where oxygen less than stoichiometric amount for complete combustion is used, partially oxidized products are obtained. In the terminology of biomass gasification reforming means, gasification in the presence of another reactant such as steam. Along with the reactions of biomass and steam, the secondary products are also transformed. The general chemistry of gasification are showed in equations from 3.1 to 3.10 [3, 6, 11].

Gasification:

$C + O_2 \rightarrow CO_2$ - 393.5 kJ **(3.1)**
$C + H_2O \rightarrow CO + H_2$ + 131.3 kJ **(3.2)**
$C + 2\ H_2O \rightarrow CO_2 + 2\ H_2$ + 90.2 kJ **(3.3)**

Boudouard Reaction:

$C + CO_2 \rightarrow 2\ CO$ + 172.4 kJ **(3.4)**

Partial Oxidation:

$C + 0.5\ O_2 \rightarrow CO$ - 110.5 kJ **(3.5)**

Water Gas Shift :

$CO + H_2O \rightarrow CO_2 + H_2$ - 41.1 kJ **(3.6)**

Methanation :

$2\ CO + 2\ H_2 \rightarrow CH_4 + CO_2$ - 247.3 kJ **(3.7)**
$CO + 3\ H_2 \rightarrow CH_4 + H_2O$ -206.1 kJ **(3.8)**
$CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O$ -165 kJ **(3.9)**
$C + 2\ H_2 \rightarrow CH_4$ - 74.8 kJ **(3.10)**

## 3.1 Fixed Bed Gasifiers

Fixed bed gasifiers can be classified into four groups; updraft, downdraft, cross draft and open core gasifiers.

### 3.1.1 Updraft Gasifiers

Updraft gasifiers are also known as countercurrent gasifiers where the fuel is fed from the top of the reactor and moves down, during which conversion and removal of ashes take place. The fuel passes through the drying, pyrolysis, reduction and hearth zones successively while it is flowing countercurrently with the product gases. The schematic presentation of an updraft gasifier is given in Figure 3.2

[3, 12].

The moisture content of the biomass is evaporated in the drying zone with the heat of the upflowing product gases and the radiation from the hearth zone. Afterwards the biomass passes through the pyrolysis zone where volatiles and char are produced. The pyrolysis zone is again heated with the hot product gases. Carbon is mainly converted in the reduction zone where the reactions between char, $CO_2$ and water vapour take place. The remaining char is combusted in the hearth zone providing the heat, $CO_2$ and water vapour required for the reactions in the reduction zone.

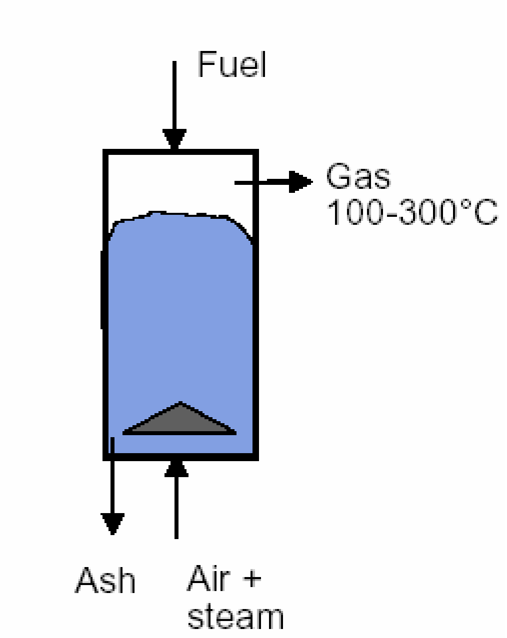


**Figure 3.2:** Schematic Presentation of Updraft Gasifiers [12]

The updraft gasifiers have the following advantages:

- Simplicity,
- High charcoal burnout,
- Low gas exit temperature due to internal heat exchange,
- High gasification efficiency,
- Flexibility of biomass moisture content (up to 60% wet basis),
- Flexibility of particle size, it enables to use small fuel particles,
- Less sensitivity to size variations.

On the other hand the major drawbacks are as follows:

- High amounts of tar in the fuel gas due to the up flow of the product gas which does not pass through the hearth zone,
- Extensive gas cleaning requirement for the end use of the gas in engines.[3]

### 3.1.2 Downdraft Gasifier

Downdraft gasifiers are also known as co-current gasifiers. The biomass and the gasifying agent are fed from the top of the reactor. The feed and the product gas flow co-currently downwards and leave at the bottom of the gasifier. The schematic presentation of an downdraft gasifier is given in Figure 3.3. The biomass passes through the drying and pyrolysis zones, the heat generated in the hearth zone mainly provides the heat for these two zones. Some of the char and pyrolysis gases are combusted in the hearth zone. The amount of combusted pyrolysis gases depends on the gasifier design and the properties of biomass feedstock. The remaining char and combustion products such as $CO_2$ and water vapour are converted to CO and $H_2$ in the reduction zone [3, 12].

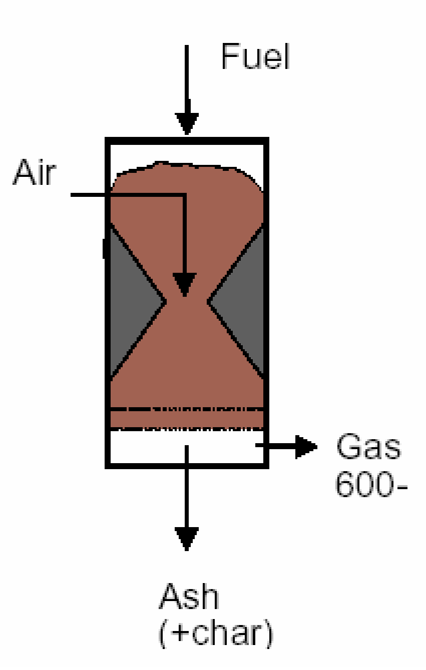


**Figure 3.3:** Schematic Presentation of Downdraft Gasifiers [12]

The main advantage of the downdraft gasifier is the low tar amount in the product gas that can be directly used in engines. It should be noted that a tar-free gas is hardly obtained in practice due to the gas does not pass through the hottest zones. The residence time in the hearth zone affects the tar content of the product gas. For application ranging between 80-500 $kW_e$ downdraft gasifiers can be used.

The major drawbacks of downdraft gasifiers are as follows:

- Relatively strict fuel requirements,

- Uniform particle size ranging between 4-10 cm so that throat blockage can be prevented and the heat and pyrolysis gases can flow easily,
- Pelletization and briquetting is often required,
- Less than 25% on wet basis of moisture content is required,
- Lower gasification efficiencies due to high temperature of the flue gas [3].

### 3.1.3 Cross-Draft Gasifiers

Cross-draft gasifiers are mainly used for charcoal gasification during which temperatures 1500 $^0$C and higher are obtained in the hearth zone. Extremely high temperatures may lead to material problems. Cross-draft gasifiers are also suitable for small scale system; however the minimal tar converting capability requires high quality charcoal [3].

### 3.1.4 Open-Core Gasifier

The main designing purpose of open core gasifiers was to gasify carbonaceous materials with low bulk densities such as rice husks. These gasifiers do not contain any throat, special devices like rotating grates may be used to stir the fuel and remove the ash. Ash removal is usually done by a basin of water, which acts as a transport medium [3].

## 3.2 Fluidized Bed Gasifiers

The operational problems encountered when gasifying high ash content fuel in a fixed bed gasifier led to the development of fluidized bed gasifiers. Fluidized bed gasifiers have the flexibility in operating with different types of biomass and coal as feedstock. These types of gasifiers are suitable for larger capacities (larger than 10 $MW_{th}$) Fluidized bed gasifiers operate at lower temperatures in the region of 750-900 $^0$C, whereas the temperature in the hearth zone of a fixed bed gasifier may be as high as 1200 $^0$C. Reaction rates of tar conversion are lower due to the low operating temperatures. The bed has high turbulence characteristics and behaves like a fluid. The advantages of fluidized bed reactors are as follows:

- Extensive mixing in the bed results in high heat exchange and reaction rates, which enables compact construction.
- Flexibility in moisture and ash contents which gives the ability to deal with fluffy and fine grained materials that have high ash content, low bulk density, or both.
- Relatively low ash melting points are observed due to low reaction temperatures.

The drawbacks of fluidized bed reactors are enlisted below:

- Producer gas has a high ash and dust content
- Alkali metals are in vapour state because of the high producer gas temperatures
- Carbon burnout is not complete
- Due to the need of controlling the supply of air and solid fuel the operation becomes complex
- Compression of the gas stream results in power consumption

Fluidized bed gasifiers can be classified into two types. The first one is the bubbling fluidized bed gasifiers (BFB). The fuel in these types of gasifiers is fed into a suspended hot sand bed. The second type of fluidized bed is the circulating fluidized bed (CFB) where the fuel is introduced into a circulating hot sand bed. Rapid mixing of the fuel with the hot bed materials results in rapid pyrolysis.

When the two types of fluidized bed gasifiers are compared, the carbon burnout in circulating fluidized bed (CFB) is considerably better than bubbling fluidized bed gasifiers (BFB). In gasification processes relatively fine fuel particle sizes are preferred [3].

## 3.3 Commercial Gasification Processes

### 3.3.1 Dry Ash Lurgi Process

It is a fixed bed process, which requires a feed that is crushed and dried. The operation conditions are in the range of 620-760 $^0$C and 2.43-3.14 MPa. The feed resides for one hour in the reactor and leaves it at 370 to 590 $^0$C.The product gas contains tar, ammonia, sulphides and particulate matter [11].

### 3.3.2 Winkler Process

Crushed coal/biomass is gasified in a fluidized bed that operates under near atmospheric pressure at 820 -1000 $^0$C. The gasifying agents of this process are steam and oxygen. The heat of the raw gas is recovered by a waste heat recovery system. The particulate matter within the gas flow can be removed by cyclone, wet scrubber or electrostatic precipitator [11].

### 3.3.3 Koppers-Totzek Process

This process does not require any pretreatment. The gasifier is a horizontal entrained flow reactor. The operating temperature and pressures are around 1820 $^0$C and atmospheric pressure. The dried and pulverized feed is gasified with oxygen. The molten ash within the raw gas is removed by quenching with water.

The gas is further purified from the entrained solids, hydrogen sulphide and some carbon dioxide by scrubbing. From this process a gas that has a syngas quality is obtained [11].

### 3.3.4 Shell Oil Co. Process

A large variety of feedstocks are converted in a high temperature and pressure entrained flow slagging gasifier. The product gas has a medium heating value that can be used in combined cycle power generation. The predried feedstock is gasified with oxygen and steam at 1500 $^0$C. A conversion in the range of 99 % is reached with this process [11].

### 3.3.5 Texaco Inc. Process

The ground feedstock is fed as water slurry to a single stage pressurized entrained flow slagging gasifier. The gasifying agent is oxygen and is mixed to the feed flow. The gasifier operates at 1200-1500 $^0$C.The amount of oxygen fed to the system has to be controlled closely in order to maintain the reductive atmosphere within the reactor so that a product gas close to syngas can be obtained [11].

### 3.3.6 IGT's U-GAS Process

A low heating value gas is produced in a single stage fluidized bed gasifier. The gasification takes place under steam and air. The gasifier operates at temperatures between 950 -1090 $^0$C and pressures ranging from atmospheric to 3.55 MPa. If air is substituted by oxygen, a medium heating value gas can be obtained [11].

# 4. TAR

## 4.1 Definition and Classification

Tar is a major problem encountered during gasification. The tar content of the product gas limits the end use of the gas. International Energy Agency defined tar in the provisional tar protocol as organic compounds with molecular weight greater than benzene the boiling point of which is 80.1 $^{0}$C. Benzene has a considerable energy content; however, it is not included in tar. Gasification of biomass at high temperature produces a tar that mainly consists of highly stable aromatic hydrocarbons such as benzene, naphthalene and other polyaromatic hydrocarbons [13, 14].

Tar is a complex mixture of condensable hydrocarbons ranging from single ring to multiple ring hydrocarbons to other oxygen containing hydrocarbons even to complex polycyclic aromatic hydrocarbons. Different classification of tars can be found in the literature. Some of them are given as follows. Milne et al. classified tars according to the reaction regimes into four groups. The schematic presentation of this classification is given by Figure 4.1. Primary tars are the cellulose-derived, hemicellulose-derived and lignin-derived products. Secondary tars are characterised by phenolics and olefins. Alkyl tertiary products are the methyl derivates of aromatic compounds whereas condensed tertiary groups are PAHs without substituent groups [15].

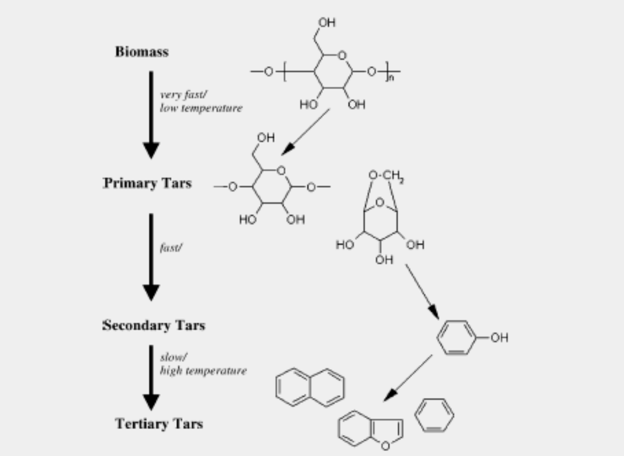
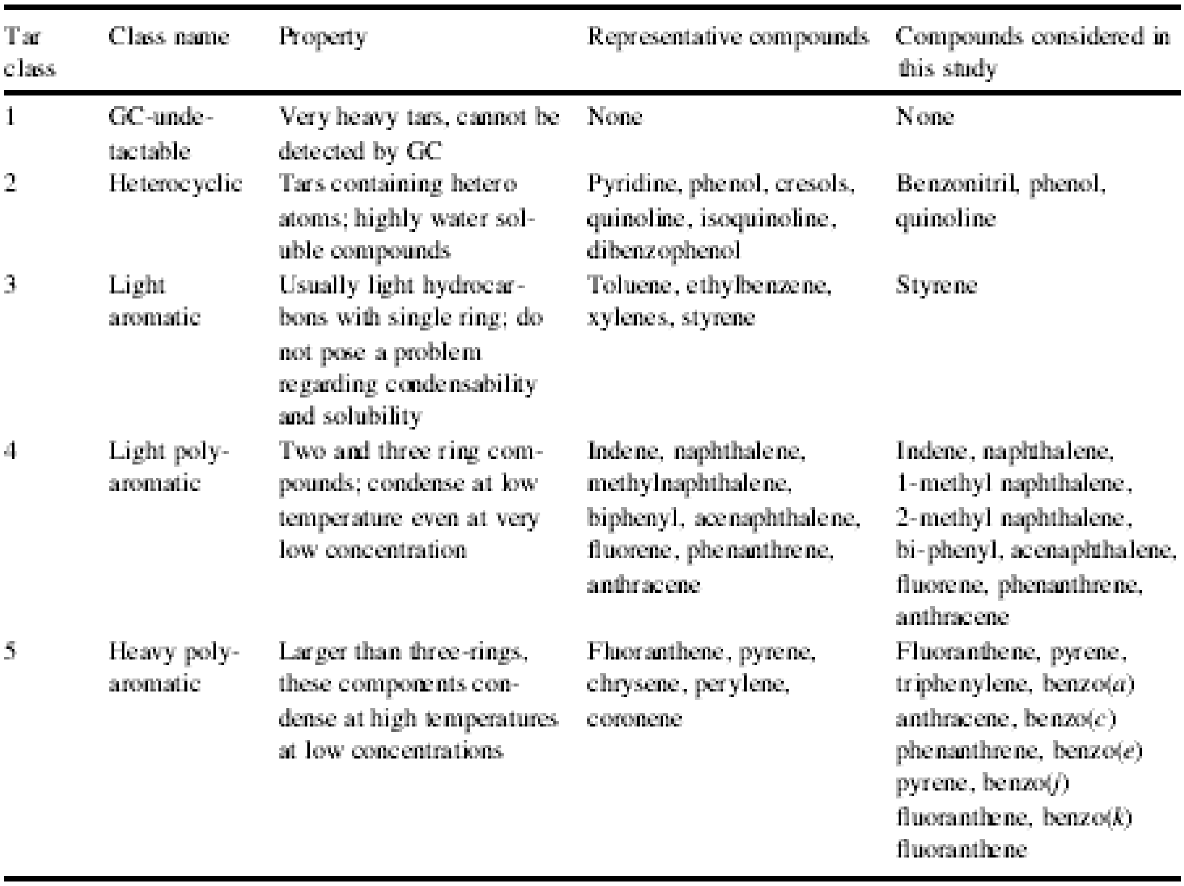


**Figure 4.1:** Tar Classes Reported by Milne et al. [15]

A different classification of tars was proposed by Corella et al, that consisted of six lumps that according to a reaction mechanism were inter-dependent. The six lumps were benzene, 1-ring compound, naphthalene, 2-ring compounds, 3 & 4-ring compounds and phenolic compounds. Perez et al. and Corella et al. suggested two main groups of tars namely “easy to destroy” consisting of the more reactive tar species and “hard to destroy” defining the less reactive tar species [15].

A classification of tars based on the solubility and condensability given in Table 4.1 of tars was developed by Energy Research Centre of The Netherlands (ECN), Toegepast Natuurwetenshappelijk Onderzoek (TNO) and University of Twente (UT) within the project “Primary measures for the inhibition/reduction of tars in biomass fuelled fluidized bed gasifiers” funded by the Dutch Agency for Research in Sustainable Energy (SDE) [15].

**Table 4.1:** Tar Classification Developed By ECN, TNO and UT [15]



| Tar class | Class name | Property | Representative compounds | Compounds considered in this study |
|---|---|---|---|---|
| 1 | GC-undetactable | Very heavy tars, cannot be detected by GC | None | None |
| 2 | Heterocyclic | Tars containing hetero atoms; highly water soluble compounds | Pyridine, phenol, cresols, quinoline, isoquinoline, dibenzophenol | Benzonitril, phenol, quinoline |
| 3 | Light aromatic | Usually light hydrocarbons with single ring; do not pose a problem regarding condensability and solubility | Toluene, ethylbenzene, xylenes, styrene | Styrene |
| 4 | Light poly-aromatic | Two and three ring compounds; condense at low temperature even at very low concentration | Indene, naphthalene, methylnaphthalene, biphenyl, acenaphthalene, fluorene, phenanthrene, anthracene | Indene, naphthalene, 1-methyl naphthalene, 2-methyl naphthalene, bi-phenyl, acenaphthalene, fluorene, phenanthrene, anthracene |
| 5 | Heavy poly-aromatic | Larger than three-rings, these components condense at high temperatures at low concentrations | Fluoranthene, pyrene, chrysene, perylene, coronene | Fluoranthene, pyrene, triphenylene, benzo(*a*) anthracene, benzo(*c*) phenanthrene, benzo(*e*) pyrene, benzo(*j*) fluoranthene, benzo(*k*) fluoranthene |

## 4.2 Tar Removal

The selected tar removal method should be an efficient and economically feasible process. It must not affect the formation of valuable gases on the contrary it should increase their yield. Tar removal can take place in the gasifier or in a secondary reactor or in auxiliary equipments as represented in Figure 4.2. The second reactor may reduce tars catalytically or thermally. Auxiliary equipments such as cyclones, filters, scrubbers, etc. can be utilized as mechanical methods for tar removal [16].

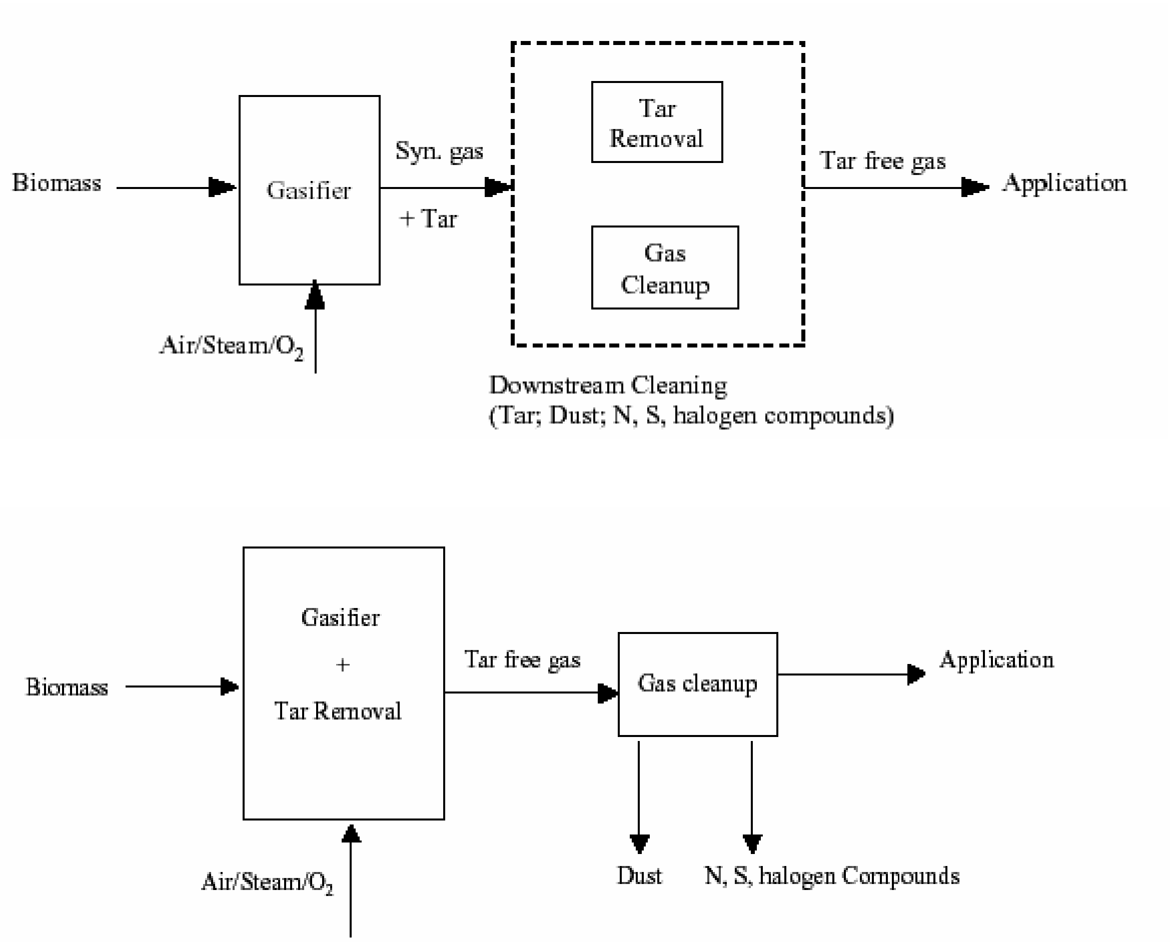


**Figure 4.2:** Tar Removal Methods [16]

Even though there are published results indicating effective tar removal by secondary reactors and auxiliary equipments, these methods are usually not economically viable. Tar reduction during gasification would eliminate the secondary methods. Many researchers have conducted studies on optimization of the gasification reactions in order to obtain a tar free gas. Corella et al. reported that product gases from a downstream catalytic reactor and a gasifier with dolomite as bed material had tar contents in the same order magnitude. The design and the operation conditions of a gasifier affect considerably the quality of the product gas; the points that should be taken into account while designing the gasifier are as follows:

1- The selection of the operating conditions,
2- The selection of the most suitable bed additives or catalysts,
3- The design of the gasifier.

The bed additives promote several chemical reactions, which do not only change the composition but also the heating value of the product gas. Agglomeration, thus bed chocking, is prevented by the introduction of active bed material into the gasifier.

Limestone is one of the first gasification additives, early works showed that even a 25% addition of limestone into the silica sand bed improved considerably the gas composition, heating value and yield, at the same time prevented agglomeration of the bed [16].

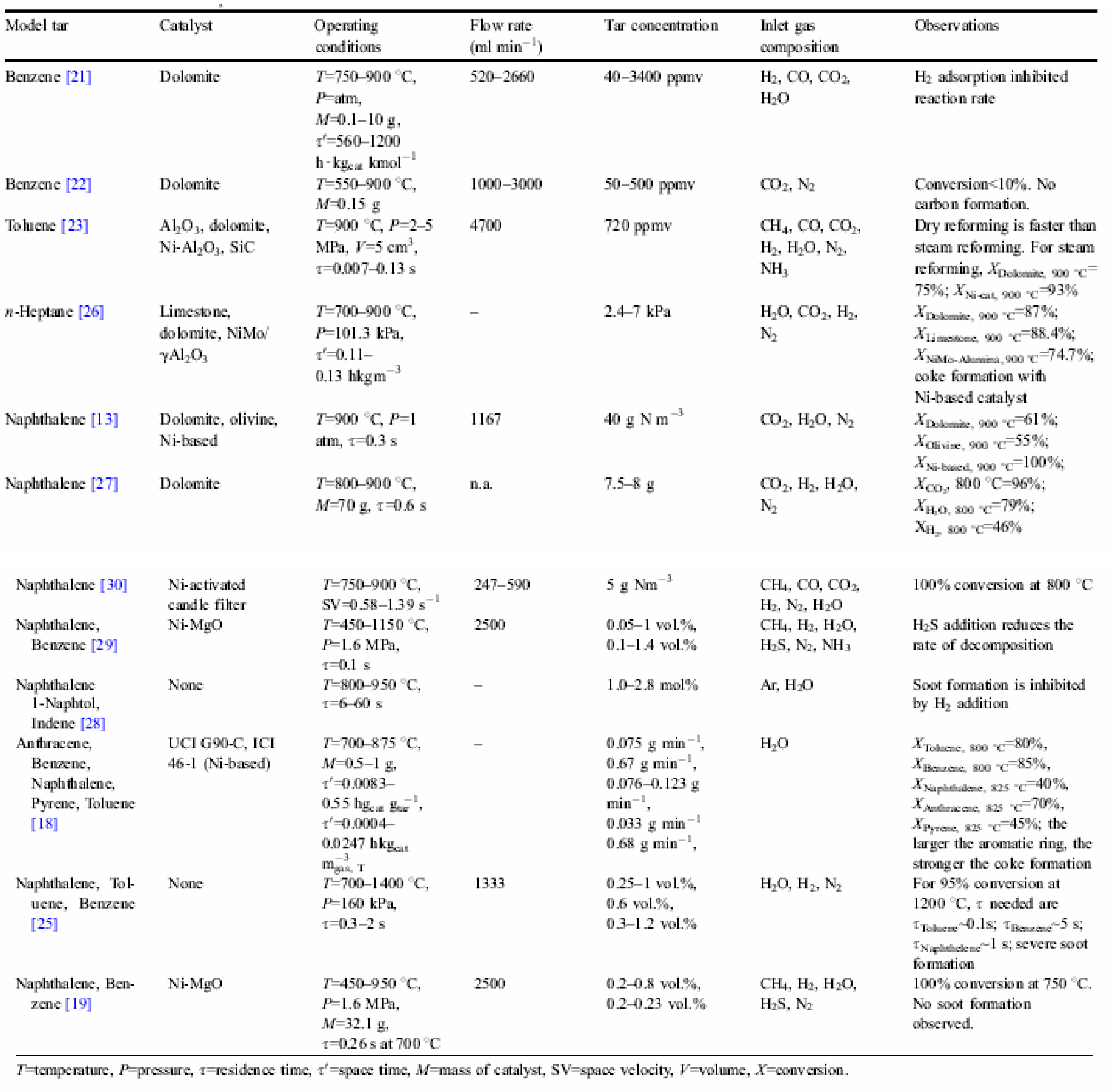
## 4.3 Catalytic Gasification

Tar and dust contents of the producer gas from a gasifier are important parameters in whether this gas can be used in an internal combustion engine or fuel cells. Besides producing a suitable gas feed for engines or fuel cells, tar cracking and reforming during gasification processes increases the overall efficiency and the gas yield. In addition to that the catalytic gasification processes require less heat requirement and achieve higher carbon conversions. Thus catalytic gasification received considerable interest from the gasification technology. Studies on coal/biomass gasification have two main purposes, which are listed below [8].

1. Understanding the kinetics of gasification which involves active mineral matters;
2. Designing process where these catalysts can be used.

A review of the catalysts used in gasification is given in Table 4.2. The gasification temperature is lower when catalysts are used. This favours product composition under equilibrium conditions and provides a high thermal efficiency. The catalytic processes can only compete with non-catalytic processes when the catalysts are inexpensive and have a high activity at low temperature.

**Table 4.2:** Review of Catalysts Used in Gasification [17]



| Model tar | Catalyst | Operating conditions | Flow rate (ml min$^{-1}$) | Tar concentration | Inlet gas composition | Observations |
|---|---|---|---|---|---|---|
| Benzene [21] | Dolomite | $T$=750–900 °C,<br>$P$=atm,<br>$M$=0.1–10 g,<br>$\tau'$=560–1200 h · kg$_{cat}$ kmol$^{-1}$ | 520–2660 | 40–3400 ppmv | $H_2$, CO, $CO_2$, $H_2O$ | $H_2$ adsorption inhibited reaction rate |
| Benzene [22] | Dolomite | $T$=550–900 °C,<br>$M$=0.15 g | 1000–3000 | 50–500 ppmv | $CO_2$, $N_2$ | Conversion<10%. No carbon formation. |
| Toluene [23] | $Al_2O_3$, dolomite, Ni-$Al_2O_3$, SiC | $T$=900 °C, $P$=2–5 MPa, $V$=5 cm$^3$,<br>$\tau$=0.007–0.13 s | 4700 | 720 ppmv | $CH_4$, CO, $CO_2$, $H_2$, $H_2O$, $N_2$, $NH_3$ | Dry reforming is faster than steam reforming. For steam reforming, $X_{\text{Dolomite, 900 °C}}$= 75%; $X_{\text{Ni-cat, 900 °C}}$=93% |
| $n$-Heptane [26] | Limestone, dolomite, NiMo/ $\gamma Al_2O_3$ | $T$=700–900 °C,<br>$P$=101.3 kPa,<br>$\tau'$=0.11– 0.13 hkgm$^{-3}$ | – | 2.4–7 kPa | $H_2O$, $CO_2$, $H_2$, $N_2$ | $X_{\text{Dolomite, 900 °C}}$=87%;<br>$X_{\text{Limestone, 900 °C}}$=88.4%;<br>$X_{\text{NiMo-Alumina, 900 °C}}$=74.7%; coke formation with Ni-based catalyst |
| Naphthalene [13] | Dolomite, olivine, Ni-based | $T$=900 °C, $P$=1 atm, $\tau$=0.3 s | 1167 | 40 g N m$^{-3}$ | $CO_2$, $H_2O$, $N_2$ | $X_{\text{Dolomite, 900 °C}}$=61%;<br>$X_{\text{Olivine, 900 °C}}$=55%;<br>$X_{\text{Ni-based, 900 °C}}$=100%; |
| Naphthalene [27] | Dolomite | $T$=800–900 °C,<br>$M$=70 g, $\tau$=0.6 s | n.a. | 7.5–8 g | $CO_2$, $H_2$, $H_2O$, $N_2$ | $X_{CO_2}$, 800 °C=96%;<br>$X_{\text{H}_2\text{O, 800 °C}}$=79%;<br>$X_{\text{H}_2\text{, 800 °C}}$=46% |
| Naphthalene [30] | Ni-activated candle filter | $T$=750–900 °C,<br>SV=0.58–1.39 s$^{-1}$ | 247–590 | 5 g Nm$^{-3}$ | $CH_4$, CO, $CO_2$, $H_2$, $N_2$, $H_2O$ | 100% conversion at 800 °C |
| Naphthalene, Benzene [29] | Ni-MgO | $T$=450–1150 °C,<br>$P$=1.6 MPa,<br>$\tau$=0.1 s | 2500 | 0.05–1 vol.%,<br>0.1–1.4 vol.% | $CH_4$, $H_2$, $H_2O$, $H_2S$, $N_2$, $NH_3$ | $H_2S$ addition reduces the rate of decomposition |
| Naphthalene 1-Naphtol, Indene [28] | None | $T$=800–950 °C,<br>$\tau$=6–60 s | – | 1.0–2.8 mol% | Ar, $H_2O$ | Soot formation is inhibited by $H_2$ addition |
| Anthracene, Benzene, Naphthalene, Pyrene, Toluene [18] | UCI G90-C, ICI 46-1 (Ni-based) | $T$=700–875 °C,<br>$M$=0.5–1 g,<br>$\tau'$=0.0083– 0.55 hg$_{cat}$ g$_{tar}^{-1}$,<br>$\tau'$=0.0004– 0.0247 hkg$_{cat}$ m$^{-3}_{\text{gas, T}}$ | – | 0.075 g min$^{-1}$,<br>0.67 g min$^{-1}$,<br>0.076–0.123 g min$^{-1}$,<br>0.033 g min$^{-1}$<br>0.68 g min$^{-1}$, | $H_2O$ | $X_{\text{Toluene, 800 °C}}$=80%,<br>$X_{\text{Benzene, 800 °C}}$=85%,<br>$X_{\text{Naphthalene, 825 °C}}$=40%,<br>$X_{\text{Anthracene, 825 °C}}$=70%,<br>$X_{\text{Pyrene, 825 °C}}$=45%; the larger the aromatic ring, the stronger the coke formation |
| Naphthalene, Toluene, Benzene [25] | None | $T$=700–1400 °C,<br>$P$=160 kPa,<br>$\tau$=0.3–2 s | 1333 | 0.25–1 vol.%,<br>0.6 vol.%,<br>0.3–1.2 vol.% | $H_2O$, $H_2$, $N_2$ | For 95% conversion at 1200 °C, $\tau$ needed are $\tau_{\text{Toluene}}$~0.1s; $\tau_{\text{Benzene}}$~5 s; $\tau_{\text{Naphthalene}}$~1 s; severe soot formation |
| Naphthalene, Benzene [19] | Ni-MgO | $T$=450–950 °C,<br>$P$=1.6 MPa,<br>$M$=32.1 g,<br>$\tau$=0.26 s at 700 °C | 2500 | 0.2–0.8 vol.%,<br>0.2–0.23 vol.% | $CH_4$, $H_2$, $H_2O$, $H_2S$, $N_2$ | 100% conversion at 750 °C. No soot formation observed. |

$T$=temperature, $P$=pressure, $\tau$=residence time, $\tau'$=space time, $M$=mass of catalyst, SV=space velocity, $V$=volume, $X$=conversion.

In a review that was published by Nishiyama the following remarks were presented.

1. The salts of alkali, alkaline earth and transition metals are active gasification catalysts.
2. The activity of a particular catalyst depends on both gasifying agent and gasification conditions.
3. When alkali and alkaline earth metal salts are used as catalysts in steam or carbon dioxide gasification, the main mechanism involves the transfer of oxygen from the catalyst to carbon through the formation and decomposition of a C-O complex [8].

Calcium is very active in the initial period during which it is well dispersed in the other promoter catalyst. However with the increase in conversion, also known as burn-off, the activity drops [8].

The catalyst in gasification is very short lived and effective only while it is in contact with the substrate, which itself changes, therefore a catalytic gasification system is more complex then other heterogeneous catalytic systems. Because of that the definition of activity for such systems is not very clear.

Along with the proceeding of gasification, changes in catalyst dispersion and increases in catalyst to carbon ratio occur which in return results in higher reaction rate when alkali metal catalysts are used. Changes in catalyst surface are due to pore opening and in the chemical state of the catalyst can be the other possible explanations of rate increase. Agglomeration of catalyst particles, cocking, reaction with sulphur or other trace elements are examples of the changes that cause catalyst deactivation.

The nature of the substrate and the gasification conditions directly affects the activity of the catalyst. The main properties of the substrate that is related to the activity are as follows

1. The reactivity of the carbonaceous constituents,
2. Catalytic effect of minerals,
3. The effect of minerals on the activity of the catalyst [8].

Some of the general trends in literature on the factors affecting the activity of the catalysts in coal as well as biomass gasification are given below:

1. Effect of coal rank: Nickel catalysts are more effective with low rank coals as they are more dispersed on them. The efficacy of potassium does not depend on coal rank. Coal rank given by carbon content is not an appropriate parameter in assessing the catalyst activity.
2. The surface area of coal char is related to the activity of the catalyst. It can be explained for the case where the amount of catalyst is large enough so that the active sites can cover the surface area. The conversion is almost proportional to the initial surface area when the catalyst is immobile.
3. Pretreatment of the substrate sometimes has an increasing effect on the rate. Although pretreatment can not always be directly applied; suitable blending or processing might have a positive effect.
4. Mineral matter can promote the reaction or deactivate the catalyst. For example, some minerals like alkali and alkaline earth metals catalyze the

reaction whereas some like silica and alumina deactivates the catalyst by interacting with it. Demineralization generally enhances the activity for potassium; it has a slight effect on the activity of calcium or nickel.

The activity of catalyst also depends on catalyst loading. The definite contact of catalyst with solid and gaseous reactants has to be ensured while loading. When catalysts are loaded from an aqueous solution, a finer dispersion of hydrophobic carbon surface compared to a hydrophilic surface is observed.

The further advantages to the overall process by catalyst are as follows.

- Increase in the rate of gasification,
- Prevention of swelling and agglomeration, and
- Promoting the methanation equilibrium [8].

### 4.3.1 Molten Medium Gasification

Molten medium gasification is the term used to define gasification processes where the feed is transported by salts of alkali metals or iron. The salts of alkali metals and iron do not only catalyzes the reaction but they also serve as a heat exchanger and provide the required heat. Two of the main commercial processes are Kellogg molten salt process and Altgas molten iron coal gasification. [8]

In Kellogg molten salt process, the coal/biomass is transported in a bath of molten sodium carbonate. The gasification agent is steam and it passes through the bath. The steam-coal reaction is strongly catalyzed by sodium carbonate, therefore the gasification is completed at relatively low temperature. Due to dispersion of coal/biomass and steam throughout the reactor by molten salt, direct gasification of coal/biomass happens without carbonization. Uniform temperature throughout the medium results in a tar free product gas [8].

Coal/biomass is injected with steam or air into a molten iron bath where steam dissociation happens along with the thermal cracking of coal/biomass volatile matters generating hydrogen and carbon monoxide in Altgas molten iron coal gasification. This process enables to capture and recover sulphur. It is a low temperature gasification process therefore mechanical problems related to feeding are discarded. In Altgas molten iron gasification process, serious factors such as coking properties, ash fusion temperature, coal/biomass fines, sulphur content are no longer problematic. It is a very flexible system in regard of the physical and chemical properties of the coal/biomass for example the pre-treatment of coarse particles is not needed. Tar elimination is achieved by operation at high temperature. A product gas with 1:3 $CO/H_2$ is obtained [8].

# 5. CATALYSTS

## 5.1 Natural (Abundant) Catalysts

### 5.1.1 Dolomite

Dolomite ($CaMg(CO_3)_2$) is a very abundant mineral rock and an inexpensive tar cracking catalyst in both steam and dry reforming processes. The usual practice is to use calcined dolomite (CaO.MgO) as bed material in biomass gasification in fluidized bed. Dolomite prevents agglomeration to a certain extent when biomass with high alkali content is gasified in a fluidized bed. The porosity of dolomite increases with calcinations, it becomes fragile and erodes. Even though it is an effective tar eliminating catalyst under the operating conditions, the product gas has rarely a tar content less than 2 $gm^{-3}$, therefore the usual application is to use it as a preliminary agent [18].

Studies in which dolomite is used in secondary reactors can be found in literature. However the results obtained by Corella et al. indicated that the lower heating values of the gases leaving a fluidized bed gasifier and a downstream catalytic reactor operating with dolomite had no difference. The tar level was considerably reduced by dolomite addition into the bed material in the fluidized bed gasifier. A tar content of 1 $gm^{-3}$ was reported for a bed material that contained 20-30% dolomite. Besides in the case when dolomite is present in the system, the operating conditions have a major influence on the production of the clean gas [16].

Lepalathi and Kurkela's work on atmospheric fluidized bed air gasification of peat showed that the tar levels were reduced to one half at 820 $^0$C. In a later work Kurkela et al. reported that dolomite was more effective when it was used in a secondary reactor rather than in a primary fluidized bed [19].

Guaxing et al. gasified wood in a pressurized fluidized bed in the presence of dolomite. They observed that the yield of naphthalene and polycyclic hydrocarbons in tar increased along with the yield of $H_2$ when dolomite and/ or steam was present in the system [19].

According to the studies of Lammers et al., a secondary feed of air into the gasifier helps to keep the activity of dolomite longer and effectively reduces the tar components including naphthalene. Carbonated rocks convert PAH more easily than benzene. Simell et al. reported that CO is a strong inhibitor of the tar decomposition on dolomite [19].

Alden et al. observed that the tars remaining in the gas stream after catalytic cracking in the presence of dolomite were non-polar. At 900 $^0$C 99.9% of the naphthalene was converted. The tar produced in steam gasification is more phenolic, thus easier to convert than the one from steam/$O_2$ gasification. Therefore increasing the ($H_2O$ + $O_2$)/biomass decreases the tar conversion [19].

Carbon deposition on the surface of dolomite was observed at 800 $^0$C when there was no steam present in the system. The same phenomenon was also reported for gasification processes operating under pressurized conditions. In order to prevent the deactivation of dolomite caused by carbon deposition under 10 bar, temperatures higher than 920 $^0$C are needed [19].

Dolomite has been used with other catalytically active substances in the aim of increasing the catalytic activity and/or the stability of both materials. Rice husk has a silica content of 95% and the producer gas from its gasification compared to producer gases from other raw materials contains lower amounts of naphthalene, which is the most stable tar component. Dolomite does not have a significant activity in the conversion of naphthalene. Myren et al. attempted to enhance the catalytic activity of calcined dolomite by the applying a layer of silica onto a layer of dolomite. Better results were obtained compared to the ones obtained when a mixture of dolomite and silica or dolomite alone was used. The naphthalene content and the amount of light tar in the gas were reduced considerably [13].

Devi et al. used calcined dolomite and olivine as additives to the sand bed in a fluidized bed gasifier. The additives increased the conversion of each tar class; the total tar conversions were 63 % and 46 % respectively. These values are lower than the results in literature which can be attributed to the fact that the additives only constituted 17 % of the sand bed. The authors concluded that the low activity of olivine was due to the fact that no pretreatment was done to olivine. Olivine has no porosity therefore there is no internal surface area where tar decomposition can take place. The iron content of olivine is believed to have a role in the moderate activity [15].

Simell et al. studied the effects of dolomite, limestone, iron sinter, nickel based catalysts, alumina and alumina silicate in hot cleaning of gasification gas. The results obtained from these materials were compared with the ones from the experiments conducted with the reference materials, silicon carbide and alphaalumina. The tests demonstrated that carbonate rocks and nickel based catalysts are the most efficient catalysts in tar cracking. The gasification gas from the updraft gasifier contained thermally unstable phenolic and aliphatic tar compounds, these compounds were converted even in the presence of inert materials whereas the tar from the fluidized bed consisted of thermally stable aromatic compounds such as benzene and naphthalene which could not be converted with SiC at 900 $^0$C. When the most active catalyst was present in the system, almost equilibrium gas composition was obtained. The conclusion drawn from the experiments were in accordance with literature that hydrocarbons were decomposed and $H_2$ and CO formation occurred via steam or $CO_2$.The results showed that dolomite and limestone were active tar cracking catalysts only when they were calcined and in order to keep them active, the operational temperature had to be around 900 $^0$C and the pressure near atmospheric pressure [20].

### 5.1.2 Olivine

Olivine is a natural occurring mineral that contains magnesium, iron oxide and silica and has $(Mg, Fe)_2SiO_4$ as chemical formula. The mineral has a Mg/Fe ratio of 9/1. It was first introduced as an tar eliminating catalyst at the end of 1990s.On the other hand, it is not as widely found as dolomite. Investigations showed that iron has an enhancing effect on tar elimination which can account for the catalytic activity of olivine. Olivine has a comparable mechanical strength to sand even at high temperatures. The particulate matter generated during gasification is negligible and does not cause significant pressure drop like dolomite [16, 18, 21].

Rapagna demonstrated that the gas yield increased 50% when the inert sand was replaced by olivine particles in the fluidized bed gasifier with steam as the gasifying agent. The tar and char were reduced by 20 fold and 30 percent respectively. The $H_2$, CO, $CO_2$ contents of the product gas increased but the methane remained the same. Consequently Rapagna et al. concluded that neither dolomite nor olivine were active in methane reforming. The operating temperature above 800 $^0$C favours the catalytic activity of olivine. Comparing the heating values of the product gases per kilogram of biomass revealed that the one obtained in the presence of olivine was 7% less than dolomite [21].

Kienneman and Cols at Strasbourg increased the activity of olivine by generating a new Ni-olivine catalyst. Hofbauer and Rapagna used this catalytic material in fluidized bed gasification with pure steam and reported good results. However Corella et al. reported poor catalytic activity when Ni-olivine was used in biomass gasification with air. In accordance with the findings of Rapagna et al. the catalyst became deactivated quickly and required periodic regeneration. Corella et al. demonstrated that sintered olivine behaved like silica sand and its activity dropped due to loss of pore structure. The tar content of raw gas was 7000-8000 mg $m^{-3}$ [18].

### 5.1.3 Alkali and Alkaline Earth Metals

The alkali and the alkaline earth metal oxides are considered to be one of the best catalysts for steam gasification. The chloride forms of these metals such as NaCl and KCl have low prices that make them very attractive even though their catalytic activities especially in coal gasification are lower than the carbonates of these metals. The low activity is due to the strong affinity between metal cation and chloride anion. Takada et al. tried to make chloride free Na and K by an ion exchange technique. The ion exchange took place between alkali metals and brown coal from an aqueous solution of alkali chloride, the pH of which was adjusted with ammonia. The remaining chloride was completely removed afterwards by water washing. A considerable increase in steam coal gasification was observed when the Cl free catalyst was used and it is as catalytically active as alkali carbonates. It was found that during gasification the active species had a carbonate form and it was easily recovered. The physical mixing of K-exchanged coal with higher rank coals promote the rate of coal gasification, which is sometimes an effective way to prepare catalyst. Potassium is a suitable catalyst for physically mixing method. Some researchers who worked with the combination of potassium carbonate and magnesium nitrate in steam gasification of brown coal reported that the coal ash and used catalyst formed a potassium silicate complex fertilizer. Encinar et al. applied steam gasification to eucalyptus char in the presence of alkaline chloride as catalyst. The process rate increased with the presence of catalysts in the system. Increasing the catalyst concentration had a positive effect up to a certain level, exceeding this level caused saturation and blockage of the pores that hindered the gas diffusion into the active sites resulting in a drop of conversion and reaction rate [8, 9].

The work of Skodras and Sakellaropoulos with Greek lignite demonstrated that there is a good correlation between the alkali index which is an indicator of the alkali content. According to their results, the specific gasification rate (k) changed almost linearly with alkali index during hydrogasification and dry reforming. Calcium, which usually found bound to the organic structure, is the most effective metal cation in gasification. The alkali content of ash is a parameter that affects the rate of gasificiation.Ca concentration has a more significant effect under $CO_2$ and $H_2$ atmospheres. However, according to the authors the gasification rate changed linearly with Ca concentration in hydrogasification, which contradicts the literature. There was no evident correlation between gasification rate and the concentration of other alkali metals such as Na, K, etc. The gasification rate under both $CO_2$ and $H_2$ atmospheres increased initially, then decreased in the presence of Mg. Fe had no effect on hydrogasification rate and no correlation could be found for dry reforming [22].

Calcium in the form of oxide was used as the catalyst of the hydrogasification reaction in a process developed by Batelle. The results obtained from experiments showed there was a reasonably good correlation between calcium content and the reactivity of coal chars with $CO_2$. It should be noted that other alkali metal compounds particularly chlorides and carbonates of sodium and potassium can increase the rate of gasification 35 to 60 %. Iron, magnesium and zinc oxides are also found to accelerate gasification by 20 to 30 % [8].

The major component of the inorganic part of the grapefruit skin char is potassium and the reactivity of carbonised grapefruit skin char in $CO_2$ and steam gasification was studied by Marquez-Montesinos et al. The results showed that the reactivity increased as the $CO_2$ gasification progressed indicating that the development of porosity accompanied by higher surface area and the presence of active species in the inorganic matter of the starting material. The metal to carbon ratio increased with the consumption of the carbon while the gasification process proceeded. According to Exxon with the impregnation of 10 to 20 % of potassium carbonate, the optimum temperature and pressure for steam gasification of bituminous coal reduced from 982 to 760 $^0$C and from 2.18 to 1.09 atm. Potassium hydroxide was preferred in their commercial scale plant design [8, 23].

Catalyst development plays a key role in the progress of novel biomass and coal conversion technologies. The most important problem encountered with catalysts in the gasification processes is the short live of catalysts due to deactivation by coke formation and difficult regeneration. According to Mochida and Sakanishi the next generation gasification processes will perform catalytic gasification at 500-750 $^0$C and they will have alkali metal salts supported on a particular type perovskite type oxide (LSCMP) as catalyst. Mochida and Sakanishi used $K_2SO_4$ on LSCMP for calcined charcoal gasification and compared the results with $K_2SO_4$. The results indicated the activity of $K_2SO_4$ on LSCMP was much higher than $K_2SO_4$ at the same conditions. Even a small amount of the catalyst had a slowing down effect on the gasification and a long time around 40 000 seconds was needed to complete the reaction. Gasification with the same amount of $K_2SO_4$ could not be completed.

$K_2SO_4$ is given as a poor catalyst in the literature and it has to be ion exchanged onto the coal surface. Therefore the $K_2SO_4$ on LSCMP has to be activated before gasification [24].

The gasification of wastepaper under $CO_2$ atmosphere proceeds mainly according to the Boudouard reaction, which is not feasible even at temperatures as high as 973 K. Jin et al. studied the effects of molten carbonate salts such as potassium, sodium and lithium carbonates on this process. The dispersion of wastepaper into the molten salts improved the contact with $CO_2$ flowing through the molten phase which in return facilitated the Boudouard reaction and increased significantly the reaction rate. Intermixtures of potassium, lithium and sodium carbonate have higher activity. Heating rate is an important factor in the determination of the end products. This process was reported to use $CO_2$ as a reactant; therefore it helps the reduction of green house emissions [25].

Alarcon et al. reported a 79% conversion of naphthalene used as a model compound for tar in steam gasification when a physical mixture of 10% CaO and 90% MgO was used as catalyst. A synergistic effect of the mixture was explained by the catalytic cooperation of separated CaO and MgO [26].

During thermal decomposition, alkali metals especially potassium promote the unzipping of the cellulose chains of woody biomass, which in return influences the product gas composition thus the heating value. Douglas et al. observed a five fold reduction of phenolic tar compounds and a ten fold reduction in PAH when 8 % potassium carbonate was used as bed additive impregnated on wood in steam gasification [16].

### 5.2 Ni Based Catalysts

The formation of hydrogen rich gas from biomass that can be used in fuel cells has a high potential of being one of the most important energy production means in the future. The hydrogen rich gas however has to have tar and CO contents less than 1 % by volume for this application. There have been a number of works on the catalytic elimination of tars which in return rendered the gas more amenable for commercial applications and increased the overall efficiency of the gasification process. Nickel based catalysts have been used as an alternative or together with calcined dolomite. Ni based catalysts are considered to be one of the most effective catalysts for syngas production. The reported works in the literature suggest that a ratio of $H_2/CO$ close to 2 could be obtained in the presence $NiO/Al_2O_3$ with only traces of olefins in the gas stream; therefore it is favourable for gasification. The experiments conducted by Bilbao et al. showed that an addition of 50 % of Ni-Al into the bed material increased the $H_2$ yield by 62% with a considerable decrease in methane. Ni/Al coprecipitated catalysts are observed to be highly effective in $CO_2$ gasification of biomass. Ni based catalysts can also decompose light hydrocarbons with high heating values, which is desired when synthesis gas is produced [16,27,28].

Zhang et al. fed the raw gas from biomass gasification to a catalytic reactor containing Ni based commercial steam reforming catalysts and reported a tar reduction of 99%. It should be noted that a guard bed of dolomite was used before the second reactor. The catalyst showed no activity loss for 12-18 hours of testing. The catalytic reactor had a positive impact on $H_2$ and $CO_2$ amounts in the product gas in the expense of CO content [29].

$H_2O$ is a very important reactant in tar elimination processes with Ni based catalysts. Ni based catalysts convert tar by steam reforming. According to the mechanism proposed by Corella et al. Ni liberates .OH radicals which then cut or open the rings of polyaromatic carbons that are the most abundant species in tar. The ratio of $H_2O/C$ in the product gas has an important role in coke removal, which directly influences the life of monolith, and it changes with the moisture content of the biomass and the steam/water fed to the system [18, 30].

Rapagna et al. conducted biomass steam gasification in a two stage system, which consisted of a fluidized bed gasifier and a secondary catalytic fixed bed reactor. When fresh catalyst was utilised, the gas composition was close to equilibrium conditions of the water-gas shift reaction. The methane was completely converted to CO and $H_2$. A 60% by volume of $H_2$ composition was reached in the product gas, which is compatible with the fuel cell feeding requirements. In the case of dolomite as the fluidized bed material, the gas yield continuously increased. The authors explained this fact with the catalytic effect of the alkaline compounds within the accumulating char. The particulate matter within the product gas increased with the depreciation of dolomite. However, increase in the overall gas yield was reported when dolomite was present in the system. Utilisation of exhaust catalyst resulted in an increase of the overall gas yield in the same order of magnitude. The major encountered problem both with dolomite and nickel based catalysts was the continuous pressure drop within the fixed bed reactor. The cause of pressure drop was the carbon deposition onto the first layer that came into contact with the gas. The addition of alkaline metals to the catalysts reduced the carbon deposition, but it

was not the ultimate solution. The sulphur content of the biomass is another cause of catalyst deactivation due to poisoning of Ni-based catalyst [28] .
NiO enhances considerably the yield of product gas; however a support is needed with a definite chemical structure that makes the material resistant to mechanical stresses. Courson et al. used olivine for this purpose. The iron content of the olivine is a factor in nickel structure stabilization. The catalyst was calcined at different temperatures. The results showed that olivine preserved its initial structure throughout the experiments. A 95% methane conversion and 80% hydrogen yield was achieved at 750 and 800 $^0$C, indicating that the impregnation of nickel on olivine did not cause a significant deactivation and accessible nickel sites existed on the support. The carbon deposition was very low and the catalyst showed good ageing behaviour [31].

Arauzo et al. worked with a modified Ni-Mg aluminate and stochiometric $NiAl_2O_4$ catalyst. Potassium was added as a promoter. The physical strength of the catalyst was achieved by partial replacement of Ni by Mg. However the amount of char increased significantly. The same catalyst was used in a fluidized bed pyrolysis and reforming experiments. A product gas with a tar content less than 100 $ppm_w$ of feed was obtained at 600 $^0$C [19].

Particles within the fuel gas reduce the activity of Ni based commercial catalysts (rings) in tar elimination. Honeycomb structured monolithic catalysts might be a solution for the particulate problem. However it should be taken into account that the monolithic catalysts require adiabatic operation conditions due to the endothermic reactions and temperature gradients occurring within them. Corella et al. reported that monoliths had activities close to dolomite. Even though hot gas cleaning is a requirement for commercial steam reforming catalysts, they are more feasible than monoliths. The life span of monoliths is very short and they need periodical regeneration. They can become feasible if only their life span becomes longer [30].

The catalytic activity of the catalyst decreases due to the reduction in dispersion, which is a consequence of the migration and aggregation of particles. Sintering of Ni catalyst happens when Ni is deposited on a support, usually on alumina, at very high temperatures. It should be noted that sintering also favours the coke deposition on the catalyst, which in return reduces the surface area. Introducing potassium based compounds into the catalyst can prevent to a certain extent the carbonization and polymerization reactions by reduction the acidity of the support material [32].

Definite chemical structures such as perovskite where the catalysts are inserted in rather than dispersed on are proposed as a solution for activity loss due to sintering and coke deposition, however some of the specific surface area is lost. Perovskite is an inert material that has two compatible elements and a general chemical formula of $ABO_3$.Studies on methane reforming where Ni based catalysts inserted in perovskite were used, showed that the nickel sintering and coke deposition are not completely eliminated. $LaNi_{0.3}Fe_{0.7}O_3$ catalyst was used by Rapagna in secondary catalytic reactor. According to the experimental setup, the raw gas from steam gasification in a fluidized bed reactor, the bed material of which was olivine, passed through the catalytic reactor. The operating temperature of the conditioning process of the hot raw gas from fluidized bed gasification was around 800 $^0$C. The presences of $H_2$ and large excess of steam in the gas stream were observed to have positive effect on Ni perovskite catalyst. $H_2$ helped to prevent the oxidation of metallic Ni sites which in return partially hindered deactivation. The results showed a very low level of tar content, less than 0.2 percent of dry gas was achieved with perovskite catalyst. Methane reduction and increase in hydrogen production in the presence of pervoskite catalyst makes it a potential catalyst for catalytic conditioning processes, which will provide hydrogen rich gases for fuel cells [32].

One of the major drawbacks of the Ni based catalysts is the deactivation due to coke deposition on the catalyst surface. Alkali addition into nickel was suggested by Zang for preventing the coke deposition. In fact during steam reforming, the coke formation on the catalyst surface is reduced according to the reaction given in equation 5.1[29].

$$C + H_2O \rightarrow CO + H_2 \qquad \textbf{(5.1)}$$

NiMo obtained by an impregnation procedure, eliminated almost 100% of tar after 10 hours of testing at 550 $^0$C and no deactivation was observed in a period of several days. The coke deposition was only in small amounts due to hydrogenation of the coke precursors. CRE Group Ltd compared the activity and cracking pattern of dolomite and Ni/Mo catalyst for reducing tars from an updraft gasifier. Although Ni/Mo had a higher activity, the more favourable cracking pattern without any coke formation was observed with dolomite. Ni/Mo had to operate in the range of 400-600 $^0$C in order to prevent carbon deposition [19, 43].

Ni-dolomite catalyst tested by Wang et al., was also deactivated by carbon decomposition. A sharp deactivation of the catalyst was observed between the first ten hours. Deactivation continued slowly for 25 hours. The regeneration of the catalyst was achieved under saturated wet air at 700 $^0$C after half an hour. The product gas had a higher content of $H_2$ and lower content of light hydrocarbons compared with thermal cracking [33].

Addition of Lanthanum to Ni-Al catalyst significantly improved the gas yield and reduced the coke formation in the steam gasification of biomass and dry reforming of methane. The CO content in the product gas increased with the presence of La in the catalyst. During the experiments conducted in a fluidized bed reactor no elutriation or attrition was observed [34].

A catalytic filter containing $Al_2O_3$ (2.5 wt %), Ni (1wt %) and MgO (0.5 wt %) removed all the naphthalene and benzene in the gas stream when $H_2S$ is absent. The benzene conversion increased at higher temperatures and benzene loading whereas the conversion of naphthalene dropped moderately when naphthalene loading was increased in the gas stream. The operational temperature was reduced by 50 $^0$C, which resulted in a considerable cost reduction in equipment and prevented problems such as blocking due to sintering of ashes [14].

## 5.3 $ZnCl_2$ Catalysts

Encinar et al. used NaCl, KCl, LiCl, $AlCl_3$. $6H_2O$ and $ZnCl_2$ as additives in the gasification/pyrolysis of grape bagasse. Increase in char yield and decrease in liquid formation were observed with all additives except for KCl. Likewise gas phase was also reduced in the presence of additives except for $AlCl_3$. $6H_2O$.When alkali metal additives were used, the fixed carbon content was higher. The product gas contained mostly CO which was followed by $H_2$ and methane. $H_2$ production significantly increased with Zn and was 5 to 8 times higher than at the presence of other additives. The productions of methane and CO were always the lowest with Zn. The fraction yields and gas production indicated that $ZnCl_2$ promoted the depolymerization process resulting in strong carbonization in other words high solid yields and higher hydrogen formation as a consequence of strong liquid phase cracking when it was compared with the case of no-additives. Higher $H_2$ yields were accompanied by low methane production, which was inhibited by the high concentration of $H_2$ [5].

According to Shafizadeh at low temperature or at the presence of inorganic additives, pyrolysis starts with dehydration, which is followed by decarboxilation, slow depolymerization and the recombination of the decomposition products to produce a carbonaceous char. If a pyrolysis process is conducted at high temperature, macromolecules are brokendown by intramolecular transglycosylation to anhydroglucose units that are then converted into lower molecular weight volatiles. Increasing the concentration of $ZnCl_2$ up to a certain level increased the formation of solid product and decreased the liquid and gaseous product except for hydrogen [5].

## 5.4 Novel Catalysts

$Rh/CeO_2/SiO_2$, first developed by Tomishige and Cols in Japan, can reduce the tar content of the raw gas by 99% but it requires a very low biomass throughput and it has a very high production cost. These catalysts are suitable for syngas production from biomass. Asadullah et al. reported that 94% carbon in the cellulose was converted to a product gas, which consisted mainly of $H_2$ and CO, at 550 K in a fluidized bed gasifier. The same conversion was achieved by a commercial steam reforming catalyst at 700 K. Steam addition into system improved considerably the performance of the catalyst. The completion of the carbon conversion and a high $H_2$ formation were attained at 500 K and $H_2O/C$ of 0.35 [18, 35].

Mixed oxides (Ni, Co, Fe) and noble metals (Pd, Rh, Ru, Pt, Ir) are reported to be highly active during the conversion of methane to synthesis gas by partial oxidation. In steam or dry reforming and partial oxidation of methane Ru and Rh have the highest catalytic activity. They are followed by Ni. Pd and Pt have a lower activity then Ni. Co and Fe have the lowest activity. Transition metal substituted hexaaluminates have also been investigated for their excellent thermal stability and catalytic activity [36, 37].

Hao et al. compared the catalytic activities of Ru/C, Pd/C, $CeO_2$ particles, nano-$CeO_2$ and nano-$(CeZr)_xO_2$ in the gasification of cellulose and sawdust under supercritical water and in the presence of CMC [$C_8H_{11}NaO_7$]. Mixing CMC with water and biomass formed a uniform and stable viscous paste that could be efficiently gasified. All of the catalysts enhanced the water-gas shift reaction and more hydrogen, carbon monoxide and less carbon dioxide were produced in their presence. Among all these catalysts Ru/C had the largest surface area and the highest catalytic activity for gasification. Although Pd/C had many similar properties to Ru/C such as large surface area, its catalytic activity was less. Ru metal had a higher activity than Pd was the conclusion drawn from these results. It was observed that in the presence of Ru/C and CMC, a 10% cellulose sample could be gasified almost completely at 500 $^0$C and 27 MPa with a yield of 11-15 g hydrogen per 100 g feedstock [38].

Zirconia is a selective catalyst and has an unusual set of acidic, basic, oxidising and reducing surface properties. It has also been used as a promoter and support. The pyrolysis of peat in the presence of zirconium oxide resulted in high conversion and $H_2$/CO ratio in the product gas. Juutilainen et al. studied bulk zirconia and alumina zirconia catalyst in comparison with dolomite and nickel catalyst. During the preliminary experiments, the high $O_2$ dependency of toluene conversion was observed. For instance, in the presence of 1% oxygen, the toluene conversion reached 20%. However, the oxidation of $H_2$ and CO, an undesired side reaction, came along with the increasing oxygen concentration. Even at temperatures below 600 $^0$C, high conversions are obtained in the presence of $O_2$. At higher temperatures, the CO and $H_2$ oxidation reactions start to compete with the decomposition reactions of toluene and ammonia. The doping of zirconia with alumina improved the selectivity, therefore the oxidations of toluene and ammonia increased and the conversion of CO and $H_2$ decreased. The alumina doped zirconia has a resistance to hydrogen sulphide poisoning which is important in gasification applications [27].

Co has been reported as an effective catalyst for steam gasification of biomass, partial oxidation of methane, dry reforming of methane and steam reforming of ethanol. Furusawa and Tsutsumi used calcined Co/MgO in steam reforming of naphthalene. Results indicated that high and stable activity was obtained with low steam to carbon ratio and naphthalene feed. The product gas mainly consisted of $H_2$ and $CO_2$ [39].

Artificial catalysts made of rare earth metals as well as molybdenum oxide ($MoO_2$) have been used in steam and $CO_2$ gasification. Good results were obtained with these catalysts, however the activity of the rare earth compounds such as $La(NO_3)_3$, $Ce(NO_3)_3$ and $Sm(NO_3)_3$ decreased with increasing burn-off of the coal. Small amounts of Na or Ca were co-loaded in order to reduce this problem. The loading of rare earth metals was done by ion exchange method [8].

## 5.5 Other Types of Catalysts

Iron has a positive effect on the decomposition of tar Nordgreen et al observed low tar levels in the gasification gas from an atmospheric fluidized bed reactor when metallic iron was present in the system, therefore it could be utilised as an tar-depleting catalyst. The catalytic activity of metallic iron under pyrolysis conditions was in the range of the capability of dolomite, however the total gas production was lower. The experiments showed that the tested iron oxides had no catalytic activity in depleting tar [21, 40].

$Al_2O_3$ was used as a bed additive in a Lurgi circulating fluidized bed. Mehrling and Reimert reported that a tar free gas was produced by this process [19].

LCM-5 a commercial catalyst with a chemical content of 37.2% of $Al_2O_3$ and 0.50 % of $Fe_2O_3$ was used in the catalytic pyrolysis of heavy oils to light olefins by Xiang-hai.The results indicated that more than 65 wt % of feedstock was cracked and the yield increased with increasing temperature. The cracked gas contained 75 to 80 % light olefins [41].

Porous particles have the ability of retaining organic gases at temperatures below 673 K above which the gases started to decompose on the particle. Shimizu et al. demonstrated that the porous particles were good alternative bed additives for fluidized bed incinerators. According to Inami et al. soot free gas with high calorific value was obtained when porous particles were used in the gasification of plastics. Namioka et al. used activated alumina and zeolite in a circulating fluidized gasifier as the bed material. A significant tar reduction and increase in both CO and $H_2$ were achieved at 873 K was observed. The yield of $H_2$ was as three times as without the porous particles [42].

Y-zeolite catalyst eliminated almost 100% of tar after 10 hours of testing at 550 $^0$C and no deactivation was observed in a period of several days. The coke deposition was only in small amounts due to hydrogenation of the coke precursors. [43]

H-zeolite catalysts are effective in the removal of the chlorinated hydrocarbons from the flue gas by combustion and considered as an alternative to the noble and metal oxide catalysts [44].

# 6. EXPERIMENTAL

## 6.1 TGA Experimental Setup

The gasification experiments were conducted in a TG 41 thermogravimetric analyzer from Shimadzu Co. The apparatus had a Pt-Rh alloy thermocouple as temperature sensor. The maximum temperature that could be reached was 1773 K. A cylindrical sample cell made of alumina with a diameter of 10 mm and height of 14 mm was used in the experiments. The illustration of the experimental apparatus is given in Figure 6.1.

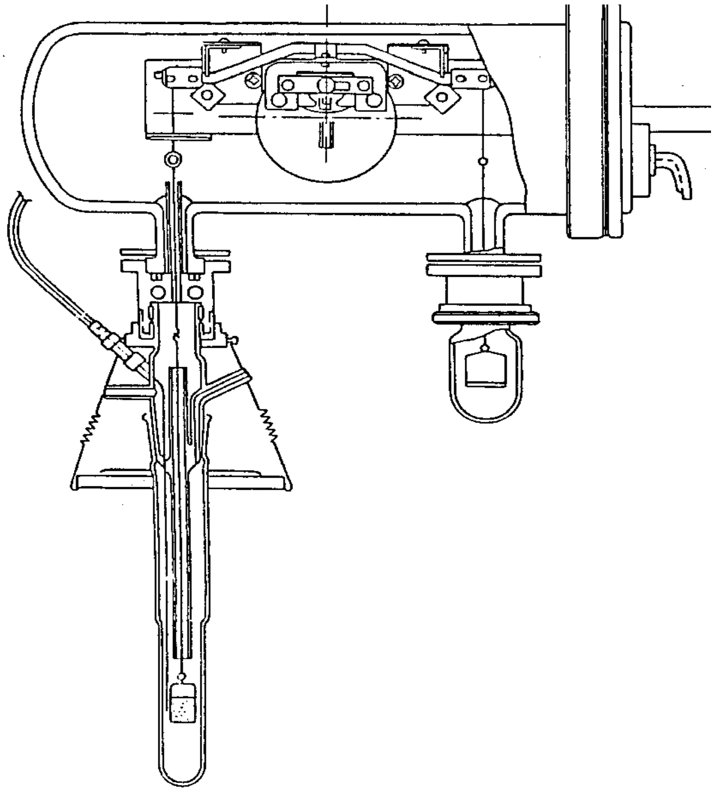


**Figure 6.1:** Illustration of TG 41

All of the experiments were conducted under the same conditions given in Table 6.1. The atmosphere within the chamber was $N_2$ and the changes in the sample mass and temperature versus time were recorded at a speed of 2.5 mmsec$^{-1}$. A four-step temperature program given in Figure 6.2 was applied. The samples were heated to 378, 673, 923 and 1223 K and kept at these temperatures for 10, 30, 30 and 300 minutes respectively. The heating rate throughout the experiments was 25 Kmin$^{-1}$. Individual thermogravimetric analyses were conducted for sunflower seed shell and each six catalytic materials. In these analyses, the initial sample mass was 40 mg. The experiments investigating the effect of catalytic materials on sunflower seed shell used a 42 mg initial mass consisting of 40 mg of sunflower seed shell and 2 mg of catalytic material.

**Table 6.1 :** Experimental Conditions

| | TGA of sunflower seed shell and each of the six catalytic material | Experiments with blend |
|---|---|---|
| Gasifying agent | $N_2$ | $N_2$ |
| Flow rate of the gasifying agent | 40 mlmin$^{-1}$ | 40 mlmin$^{-1}$ |
| Heating rate | 25 Kmin$^{-1}$ | 25 Kmin$^{-1}$ |
| Recording speed | 2.5 mmmin$^{-1}$ | 2.5 mmmin$^{-1}$ |
| Maximum temperature | 1223 K | 1223 K |
| Initial sample mass | 40 mg | 42 mg |

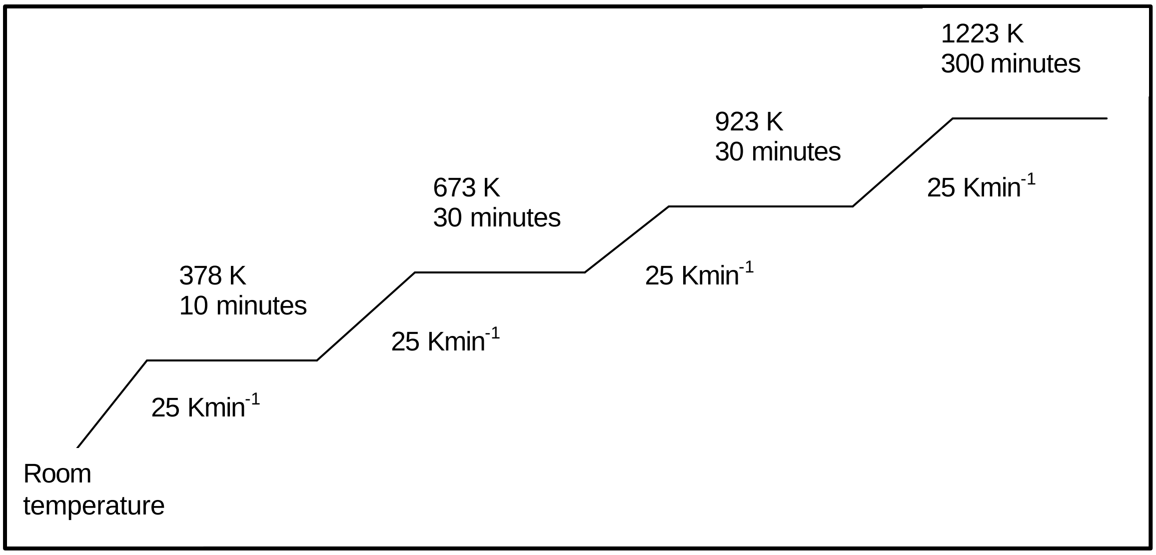


**Figure 6.2:** Temperature Program

## 6.2 Experimental Setup and Conditions for Pyrolysis

The experiments were conducted in batch mode. In each experiment a 10g biomass sample was used. The blends with the catalysts consisted of catalysts with an amount of 5 wt % of biomass feed, and the biomass sample itself. The total initial mass for the experiments with the blends was 10.5 g. After the biomass alone or the blends were fed into the reactor, the reactor was purged with $N_2$ for 20 minutes at room temperature. Then the reactor was placed within the tube furnace where it was heated to the pre-selected temperatures with a heating rate of 20 $Kmin^{-1}$. The temperature program of the experiments is given in Figure 6.3. The data obtained during the TG analysis was the basis of the design of the temperature program applied in the pyrolysis experiments. The maximum weight loss occurred in the interval of 673-773 K; therefore the maximum temperature for the experiments was set to 773 K. The sample lost its moisture during the heating up period The CO, $CO_2$, $CH_4$ contents were determined by GASMET DX-Series FTIR Gas Analyzer.

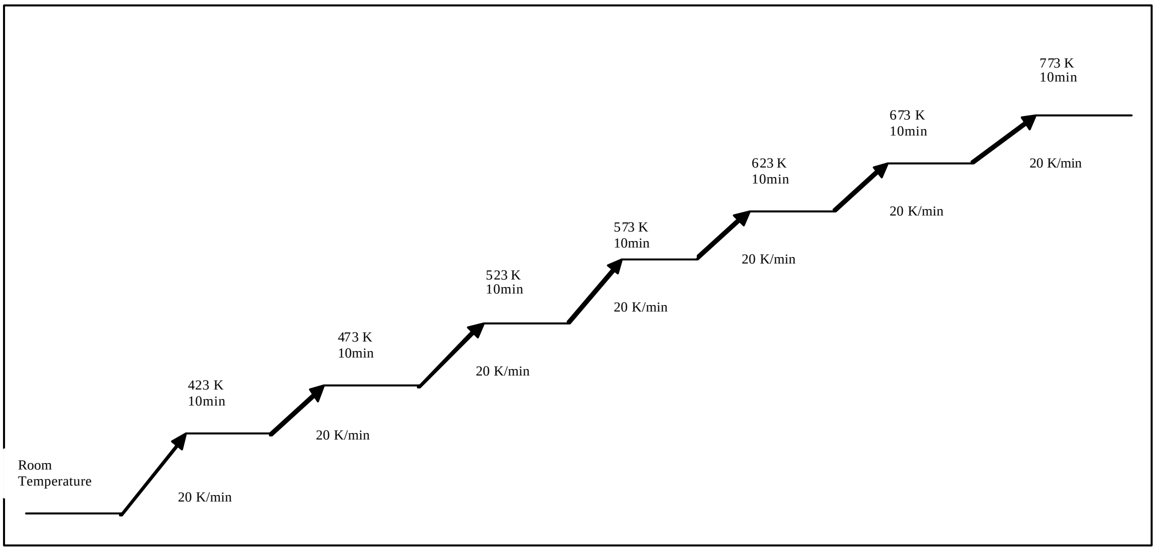


**Figure 6.3:** The Applied Temperature Program during The Pyrolysis Experiments

The experimental setup used during the experiments is given in Figure 6.4. The pyrolysis experiments were conducted in a Pyrex reactor placed within a tube furnace through which the process heat was supplied. The inert atmosphere within the system was $N_2$ and it has a flow rate of 1 $lmin^{-1}$. The product gas passes through a condenser where the moisture and some of the tar was retained. The gas then flew into a microfibre filter where the rest of the tar and particulate matter was captured. A flowmeter was placed right after the filter so that the volumetric flow rate of the total gas leaving the system can be monitored. A stream of the clean product gas was fed into a dilution unit where it was diluted with He and sent to the FTIR. The gas flow to the FTIR has a flow rate of 3,92 $lmin^{-1}$. The rest of the product gas was vented.

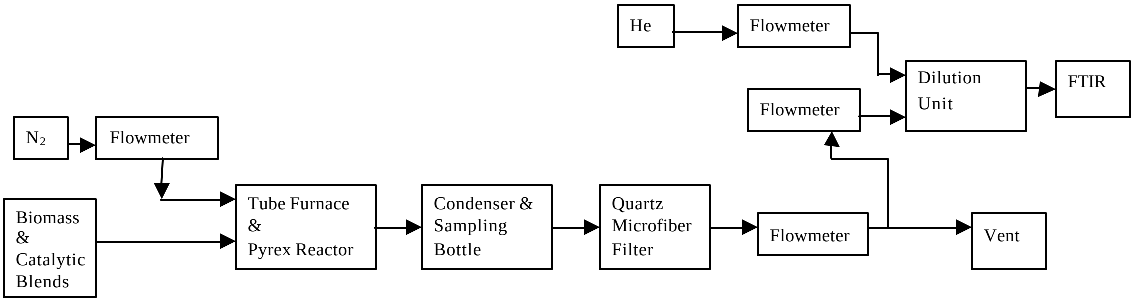


**Figure 6.4:** The Pyrolysis Experimental Setup

## 6.3 The Biomass Sample

The starting material of the experiments was sunflower seed shell from Tekirdag and had moisture content of 10.3 % [45]. The desired particle size (< 250 µm) of the biomass sample was obtained by grinding and sieving. The proximate and the higher heating value analyses were performed according to ASTM standards. The ultimate analyses were carried out using Euro EA 3000 elemental analyzer. The proximate and ultimate analysis data of the biomass sample used in the experiments are tabulated in Table 6.2. The lower and higher heating values of the biomass sample are 16 and 17.6 MJ/kg respectively [45 ]. The lignin, holocellulose and a-cellulose contents of the biomass sample are given in Table 6.3.

**Table 6.2:** Proximate and Ultimate Analysis Data of Sunflower Seed Shell [45]

| Proximate analysis (dry basis) | | |
|---|---|---|
| Ash | wt% | 3.6 |
| Volatile Matter | wt% | 84.7 |
| Fixed Carbon | wt% | 11.7 |

| Ultimate analysis (dry ash free basis) | | |
|---|---|---|
| C | wt% | 51,9 |
| H | wt% | 6,2 |
| N | wt% | 0 |
| O | wt% | 41,9 |

**Table 6.3:** Extractives, Lignin, Holocellulose and ?-Cellulose Content of The Biomass Sample on Dry Basis and The Analysis Methods Used. [45]

| | wt % | Method of Analysis |
|---|---|---|
| Extractives | 13.8 | ASTM-D1105 [46] |
| Lignin | 31.4 | Van Soest Method [47] |
| Holocellulose | 62.5 | $NaClO_2$ - acetic acid extraction [48] |
| a-cellulose | 25.6 | TAPPI T203 om-88 standard [49] |

## 6.4 The Catalytic Materials

The catalytic effects of six materials on the gasification of sunflower seed shell under $N_2$ atmosphere had been investigated in this study. The materials were; natural catalysts such as limestone, dolomite, zeolite, olivine and $Na_2CO_3$ and $K_2CO_3$. Limestone, dolomite, natural olivine and zeolite were calcined at 1173 K under dry air for 1 hour. Analytical grade $Na_2CO_3$ and $K_2CO_3$were used and no pre-treatment was applied. The properties of limestone, dolomite, zeolite and olivine are given in Table 6.4.

**Table 6.4:** Properties of The Natural Catalysts [50-52]

| Species | Limestone from Çanakkale [50 ] | Dolomite from Sivrihisar-Eskisehir [50 ] | Olivine Burhaneli Bursa [51 ] | Zeolite Bigadiç [52 ] |
|---|---|---|---|---|
| Chemical Properties | | | | |
| $CaCO_3$ (wt%) | 92 | 20.3 | - | - |
| MgO (wt%) | 2.4 | 22.6 | 42.1 | 2 |
| $P_2O_3$ (wt%) | 0.2 | - | - | - |
| $Al_2O_3$ (wt%) | 1.6 | 1.9 | 1.9 | 12.7 |
| $Fe_2O_3$ (wt%) | - | 0.3 | 9.6 | 1.3 |
| $SiO_2$ (wt%) | 1.1 | 13.3 | 35.7 | 60 |
| Other | 2.7 | 40.7 | 10.7 | 24 |
| Moisture (wt%) | - | 0.9 | - | - |
| Particle size distribution | 420- 710 µm | Less than 250 µm | Less than 250 µm | Less than 250 µm |

# 7. RESULTS AND DISCUSSIONS

## 7.1 Results of the TGA

In this study the effect of six catalytic materials on the gasification of sunflower seed shell, chosen as the biomass sample was discussed. The remaining mass after drying was taken as the basis of the calculations. The ultimate analysis of sunflower seed shell showed that the biomass sample had a high volatile matter and low ash percentages; therefore a high yield of gas product was expected. The TGA data obtained during the pyrolysis of sunflower seed shell confirmed this expectation; an almost complete conversion was reached. On the DTG of the biomass sample, which can be seen in Figure 7.1, two following peaks occurring in the interval of 416-575 K were observed. The maximum rate was obtained at 518 K and had a value of 6.45 mg/min. The gasification reached completion after 2.8 hours. The very low amount of solid residue can be explained by the effect of alkali metals in the structure which enhanced the formation of fly ash. The produced fly ash is carried out from the system with the gasification agent.

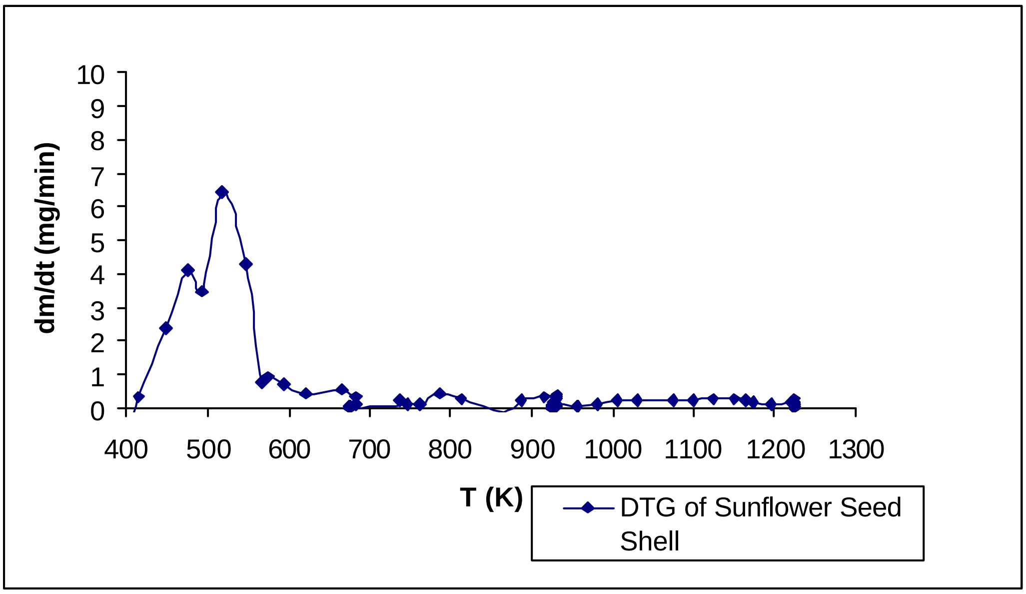


**Figure 7.1:** The DTG of The Sunflower Seed Shell

Calcined olivine did almost not change during thermal analysis, only a small peak of 0.71 mg/min was observed. However this peak was not observable on the DTG of the blend, due to small amount of catalyst present in the system. The DTGs of the biomass sample, calcined olivine and blend are plotted in Figure 7.2. When the DTG of the sunflower seed shell and the blend was compared the continuing two peaks seen in the sunflower seed shell alone was not observed on the DTG of the blend.

The peak observed on the DTG of the blend was the sum of the peaks of the conversion of hemicellulose and cellulose. The total conversion reached in the presence of calcined olivine was 74%. The maximum rate observed with blend was around 8.7 mg/min at 504 K, 2.2 mg/min higher than the one with the biomass sample, obtained at 518 K. The maximum peaks were observed between 450-550 K and 493 -595 K for the blend and sunflower seed shell respectively. It can be deduced from that, the thermolysis of lignins within the biomass sample shifted towards lower temperatures. The completion of the gasification process of the blend took 3.5 hours, which is almost half an hour more than the duration of the gasification of the biomass sample alone.

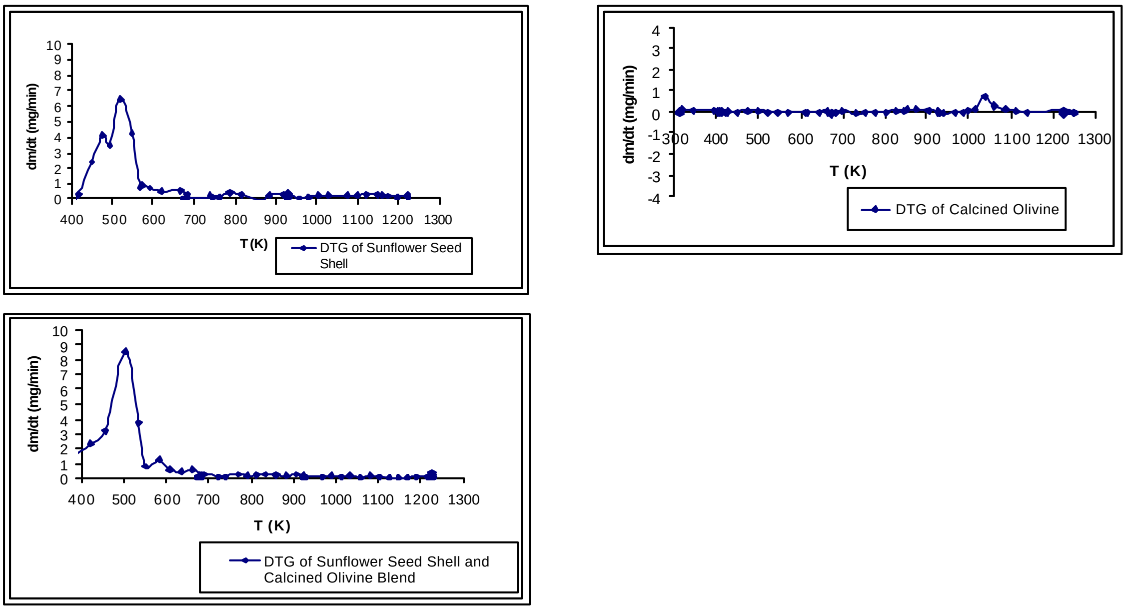


**Figure 7.2:** DTGs of The Sunflower Seed Shell, Calcined Olivine and The Blend

A peak with an intensity of 2.98 was observed at 1221 K on the DTG of calcined dolomite given in Figure 7.3, which was the maximum rate obtained in TGA of calcined dolomite. In the region from 976 to 1026 K an increase in the mass of the calcined dolomite was observed. This phenomenon could be explained by the gas adsorption and retention within the calcined dolomite sample. However the change in the mass was not very obvious in the gasification of the blend and no increase in the mass was observed for this temperature interval. Therefore it could be said that there had been a synergetic effect. The maximum rate increased from 6.45 mg/min to 7.71 mg/min. The maximum peak was observed at 514 K close to the one of the biomass sample. The continuous two peaks started at 406 K and ended at 671 K, which was a larger interval than the one of the biomass sample alone. The total conversion achieved was 89 %. The time of gasification was 5.9 hours and almost twice as the time of gasification of biomass sample alone and the total conversion was lower.

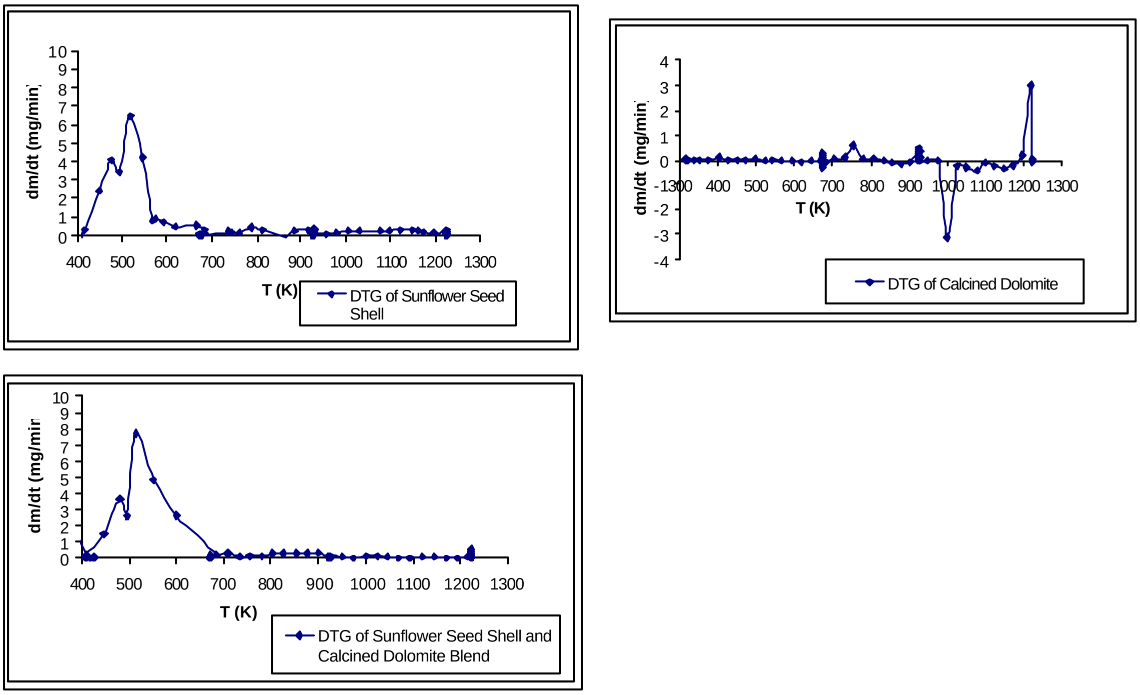


**Figure 7.3:** DTGs of The Sunflower Seed Shell, Calcined Dolomite and The Blend

The DTG of the calcined limestone given in Figure 7.4 had two peaks between 494-672 K and 826-937 K. These peaks could also be observed on the DTG of the blend, however they were smaller due to the small amount of the catalyst in the blend. The maximum rate of the blend was achieved at the same temperature as the one reached with the biomass sample but had a considerably higher value. Calcined limestone had an enhancing effect on the maximum rate. The maximum rate had a value of 8.85 mg/min. The first peak on the DTG of the blend is smaller than the biomass sample. The conversion of hemicelluloses was slower. The completion of gasification was achieved after 6.2 hours. An almost complete conversion like in the biomass sample was attained. The very low amount of solid residue can be explained by the effect of alkali metals in the structures which enhances the formation of fly ash. The produced fly ash is carried out from the system with the gasification agent.

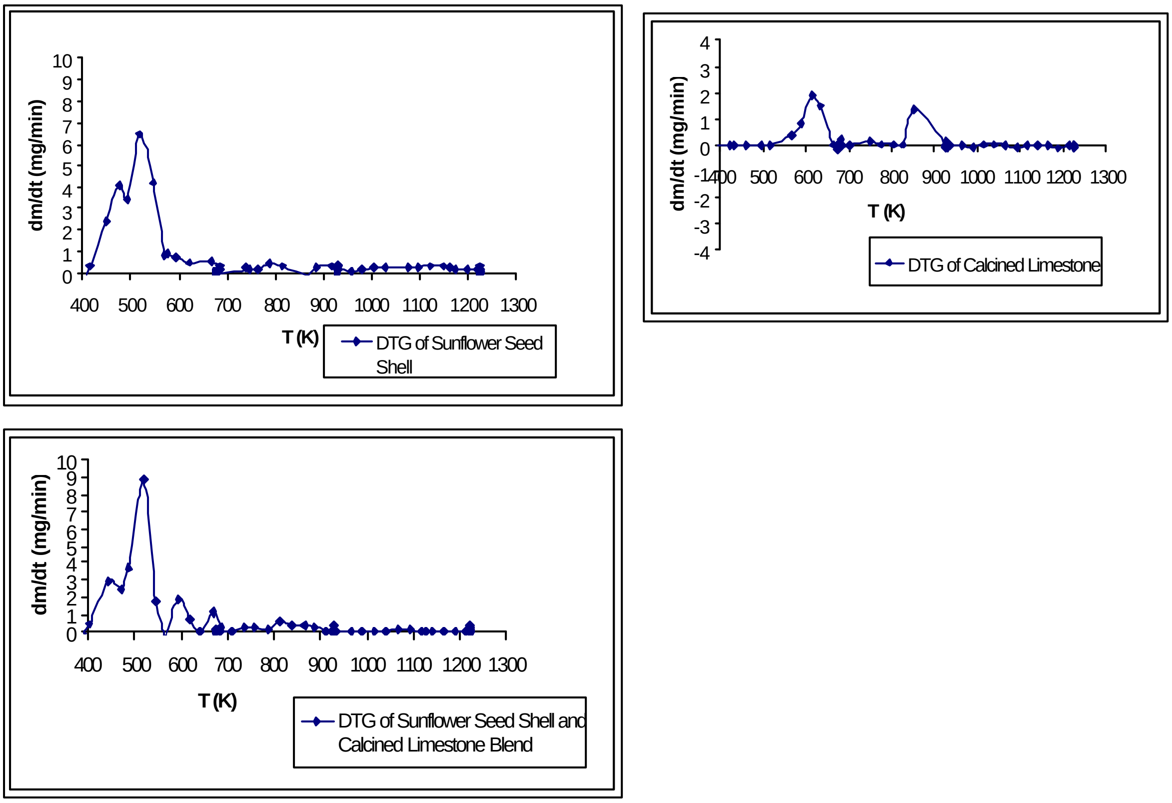


**Figure 7.4:** DTGs of The Sunflower Seed Shell, Calcined Limestone and The Blend

Similar to the phenomenon observed with calcined dolomite, increases in the mass are observed during thermal analysis of calcined zeolite However these increases were not present in the gasification of the blend. DTGs of the sunflower seed shell, calcined zeolite and the blend are given in Figure 7.5. The maximum rate was 8.74 mg/min at 543 K. Although a higher maximum rate was reached, the temperature at which it was observed was also higher. The completion of gasification took almost 7 hours. After 700 K a very slow conversion was observed, 66 % of the sample was converted. The very low amount of solid residue could be explained by the effect of alkali metals in the structures of the biomass and the catalyst which enhances the formation of fly ash. The produced fly ash is carried out from the system with the gasification agent.

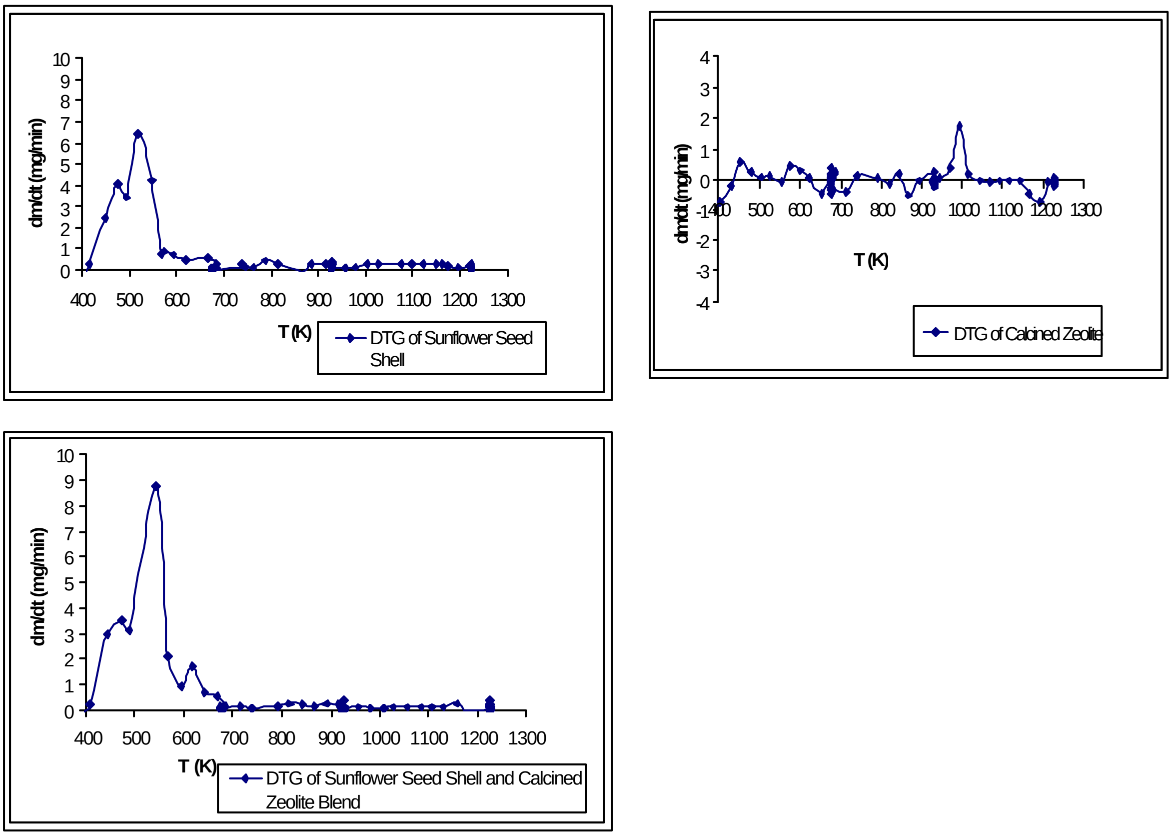


**Figure 7.5:** DTGs of The Sunflower Seed Shell, Calcined Zeolite and The Blend

The DTG of $Na_2CO_3$ showed no peaks. Instead of the continuous two peaks observed on the DTG of the biomass sample, only one sharp peak is present on the DTG of the blend. The temperature interval within which the peak took place was narrower than that the one of biomass sample. The maximum rate, reached at 490 K, had a considerably higher value of 9.15 mg/min. In the presence of $Na_2CO_3$ maximum rate increased. A slow but stable loss of mass continued till high temperatures. The gasification process took almost 3.4 hours and ended with an almost complete conversion. The very low amount of solid residue can be explained by the effect of alkali metals present which enhanced the formation of fly ash. The produced fly ash is carried out from the system with the gasification agent.

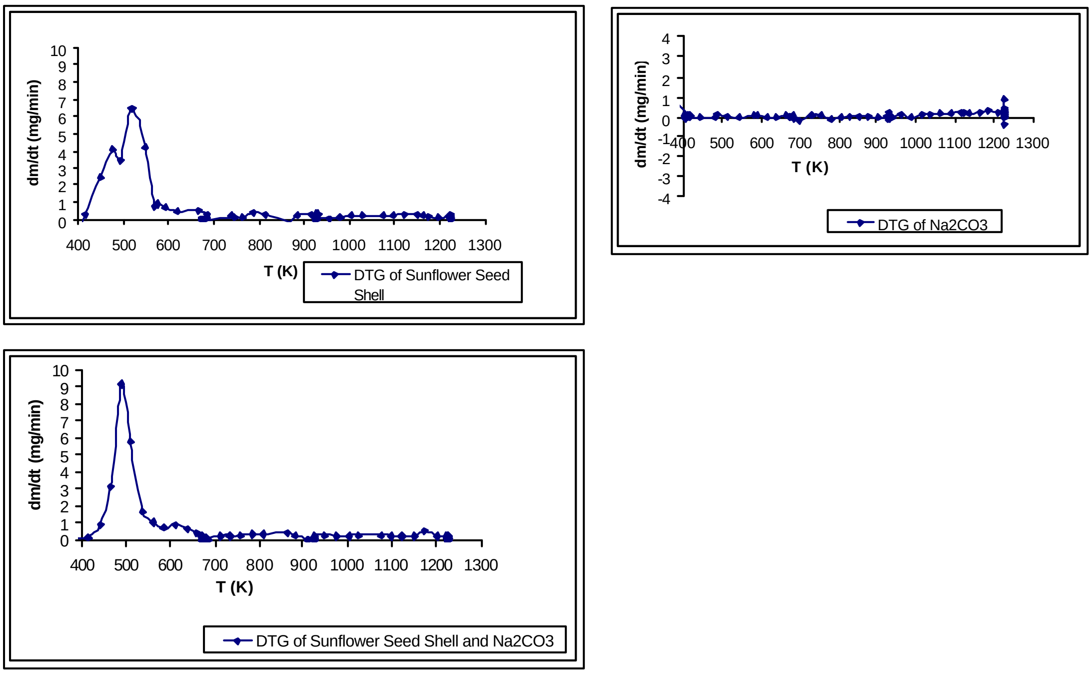


**Figure 7.6:** DTGs of The Sunflower Seed Shell, $Na_2CO_3$ and The Blend

On the DTG of $K_2CO_3$ a large peak was observed at 1223 K, indicating the decomposition of $K_2CO_3$ and the release of $CO_2$. This phenomenon could also be seen on the DTG of the blend; however the peak was smaller due to the low amount of $K_2CO_3$ in the blend. At high temperatures the conversion was due to the decomposition of the catalyst. Therefore operating at high temperatures is not recommended. On the DTG of the blend one broad peak instead of two could be seen. As in the case of $Na_2CO_3$ the maximum rate increased and reached the value of 8.23 mg/min at 518 K. An almost total conversion was reached after 3.4 hours. The very low amount of solid residue can be explained by the effect of alkali metals in the structures which enhances the formation of fly ash. The produced fly ash is carried out from the system with the gasification agent.

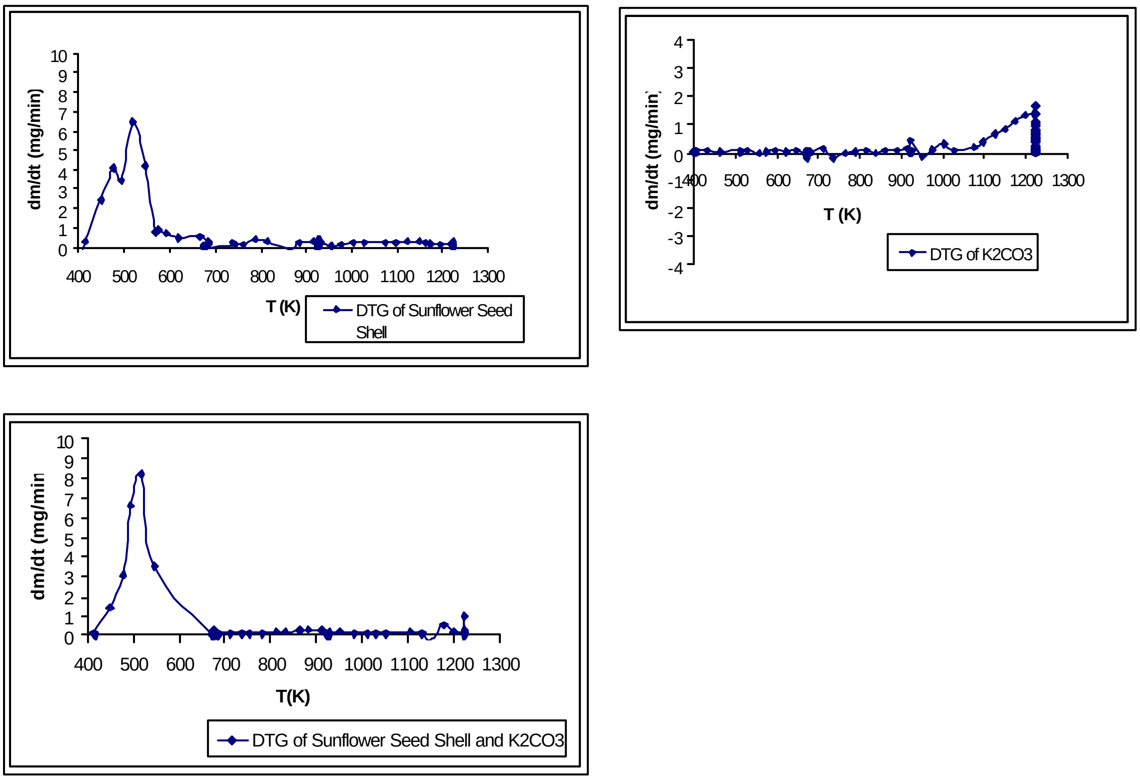


**Figure 7.7:** DTGs of The Sunflower Seed Shell, $K_2CO_3$ and The Blend

## 7.2 The Pyrolysis Experiments

FTIR analysis results of the gaseous products from the biomass sample are given in Table 7.1. Twenty one different chemical compounds could be identified from this analysis. Chloroform was detected as the dominant compound at 423, 473, 523, 623, 673 K. Besides, concentration of carbon monoxide at 573 K was so high that its concentration was the highest concentration detected for the sample throughout the experiments. When temperature reached 773 K, concentration of methane rapidly increased and methane became the most apparent compound at this temperature.

It was concluded that methane and propane concentrations almost increased linearly as temperature increased. The highest concentrations of low molecular weight saturated aliphatic hydrocarbons such as methane, ethane, and propane were determined in the gaseous product that obtained at the highest temperature. In contrast to this, higher molecular weight saturated aliphatic hydrocarbons such as butane, hexane, heptane, octane, and nonane had their maximum concentrations in the gaseous product forming at 423 K. This can be explained by the fact that these higher molecular weight saturated aliphatic hydrocarbons decomposed into smaller ones upon heating. Similarly, chloroform concentration also decreased as a result of increasing temperature.

**Table 7.1:** Gaseous Species from Pyrolytic Gasification Performed without Catalyst

| | | Temperature (K) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Compound | | 423 | 473 | 523 | 573 | 623 | 673 | 773 |
| Carbon monoxide | ppm | 0,0 | 16,9 | 2810,9 | 31754,8 | 2990,5 | 2758,6 | 2389,7 |
| Nitrogen dioxide | ppm | 570,4 | 1004,3 | 1216,8 | 320,3 | 613,3 | 705,6 | 2038,4 |
| Ammonia | ppm | 265,1 | 0,0 | 20,5 | 0,0 | 30,0 | 137,2 | 57,1 |
| Methane | ppm | 81,2 | 54,1 | 0,0 | 232,5 | 788,0 | 3223,9 | 8775,7 |
| Ethane | ppm | 441,2 | 181,2 | 179,1 | 434,5 | 320,7 | 366,5 | 1049,3 |
| Propane | ppm | 63,5 | 92,9 | 51,3 | 110,0 | 184,7 | 281,9 | 679,0 |
| Butane | ppm | 1186,1 | 67,5 | 215,3 | 120,6 | 141,8 | 74,4 | 168,8 |
| Hexane | ppm | 438,0 | 0,0 | 0,0 | 290,9 | 270,0 | 130,7 | 86,5 |
| Isohexane | ppm | 191,9 | 17,3 | 0,0 | 25,8 | 11,1 | 0,0 | 26,2 |
| Heptane | ppm | 547,6 | 26,5 | 0,0 | 0,0 | 64,0 | 135,5 | 289,8 |
| Octane | ppm | 192,0 | 9,7 | 0,0 | 0,0 | 18,4 | 8,2 | 44,1 |
| Nonane | ppm | 102,7 | 89,5 | 0,0 | 0,0 | 4,8 | 79,1 | 3,4 |
| Benzene | ppm | 190,9 | 260,3 | 108,8 | 22,6 | 0,0 | 215,6 | 166,6 |
| Toluene | ppm | 79,3 | 425,1 | 397,4 | 296,4 | 87,2 | 209,9 | 160,3 |
| m-Xylene | ppm | 213,2 | 45,5 | 128,6 | 233,6 | 203,1 | 174,7 | 68,5 |
| o-Xylene | ppm | 0,0 | 0,0 | 220,7 | 578,8 | 209,9 | 152,9 | 317,9 |
| p-Xylene | ppm | 0,0 | 50,8 | 69,8 | 120,6 | 143,5 | 31,9 | 39,1 |
| Formic acid | ppm | 508,7 | 108,8 | 118,9 | 7,2 | 98,7 | 55,1 | 14,3 |
| Methanol | ppm | 0,0 | 250,7 | 400,3 | 206,6 | 152,9 | 158,7 | 311,4 |
| Ethanol | ppm | 1223,4 | 460,2 | 0,0 | 179,7 | 775,2 | 695,0 | 320,0 |
| Chloroform | ppm | 12585,2 | 6258,7 | 7874,5 | 5928,5 | 3888,4 | 3296,2 | 2380,2 |

FTIR analyses results of the gaseous products obtained using catalytic materials are shown in Tables 7.2-7.7.

**Table 7.2:** Gaseous Species from Pyrolytic Gasification Performed with Dolomite

| | | Temperature (K) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Compound | | 423 | 473 | 523 | 573 | 623 | 673 | 773 |
| Carbon monoxide | ppm | 53,0 | 218,1 | 23282,8 | 95501,8 | 73827,4 | 9602,7 | 17569,6 |
| Ammonia | ppm | 224,4 | 0,0 | 184,1 | 0,0 | 73,1 | 48,8 | 0,0 |
| Methane | ppm | 20,0 | 89,5 | 95,1 | 450,6 | 4837,8 | 9813,3 | 40863,3 |
| Ethane | ppm | 127,7 | 74,4 | 544,7 | 106,2 | 764,7 | 1423,6 | 5484,7 |
| Propane | ppm | 163,4 | 133,2 | 424,4 | 632,0 | 1193,3 | 1459,1 | 2909,0 |
| Butane | ppm | 128,6 | 108,8 | 28,9 | 110,3 | 24,4 | 60,4 | 3,4 |
| Hexane | ppm | 421,6 | 134,2 | 181,2 | 422,3 | 97,5 | 126,7 | 16,0 |
| Isohexane | ppm | 27,5 | 25,2 | 41,0 | 103,0 | 110,3 | 142,5 | 150,5 |
| Heptane | ppm | 49,0 | 0,0 | 469,5 | 163,6 | 76,8 | 163,9 | 111,3 |
| Octane | ppm | 48,5 | 18,4 | 0,0 | 179,9 | 16,4 | 132,9 | 122,1 |
| Nonane | ppm | 26,7 | 30,4 | 92,5 | 0,0 | 3,0 | 9,1 | 24,9 |
| Decane | ppm | 33,6 | 0,3 | 0,0 | 11,7 | 2,6 | 0,0 | 59,0 |
| Benzene | ppm | 238,0 | 63,6 | 51,0 | 11,0 | 288,5 | 310,7 | 275,5 |
| Toluene | ppm | 248,5 | 202,4 | 122,8 | 5,5 | 269,3 | 226,3 | 303,0 |
| m-Xylene | ppm | 168,6 | 89,9 | 99,0 | 172,4 | 59,2 | 27,2 | 191,9 |
| o-Xylene | ppm | 0,0 | 213,4 | 0,0 | 0,0 | 191,1 | 0,0 | 347,4 |
| p-Xylene | ppm | 45,2 | 9,7 | 34,2 | 27,7 | 31,9 | 0,0 | 579,8 |
| Formic acid | ppm | 48,2 | 86,5 | 166,1 | 359,9 | 78,4 | 2,1 | 0,0 |
| Formaldehyde | ppm | 4,3 | 47,5 | 230,6 | 424,5 | 299,6 | 298,7 | 276,0 |
| Methanol | ppm | 0,0 | 109,8 | 2430,3 | 6307,2 | 5108,0 | 7348,5 | 2138,2 |
| Chloroform | ppm | 558,6 | 438,1 | 485,2 | 371,1 | 512,5 | 800,8 | 592,8 |

Blending the biomass sample with dolomite resulted in important variations in the compositions of the gases. For example, compared to the case without catalyst, carbon monoxide concentrations augmented unexpectedly. Methane, ethane, and propane concentrations also increased apparently. Similarly, methanol became more concentrated as a result of catalytic effect of dolomite. Behaviors of benzene and toluene were not so easy to interpret and their concentrations showed some reductions and increases depending on temperature. However, their concentrations couldn’t reach the levels of the carbon monoxide, methane, ethane, propane, and methanol especially at higher temperatures, while they were comparable at lower temperatures.

**Table 7.3:** Gaseous Species from Pyrolytic Gasification Performed with Limestone

| | | Temperature (K) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Compound | | 423 | 473 | 523 | 573 | 623 | 673 | 773 |
| Carbon monoxide | ppm | 0,0 | 12,4 | 221,4 | 57,9 | 27942,6 | 59699,3 | 3920,4 |
| Ammonia | ppm | 61,6 | 148,0 | 107,7 | 21,8 | 68,8 | 104,4 | 14,1 |
| Methane | ppm | 0,0 | 159,1 | 654,5 | 1798,4 | 200,1 | 1083,2 | 11106,0 |
| Ethane | ppm | 880,6 | 198,3 | 88,3 | 370,6 | 321,0 | 7,4 | 1357,9 |
| Propane | ppm | 183,6 | 119,3 | 50,1 | 74,3 | 201,8 | 137,4 | 1257,7 |
| Butane | ppm | 352,9 | 74,7 | 0,0 | 132,7 | 17,2 | 0,0 | 408,7 |
| Hexane | ppm | 55,7 | 236,1 | 205,5 | 163,8 | 46,4 | 53,0 | 121,5 |
| Isohexane | ppm | 0,0 | 8,1 | 404,3 | 64,7 | 48,7 | 39,5 | 96,3 |
| Heptane | ppm | 69,0 | 222,8 | 75,8 | 67,3 | 51,0 | 84,7 | 5,9 |
| Octane | ppm | 0,0 | 22,7 | 55,2 | 19,6 | 23,4 | 12,9 | 12,8 |
| Nonane | ppm | 0,0 | 10,7 | 100,1 | 3,3 | 266,0 | 246,4 | 215,9 |
| Decane | ppm | 2,2 | 0,0 | 17,4 | 3,7 | 5,5 | 37,6 | 21,0 |
| Benzene | ppm | 14,9 | 110,8 | 279,5 | 546,4 | 94,7 | 44,0 | 453,9 |
| Toluene | ppm | 653,5 | 25,0 | 238,5 | 296,9 | 44,4 | 92,5 | 623,2 |
| m-Xylene | ppm | 693,4 | 15,7 | 0,0 | 17,2 | 33,4 | 46,8 | 318,2 |
| o-Xylene | ppm | 16,4 | 50,5 | 221,3 | 96,3 | 151,5 | 690,2 | 108,9 |
| p-Xylene | ppm | 79,3 | 6,4 | 4,3 | 19,7 | 0,0 | 10,6 | 488,0 |
| Methanol | ppm | 0,0 | 1467,1 | 1314,5 | 654,9 | 2473,9 | 1046,6 | 40,4 |
| Ethanol | ppm | 795,0 | 215,3 | 24,8 | 181,2 | 34,2 | 0,0 | 942,4 |
| Propanol | ppm | 0,0 | 37,7 | 1,7 | 35,4 | 4,4 | 81,8 | 33,3 |
| Chloroform | ppm | 1105,4 | 213,2 | 311,5 | 2083,7 | 277,6 | 138,8 | 187,3 |

As a general conclusion, the effects of limestone showed some similarity to that of dolomite. At 673 K carbon monoxide and at 773K methane, ethane, propane, and ethanol became more evident. Propanol was also detected.

**Table 7.4:** Gaseous Species from Pyrolytic Gasification Performed with Zeolite

| | Temperature (K) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Compound | | 423 | 473 | 523 | 573 | 623 | 673 | 773 |
| Carbon monoxide | ppm | 0,0 | 0,0 | 13215,0 | 51607,1 | 188375,8 | 38445,8 | 0,0 |
| Ammonia | ppm | 142,0 | 41,9 | 158,8 | 16,3 | 0,0 | 0,6 | 0,0 |
| Methane | ppm | 0,0 | 14,0 | 55,4 | 127,5 | 3811,7 | 19016,6 | 2365,5 |
| Ethane | ppm | 195,7 | 0,0 | 274,5 | 141,2 | 950,7 | 2043,3 | 278,3 |
| Propane | ppm | 160,9 | 0,0 | 100,9 | 243,5 | 1226,0 | 1586,3 | 0,0 |
| Butane | ppm | 510,0 | 204,1 | 139,2 | 79,3 | 0,0 | 0,0 | 283,3 |
| Hexane | ppm | 0,0 | 45,0 | 178,5 | 0,0 | 0,0 | 339,7 | 667,5 |
| Isohexane | ppm | 0,0 | 27,1 | 0,0 | 56,2 | 10,8 | 216,6 | 38,0 |
| Heptane | ppm | 0,0 | 0,0 | 22,4 | 3,4 | 49,9 | 481,5 | 149,3 |
| Octane | ppm | 0,0 | 0,0 | 0,0 | 124,7 | 22,2 | 150,0 | 0,0 |
| Nonane | ppm | 0,0 | 0,0 | 14,3 | 10,4 | 35,8 | 547,0 | 687,0 |
| Decane | ppm | 0,0 | 0,0 | 23,0 | 54,1 | 26,7 | 0,0 | 0,0 |
| Benzene | ppm | 107,7 | 184,1 | 206,5 | 125,4 | 101,4 | 47,2 | 600,1 |
| Toluene | ppm | 1020,3 | 42,6 | 425,4 | 132,2 | 56,5 | 128,7 | 167,7 |
| m-Xylene | ppm | 390,7 | 0,0 | 0,0 | 137,0 | 43,8 | 23,5 | 0,0 |
| o-Xylene | ppm | 217,9 | 3,7 | 24,7 | 3,0 | 0,0 | 154,5 | 0,0 |
| p-Xylene | ppm | 0,0 | 0,0 | 25,0 | 11,2 | 11,8 | 214,7 | 0,0 |
| Methanol | ppm | 211,7 | 473,3 | 333,1 | 710,7 | 9276,5 | 19050,4 | 0,0 |
| Ethanol | ppm | 290,3 | 210,8 | 18,8 | 0,0 | 786,3 | 695,2 | 0,0 |

Zeolite was observed to have different effects than the above mentioned two catalytic materials. It led to high carbon monoxide concentrations in the temperature interval of 523-673 K. But outside of this interval carbon monoxide was not detected. Methane concentration gradually increased as temperature increased. However, their levels were not as high as the levels in cases of dolomite and limestone. On the other hand, concentration of nonane was superior to the previous catalytic materials at a higher temperature. Benzene concentration was also higher at 773 K. With respect to methanol concentrations zeolite provided considerable yields.

**Table 7.5:** Gaseous Species from Pyrolytic Gasification Performed with Olivine

| | | Temperature (K) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Compound | | 423 | 473 | 523 | 573 | 623 | 673 | 773 |
| Carbon monoxide | ppm | 39,1 | 70,1 | 1578,7 | 103657,3 | 151075,2 | 18839,2 | 14251,4 |
| Ammonia | ppm | 210,1 | 30,3 | 0,0 | 110,0 | 15,1 | 0,0 | 31,6 |
| Methane | ppm | 279,1 | 24,3 | 3,7 | 254,1 | 1848,0 | 1025,8 | 11288,6 |
| Ethane | ppm | 385,6 | 426,9 | 146,2 | 428,0 | 1302,9 | 160,4 | 2193,0 |
| Propane | ppm | 359,2 | 164,4 | 88,5 | 660,7 | 1725,0 | 287,9 | 1203,7 |
| Butane | ppm | 0,0 | 337,3 | 362,3 | 194,0 | 13,4 | 27,9 | 50,2 |
| Hexane | ppm | 324,1 | 154,7 | 168,1 | 13,8 | 393,2 | 56,1 | 332,9 |
| Isohexane | ppm | 61,0 | 52,3 | 137,0 | 55,4 | 108,0 | 79,7 | 79,4 |
| Heptane | ppm | 96,0 | 11,6 | 120,3 | 101,5 | 121,0 | 117,8 | 961,9 |
| Octane | ppm | 42,0 | 22,7 | 70,5 | 15,0 | 213,5 | 44,6 | 82,7 |
| Nonane | ppm | 3,5 | 25,4 | 318,6 | 10,7 | 807,5 | 320,4 | 11,8 |
| Decane | ppm | 40,0 | 52,0 | 2,6 | 3,1 | 36,2 | 4,4 | 10,0 |
| Cyclopentane | ppm | 19,3 | 37,8 | 57,9 | 108,3 | 23,6 | 105,9 | 70,1 |
| Cyclopentene | ppm | 20,9 | 101,8 | 0,0 | 28,4 | 20,1 | 0,0 | 0,0 |
| Methyl cyclopentane | ppm | 81,7 | 0,0 | 7,9 | 79,3 | 84,6 | 7,3 | 16,6 |
| Benzene | ppm | 126,4 | 121,0 | 132,1 | 7,2 | 16,9 | 2,5 | 193,8 |
| Toluene | ppm | 123,1 | 189,4 | 197,3 | 52,1 | 29,9 | 30,5 | 8,4 |
| m-Xylene | ppm | 0,0 | 69,7 | 40,9 | 44,3 | 3,3 | 38,2 | 58,3 |
| o-Xylene | ppm | 40,5 | 78,0 | 123,8 | 281,5 | 0,0 | 28,9 | 167,6 |
| p-Xylene | ppm | 77,7 | 24,7 | 16,2 | 123,1 | 0,0 | 14,9 | 94,0 |
| Formaldehyde | ppm | 26,3 | 124,1 | 125,6 | 304,5 | 548,7 | 72,8 | 28,0 |
| Methanol | ppm | 5727,2 | 5080,3 | 5624,3 | 4741,2 | 13188,9 | 4301,1 | 3835,3 |
| Ethanol | ppm | 82,4 | 414,8 | 44,6 | 55,6 | 467,2 | 300,1 | 704,7 |
| Propanol | ppm | 34,8 | 110,9 | 0,0 | 0,0 | 0,0 | 0,0 | 28,0 |
| Chloroform | ppm | 646,3 | 691,3 | 693,4 | 469,3 | 1175,0 | 353,4 | 406,4 |

General characteristics of olivine as a gasifying catalyst can be summarized as forming new compounds such as cyclopentane, cyclopentene, methylcyclopentane, and formaldehyde. Furthermore, increasing concentrations of carbon monoxide, methane, ethane, propane, heptane, ethanol, and methanol are also striking effect of olivine. Toluene concentration was seen to reduce considerably.

**Table 7.6:** Gaseous Species from Pyrolytic Gasification Performed with $Na_2CO_3$

| | | Temperature (K) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Compound | | 423 | 473 | 523 | 573 | 623 | 673 | 773 |
| Carbon monoxide | ppm | 259,9 | 706,4 | 27583,7 | 12469,7 | 24441,3 | 41579,2 | 25058,4 |
| Ammonia | ppm | 48,8 | 35,0 | 65,4 | 0,0 | 147,6 | 0,0 | 0,0 |
| Methane | ppm | 3706,5 | 2891,1 | 3176,3 | 3318,6 | 3924,4 | 9368,0 | 17485,5 |
| Ethane | ppm | 162,9 | 99,0 | 0,0 | 52,8 | 94,1 | 798,2 | 1798,6 |
| Propane | ppm | 34,3 | 27,6 | 129,6 | 74,5 | 294,2 | 630,6 | 417,4 |
| Butane | ppm | 168,7 | 47,3 | 260,8 | 231,5 | 122,1 | 264,1 | 651,1 |
| Hexane | ppm | 156,2 | 428,3 | 470,2 | 385,6 | 193,2 | 1165,9 | 247,0 |
| Isohexane | ppm | 259,5 | 56,6 | 101,5 | 30,8 | 207,9 | 117,0 | 203,4 |
| Heptane | ppm | 188,7 | 63,6 | 48,7 | 57,3 | 81,5 | 0,0 | 12,8 |
| Octane | ppm | 39,4 | 0,0 | 7,1 | 13,6 | 3,5 | 16,6 | 59,9 |
| Nonane | ppm | 145,9 | 0,0 | 0,0 | 200,7 | 9,1 | 0,1 | 154,1 |
| Decane | ppm | 0,8 | 0,0 | 0,1 | 3,4 | 32,0 | 0,6 | 2,1 |
| Benzene | ppm | 421,9 | 125,0 | 104,7 | 274,9 | 235,8 | 298,0 | 381,8 |
| Toluene | ppm | 96,6 | 26,4 | 149,3 | 166,9 | 98,7 | 193,6 | 116,3 |
| m-Xylene | ppm | 32,8 | 6,9 | 0,0 | 56,1 | 41,6 | 0,0 | 64,9 |
| o-Xylene | ppm | 146,2 | 273,8 | 480,0 | 68,8 | 173,5 | 376,3 | 559,6 |
| p-Xylene | ppm | 221,6 | 16,7 | 37,7 | 179,6 | 69,7 | 19,5 | 121,6 |
| Formic acid | ppm | 108,3 | 33,7 | 189,5 | 167,7 | 209,1 | 176,4 | 80,5 |
| Form aldehyde | ppm | 156,8 | 21,8 | 29,1 | 23,9 | 0,0 | 110,4 | 4,2 |
| Methanol | ppm | 7345,1 | 2596,5 | 4178,3 | 1881,3 | 1689,3 | 7000,6 | 1796,3 |
| Ethanol | ppm | 585,4 | 119,9 | 47,1 | 51,5 | 135,8 | 35,5 | 749,7 |
| Propanol | ppm | 0,0 | 20,1 | 13,1 | 106,1 | 87,1 | 0,0 | 0,0 |

The presence of $Na_2CO_3$ produced a gaseous mixture consisting mainly from carbon monoxide and methane. In addition, ethane, methanol, and ethanol were the other important compounds in the mixture. Concentrations of the tar forming high molecular weight compounds were in reasonable quantities.

**Table 7.7:** Gaseous Species from Pyrolytic Gasification Performed with $K_2CO_3$

| | Temperature (K) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Compound | | 423 | 473 | 523 | 573 | 623 | 673 | 773 |
| Carbon monoxide | ppm | 0,0 | 1317,9 | 3551,9 | 124744,3 | 131793,0 | 114206,7 | 55212,6 |
| Ammonia | ppm | 71,5 | 128,3 | 0,0 | 126,9 | 0,0 | 17,8 | 0,0 |
| Methane | ppm | 1560,8 | 3002,2 | 2950,0 | 3134,7 | 6166,9 | 13270,2 | 64340,4 |
| Ethane | ppm | 444,6 | 267,9 | 47,7 | 595,9 | 2035,7 | 2245,4 | 14171,6 |
| Propane | ppm | 661,3 | 0,0 | 123,0 | 757,3 | 2509,0 | 162,0 | 4325,8 |
| Butane | ppm | 0,0 | 148,7 | 113,9 | 0,0 | 0,0 | 0,0 | 2,8 |
| Hexane | ppm | 307,8 | 182,3 | 396,8 | 0,0 | 0,0 | 0,0 | 90,8 |
| Isohexane | ppm | 339,4 | 213,1 | 149,8 | 197,1 | 56,1 | 175,4 | 660,8 |
| Heptane | ppm | 180,8 | 563,5 | 0,0 | 0,0 | 0,0 | 159,4 | 1379,4 |
| Octane | ppm | 31,3 | 0,0 | 0,0 | 82,2 | 634,8 | 460,5 | 548,6 |
| Nonane | ppm | 248,3 | 7,6 | 26,9 | 1,6 | 21,4 | 950,8 | 3544,8 |
| Decane | ppm | 43,1 | 0,0 | 2,6 | 0,0 | 460,3 | 0,0 | 472,6 |
| Benzene | ppm | 343,1 | 320,4 | 71,9 | 63,6 | 59,5 | 582,1 | 1677,8 |
| Toluene | ppm | 220,8 | 63,1 | 50,2 | 0,0 | 625,7 | 256,4 | 0,0 |
| Styrene | ppm | 495,4 | 250,8 | 599,2 | 171,3 | 1522,9 | 1556,4 | 2149,5 |
| m-Xylene | ppm | 374,9 | 31,1 | 7,5 | 0,0 | 0,0 | 0,0 | 0,0 |
| o-Xylene | ppm | 235,3 | 132,4 | 180,0 | 0,0 | 0,0 | 18,2 | 1268,9 |
| p-Xylene | ppm | 450,7 | 116,4 | 15,4 | 61,3 | 8,0 | 66,3 | 893,9 |
| Form aldehyde | ppm | 410,6 | 151,1 | 175,3 | 913,3 | 688,3 | 526,3 | 288,1 |
| Methanol | ppm | 12552,8 | 5983,5 | 1486,1 | 10201,3 | 31044,0 | 23083,7 | 9342,8 |
| Ethanol | ppm | 725,0 | 600,7 | 169,8 | 0,0 | 0,0 | 212,1 | 3940,6 |
| Propanol | ppm | 111,5 | 0,0 | 0,0 | 0,0 | 0,0 | 0,0 | 366,1 |
| Chloroform | ppm | 2661,5 | 1964,2 | 610,2 | 536,6 | 8511,0 | 5485,8 | 2910,4 |

Extremely high carbon monoxide and methane concentrations were found when $K_2CO_3$ was used. Besides, the gas product was rich in methanol and chloroform. Styrene which is a potential tar forming chemical was detected only when pyrolysis experiments were carried out using $K_2CO_3$. This demonstrates that presence of potassium contributes to tar formation and this is in accordance with literature [53-55]. Likewise, benzene, octane, nonane, and decane concentrations were also the highest among all the experiments performed. This indicates that usage of $K_2CO_3$ as a catalytic material leads to important tar and deposition problems. In spite of the very high yields of carbon monoxide and methane, $K_2CO_3$ addition to the gasification medium is not preferable. Table 7.8 shows the percentages of the variations in the concentrations of the gaseous species at 773 K. In this table, the value of -100 means that the species in question is thoroughly disappeared in the gaseous product as a result of the catalyst used. Positive values indicate the extents of the increases in the concentration of the gaseous species.

**Table 7.8:** Percentages of Variations in The Concentrations of The Gaseous Species at 773 K

| Gaseous Species | Dolomite | Limestone | Zeolite | Olivine | $Na_2CO_3$ | $K_2CO_3$ |
|---|---|---|---|---|---|---|
| Carbon monoxide (CO) | 635 | 64 | -100 | 496 | 948 | 2210 |
| Nitrogen dioxide ($NO_2$) | -100 | -100 | -100 | -100 | -100 | -100 |
| Ammonia ($NH_3$) | -100 | -75 | -100 | -44 | -100 | -100 |
| Methane ($CH_4$) | 365 | 26 | -73 | 28 | 99 | 633 |
| Ethane ($C_2H_6$) | 422 | 29 | -73 | 109 | 71 | 1250 |
| Propane ($C_3H_8$) | 328 | 85 | -100 | 77 | -38 | 537 |
| Butane ($C_4H_{10}$) | -98 | 142 | 68 | -70 | 285 | -98 |
| Hexane ($C_6H_{14}$) | -81 | 40 | 672 | 284 | 185 | 5 |
| Isohexane ($C_6H_{14}$) | 474 | 267 | 45 | 202 | 676 | 2421 |
| Heptane ($C_7H_{16}$) | -61 | -97 | -48 | 232 | -96 | 376 |
| Octane ($C_8H_{18}$) | 177 | -70 | -100 | 87 | 36 | 1144 |
| Nonane ($C_9H_{20}$) | 623 | 6181 | 19890 | 244 | 4384 | 103047 |
| Benzene ($C_6H_6$) | 65 | 172 | 260 | 16 | 129 | 907 |
| Toluene ($C_7H_8$) | 89 | 288 | 4 | -94 | -27 | -100 |
| m-Xylene ($C_8H_{10}$) | 180 | 365 | -100 | -14 | -5 | -100 |
| o-Xylene ($C_8H_{10}$) | 9 | -66 | -100 | -47 | 76 | 299 |
| p-Xylene ($C_8H_{10}$) | 1384 | 1149 | -100 | 141 | 211 | 2188 |
| Formic Acid ($CH_2O$) | -100 | -100 | -100 | -100 | 463 | -100 |
| Methanol ($CH_4O$) | 586 | -87 | -100 | 1131 | 476 | 2900 |
| Ethanol ($C_2H_6O$) | -100 | 194 | -100 | 120 | 134 | 1131 |
| Chloroform ($CHCl_3$) | -75 | -92 | -100 | -83 | -100 | 22 |

Nitrogen dioxide was completely eliminated from the product gas irrespective of the type of the catalyst. All catalysts except $Na_2CO_3$ were able to remove the formic acid from the product gas entirely. Concentrations of chloroform, which is rich in chlorine content, were also diminished in various ratios except for $K_2CO_3$. Concentrations of ammonia were determined either to be lower or zero for every catalyst materials as well.

Concentrations of isohexane, nonane, and benzene increased in all cases. Similarly, carbon monoxide, methane, ethane, hexane, and p-xylene were detected to be more concentrated for most of the catalytic materials.

Light hydrocarbons such as methane, ethane, and propane, which are widely used as gaseous fuel and have less tar forming characteristics, became concentrated for dolomite, limestone, olivine, and $K_2CO_3$. In particular, dolomite or $K_2CO_3$ obviously increased the concentrations of light hydrocarbons. In case of dolomite; methane, ethane, and propane concentrations increased 365, 422, and 328 %, respectively. Usage of $K_2CO_3$ further improved these values, and 633, 1250, and 537 % increases were determined in the concentrations of methane, ethane, and propane, respectively. On the other hand, concentrations of some tar forming compounds also became concentrated in case of $K_2CO_3$. This indicates that some of these catalytic materials can be used in the gasification of sunflower seed shell for specific purposes like light-hydrocarbon-rich gas production provided that taking technological and environmental restrictions into account.

It can be seen from the Table 7.8 that zeolite acted in such a way that the number of the existing species decreased considerably. This can be explained by the fact that zeolite has an important potential for capturing of a number types of gases. In this context, carbon monoxide, nitrogen dioxide, ammonia, propane, octane, m-xylene, o-xylene, p-xylene, formic acid, methanol, ethanol, and chloroform were fully eliminated as a result of zeolite usage as a catalyst during pyrolytic gasification. Similarly, important reductions in the concentrations of methane and ethane were also detected. Concentrations of six species increased whereas fifteen of them decreased or became zero. On the other hand, concentration of nonane which is relatively larger molecule was determined to increase enormously. This increase may compensate the above mentioned reductions in concentrations. For this reason, it can be concluded that zeolite is not a suitable catalytic material to use in the gasification processes.

Olivine favors the reduction of some tar forming species such as toluene, m-xylene, and o-xylene. This characteristics of olivine in reducing tar components differs it from the other catalytic materials used in this study. This is in good agreement with the findings of the investigations in literature [16].

### 7.2.1 Effects of Temperature on The Concentrations of CO, CH4, And Combustibles

Gasification usually aims to obtain a gaseous product having high concentrations of combustibles, low molecular weight hydrocarbons such as methane, and carbon monoxide for synthesis purposes. From this point of the view, concentrations of these compounds were considered at various temperatures. Figure 7.8 illustrates the variations of these components depending on temperature. The highest CO concentration and consequently the highest combustible compound concentrations were detected at 573 K.

Influences of the catalytic materials on these concentrations are presented in Figures 7.9- 7.14.

The effect of temperature on the yield of CO, $CH_4$ and total combustibles are given in Figure 7.8. The pyrolysis of sunflower seed shell alone yielded a 3% of CO maximum at 573 K. The methane production reached maximum at 773 K. The maximum methane yield in this process was 0.87 %. The maximum value for the concentration of total combustibles was obtained at 573 K due to the fact that the larger amount of CO in the product stream.

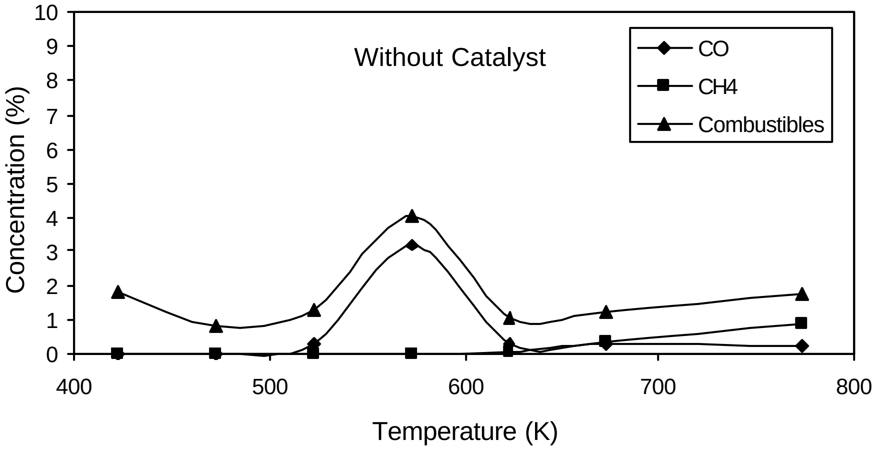


**Figure 7.8:** Effect of Temperature on CO, $CH_4$, and Combustible Product Concentrations

A considerable increase in CO can be observed in the presence of calcined dolomite at 573 K in Figure 7.9. The sharp increase of CO was followed by a sharp decrease at 673 K. A small increase at 773 K can result from the increase in temperature, which had a positive effect on the process. Methane production showed a constantly increased hence the maximum concentration during the experiment was achieved at 773 K. The total combustible concentration had a maximum at 573 K due to high CO concentration. Although after 573 K a decrease is observed, the increase in methane release partly compensated the decrease of CO at 773 K.

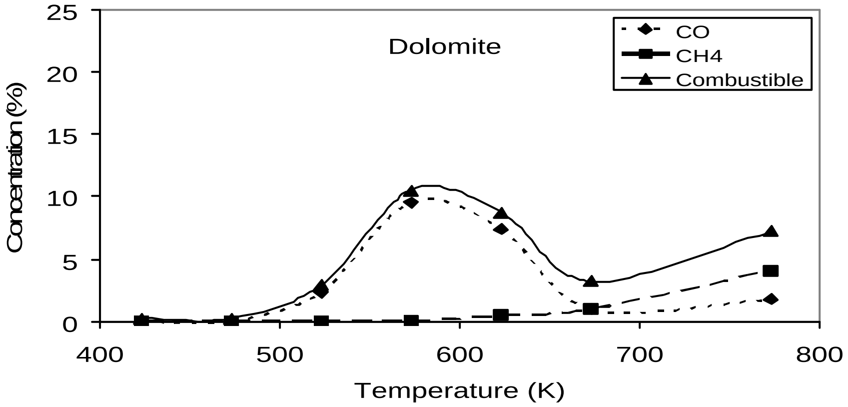


**Figure 7.9:** Effect of Temperature on CO, $CH_4$, and Combustible Product Concentrations Using Dolomite

Figure 7.10 represents the concentration change versus temperature. The pyrolysis of the biomass sample with calcined limestone did not yield CO as much as dolomite. Calcined limestone was not as active as calcined dolomite in the production of CO. The methane production was also less than calcined dolomite. CO and the total combustibles showed a maximum at 673 K. A 100 K shift from the one observed during the pyrolysis of the blend containing calcined dolomite. Methane followed the same increase trend however the concentrations obtained during the experiment was lower than the previous one.

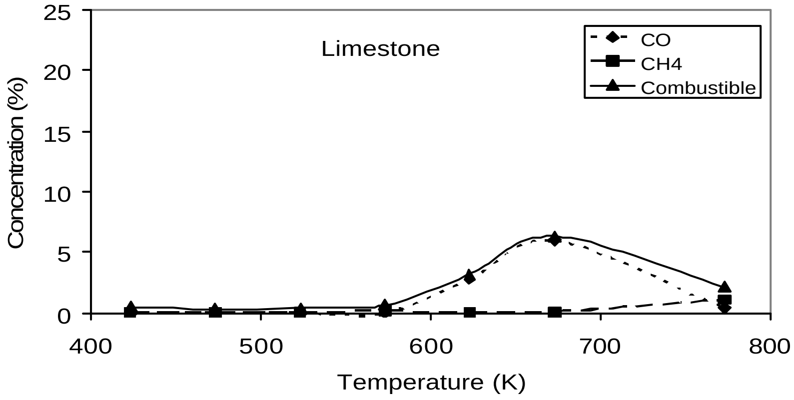


**Figure 7.10:** Effect of Temperature on CO, $CH_4$, and Combustible Product Concentrations Using Limestone

Calcined zeolite enhanced the CO production considerably. The maximum production was reached at 623 K. Only a small increase in methane production was observed. Among the six catalysts the highest total combustibles and CO yield was obtained with calcined zeolite. A sharp decrease in the CO and total combustibles might be due to the loss of catalytic activity.

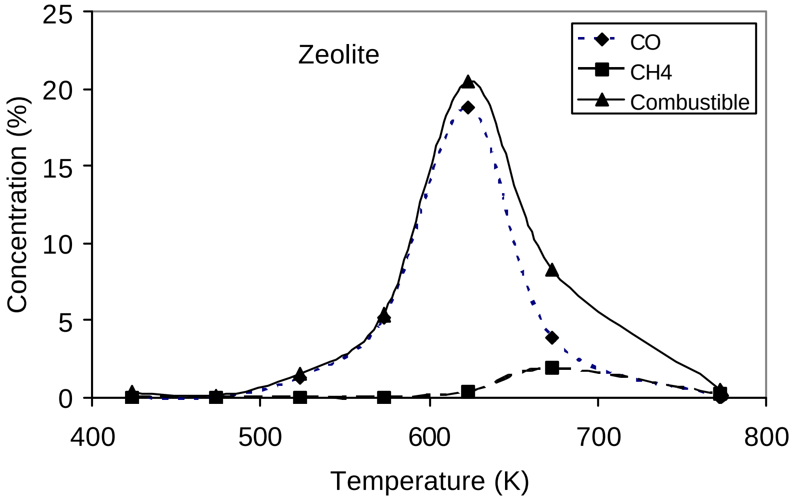


**Figure 7.11:** Effect of Temperature on CO, $CH_4$, and Combustible Product Concentrations Using Zeolite

In the presence of calcined olivine a maximum CO concentration is reached at 623 K as seen in Figure 7.12. The maximum value is lower than the one obtained in the presence of calcined zeolite. However a considerable increase is also achieved. The sharp decrease observed in concentration can result from the activity loss of the catalysts. Methane production was not very much pronounced. The maximum methane production was achieved at 773 K. The calcination of olivine favors the porous structure hence its catalytic activity. The experiments showed that a high yield of CO at relatively low temperatures could be obtained in the presence of catalysts such as calcined zeolite and calcined olivine. Both of these natural catalysts contain $Fe_2O_3$. This is also in accordance with literature [56].

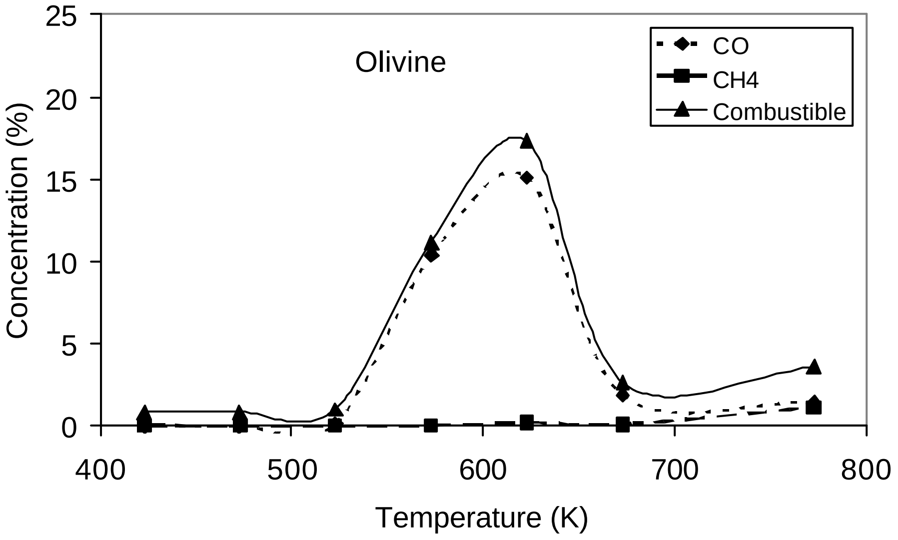


**Figure 7.12:** Effect of Temperature on CO, $CH_4$, and Combustible Product Concentrations Using Olivine

$Na_2CO_3$ did not favour the CO production as calcined zeolite or olivine. Some small increases and decreases are observed during the experiment. The methane production had a small increase in the presence of $Na_2CO_3$ but these values are not very much pronounced.

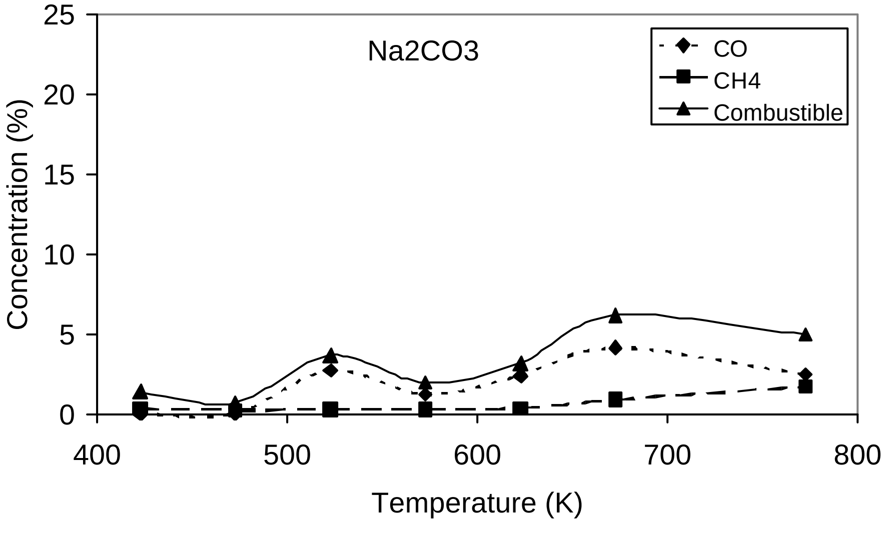


**Figure 7.13:** Effect of Temperature on CO, $CH_4$, and Combustible Product Concentrations Using $Na_2CO_3$

The presence $K_2CO_3$ in the reactor resulted in a sharp increase of CO production and the maximum concentration of CO was reached at 623 K. The methane formation was considerably enhanced in the presence of $K_2CO_3$. Potassium carbonate has a higher activity than sodium carbonate this finding is supported also by the literature; however it is worth to note that the experiments referred in the literature were conducted at higher temperatures and gasification medium was steam in most of them [56].

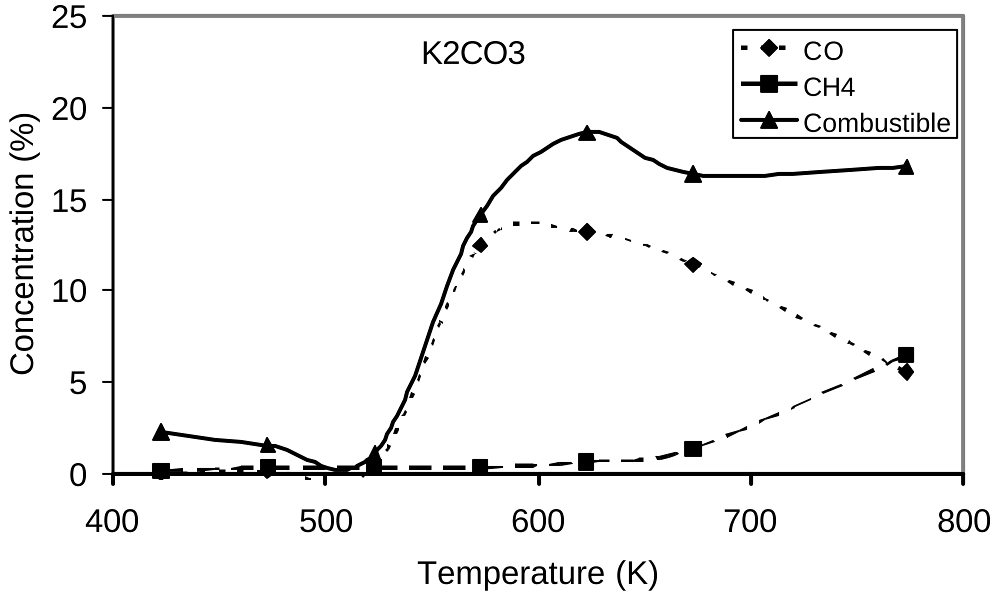


**Figure 7.14:** Effect of Temperature on CO, $CH_4$, and Combustible Product Concentrations Using $K_2CO_3$

Figure 7.15 summarizes the changes in the concentrations of concentrations of CO, $CH_4$ and total combustibles versus temperature and the catalysts hence the findings mentioned above.

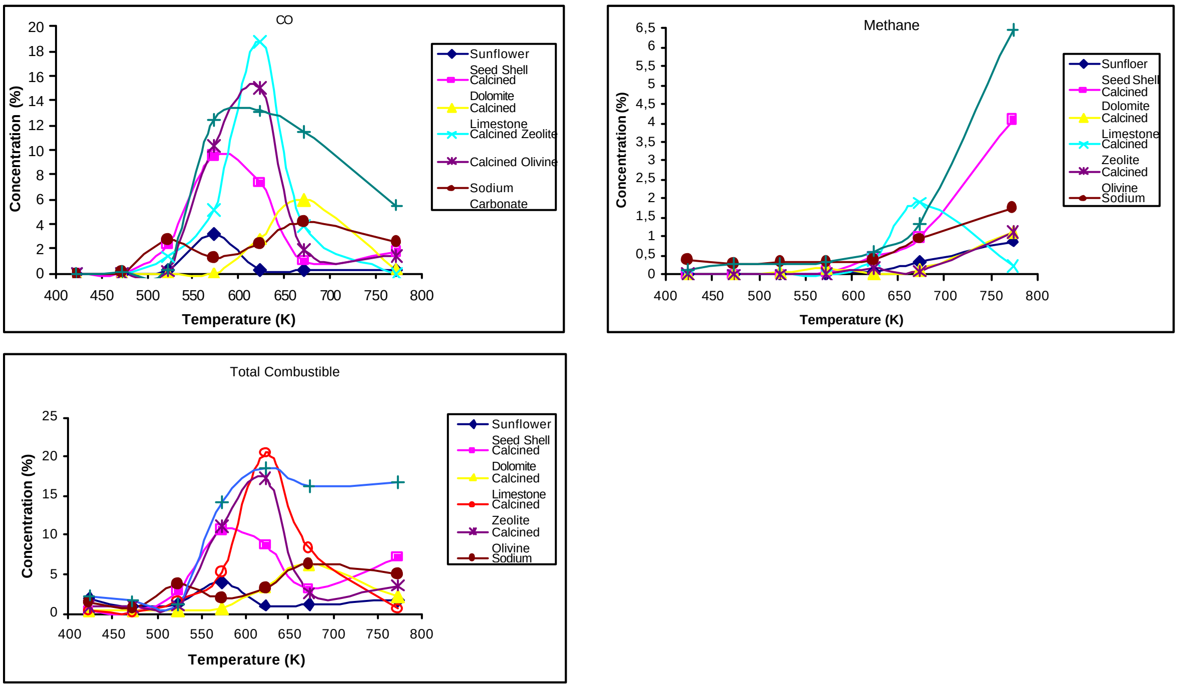


**Figure 7.15:** The Concentration Changes versus Temperature with/without Catalysts

From these figures, maximum carbon monoxide, methane, and combustibles concentrations and their temperatures were extracted and tabulated. These results are given in Table 7.9.

**Table 7.9:** Maximum Concentrations (%) and The Temperatures at which They are Attained

| Catalyst | $C_{(CO)max}$ | T (K) | $C_{(CH4)max}$ | T(K) | $C_{(Combustibles)max}$ | T(K) |
|---|---|---|---|---|---|---|
| n/a | 3.17 | 573 | 0.87 | 773 | 4.05 | 573 |
| Dolomite | 9.55 | 573 | 4.08 | 773 | 8.78 | 623 |
| Limestone | 5.97 | 673 | 1.11 | 773 | 6.36 | 673 |
| Zeolite | 18.84 | 623 | 1.90 | 673 | 8.31 | 673 |
| Olivine | 15.11 | 623 | 1.12 | 773 | 17.32 | 623 |
| $Na_2CO_3$ | 4.16 | 673 | 1.74 | 773 | 6.22 | 673 |
| $K_2CO_3$ | 12.47 | 573 | 6.43 | 773 | 18.61 | 623 |

It can be seen from Table 7.9 that the maximum concentrations of carbon monoxide increased for every catalytic material compared to the case performed without catalyst. On the other hand, the temperatures of these concentrations mostly shifted to higher temperatures. When zeolite was used 18.84 % of the gaseous product consisted of carbon monoxide at 623 K. The lowest increase in the carbon monoxide concentration was determined in case of $Na_2CO_3$. Methane concentrations were relatively lower for gasification of sunflower shell without catalytic material. The highest value was 0.87 % at 773 K. The most apparent increases in the methane concentration were obtained in the cases of dolomite and $K_2CO_3$. The highest concentrations of methane were determined at the highest temperature of the experiments. This is in accordance with the results in literature [57]. Since carbon monoxide and methane, which are the most abundant constituents of gasification processes carried out at relatively low temperatures, were in low concentrations, consequently sum of the combustible part of the gaseous products was also low in case of without catalyst. However, addition of the catalytic materials into the gasification medium improved the concentration of the combustibles to some extent. For instance, $K_2CO_3$ led to an increase from 4.05 % to 18.61 % in its concentration. The temperatures at which the highest concentrations of the combustibles were detected also shifted to the higher temperatures in case of catalytic materials.

### 7.2.2 Solid Product Yields

The initial mass of the samples are taken as dry basis. The initial mass of the blends include the amount of catalyst which was 5 wt % of the sunflower seed shell. The natural catalysts used in the experiments like dolomite, limestone; zeolite and olivine were all calcined. Therefore in the calculations of the solid product yield they are assumed not to lose any weight. The solid product yields along with the initial mass and the remaining mass after the experiments are tabulated in Table 7.10.

The solid product yields were higher than the TG analysis due to the temperature program selected, which can clearly be seen in Table 7.10. During TG analysis temperatures up to 1223 K were applied to the samples resulting in low the solid yields. However the maximum operation temperature applied during the pyrolysis experiments was 773 K. Therefore high solid yields were an expected outcome due to low operation temperatures and heating rates favoring the solid product formation during gasification. The highest solid product yield was achieved in the presence of calcined zeolite which was followed by $Na_2CO_3$ and calcined limestone. The calcined zeolite resulted in 10% increase in the solid product yield.

**Table 7.10:** The Solid Product Yields for the Catalytic Materials

| Species | Initial Mass (dry basis) (g) | Remaining Mass (g) | Solid Product Yield (%) |
|---|---|---|---|
| Sunflower seed shell | 8,97 | 3,19 | 35,56 |
| Blend with calcined dolomite | 9,47 | 3,52 | 37,17 |
| Blend with calcined limestone | 9,47 | 3,98 | 42,03 |
| Blend with calcined zeolite | 9,47 | 4,35 | 45,93 |
| Blend with calcined olivine | 9,47 | 3,58 | 37,80 |
| Blend with $Na_2CO_3$ | 9,47 | 4,09 | 43,19 |
| Blend with $K_2CO_3$ | 9,47 | 3,63 | 38,33 |

# 8. CONCLUSION AND REMARKS

During TG analysis high conversions were obtained with all catalytic matters except for calcined olivine. The gasification ended before the total conversion was achieved. The time period needed for the gasification process to be completed was longer for the blends than for sunflower seed shell alone. It was deduced that these catalytic materials had a slowing down effect on the process. The gasification process required times in the range of 5.5 to 7 hours when calcined dolomite, limestone and zeolite were used as the catalytic material whereas this period was around 3.5 hours for blends containing calcined olivine, $Na_2CO_3$ and $K_2CO_3$. These findings were in accordance with the results in the literature. The longest gasification process was the one of the blend that contained calcined zeolite. All the catalytic materials increased the maximum rate of gasification. The highest maximum rate was achieved with $Na_2CO_3$. The DTGs of the blends containing $Na_2CO_3$ and $K_2CO_3$ had one peak instead of two; the observed peaks were sharper in the case of $Na_2CO_3$ whereas it was broader in the presence of $K_2CO_3$. At high temperature $K_2CO_3$ decomposed to $K_2O$ and $CO_2$, therefore high operation temperatures are not recommended when it is used as the catalyst in gasification. Calcined dolomite and limestone had two peaks alike to the ones of the biomass sample, however shifts in the temperature range were observed. A synergetic effect was observed in the gasification of the blend containing calcined dolomite as the catalytic material.

The TGA data was the basis of the pyrolysis experiments. The highest conversion rates were achieved in the range of 673-773 K. The temperature program for the pyrolysis experiments were designed accordingly. The maximum CO yields were achieved in the interval of 573-673 K. In the presence of calcined zeolite the maximum CO concentration was observed. The maximum operation temperature was 773K at which the maximum $CH_4$ concentrations were achieved both with the sunflower seed shell and the blends. $K_2CO_3$ was the catalyst that promotes the production of $CH_4$ at most. The concentrations of the total combustibles were mainly dependent on the changes in CO concentrations. The increases and decreases in the CO concentrations were mimicked in the behaviour of the total combustibles. The highest solid product yield was also obtained in the presence of calcined zeolite which was followed by $Na_2CO_3$. High solid product yields were an expected outcome due to the low operation temperatures.

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## CURRICULUM VITAE

Elif ÇAGLAYAN was born in Istanbul in 1979. She finished Kabatas High School in 1997. She started her Bachelor of Science degree at Chemical Engineering Department of Istanbul Technical University in 1997 and completed in 2001. In 2004 she started her Master of Science degree at the same department. She works as a researcher in the Institute of Energy of TUBITAK Marmara Research Center (MRC). The main projects she is involved in at MRC are related to biomass and coal gasification.