

## CHAPTER II

### THEORY AND LITERATURE REVIEW

Gasification technologies have been commercially applied for more than a century for the production of both fuels and chemicals. Current trends in the power generation and refinery industries support the observation that advanced stages of the technology will continue to be applied toward the synthesis of syngas, with an increasing number of applications in power generation, fuels, and basic chemicals manufacturing.

Attractive features of technology include:

- The ability to produce a consistent product that can be used for the generation of electricity or as primary building blocks for manufacturers of chemicals and transportation fuels.
- The ability to produce from a wide range of feedstocks including coal, heavy oils, petroleum coke, heavy refinery residues, refinery wastes, hydrocarbon contaminated soils, biomass, and agricultural wastes.
- The ability to remove contaminants in the feedstock and to produce a clean syngas product.
- The ability to convert wastes or low-value products to higher value products.
- The ability to minimize the amount of solid waste requiring landfill disposal. Solid by-products have a market value that can be used as fuel or construction material, and are non-hazardous.

#### 2.1 Gasification process

Gasification is a process for converting carbonaceous materials to a combustible or synthetic gas (e.g.,  $H_2$ ,  $CO$ ,  $CO_2$ ,  $CH_4$ ). In general, gasification involves the reaction of carbon with air, oxygen, steam, carbon dioxide, or a mixture of these gases at  $700\text{ }^\circ\text{C}$  or higher to produce a gaseous product that can be used to provide electric power and heat or as a raw material for the synthesis of chemicals, liquid fuels,

or other gaseous fuels such as hydrogen. Once a carbonaceous solid or liquid material is converted to a gaseous state, undesirable substance such as sulfur compounds and ash may be removed from the gas. In contrast to combustion processes, which work with excess air, gasification processes operate at substoichiometric conditions with the oxygen supply controlled (generally 35 percent of the amount of  $O_2$  theoretically required for complete combustion or less) such that both heat and a new gaseous fuel are produced as the feed material is consumed. Some gasification processes also use indirect heating, avoiding combustion of the feed material in the gasification reactor and avoiding the dilution of the product gas with nitrogen and excess  $CO_2$ . Figure 2.1 shows the principal methods for gasifying a carbonaceous material.

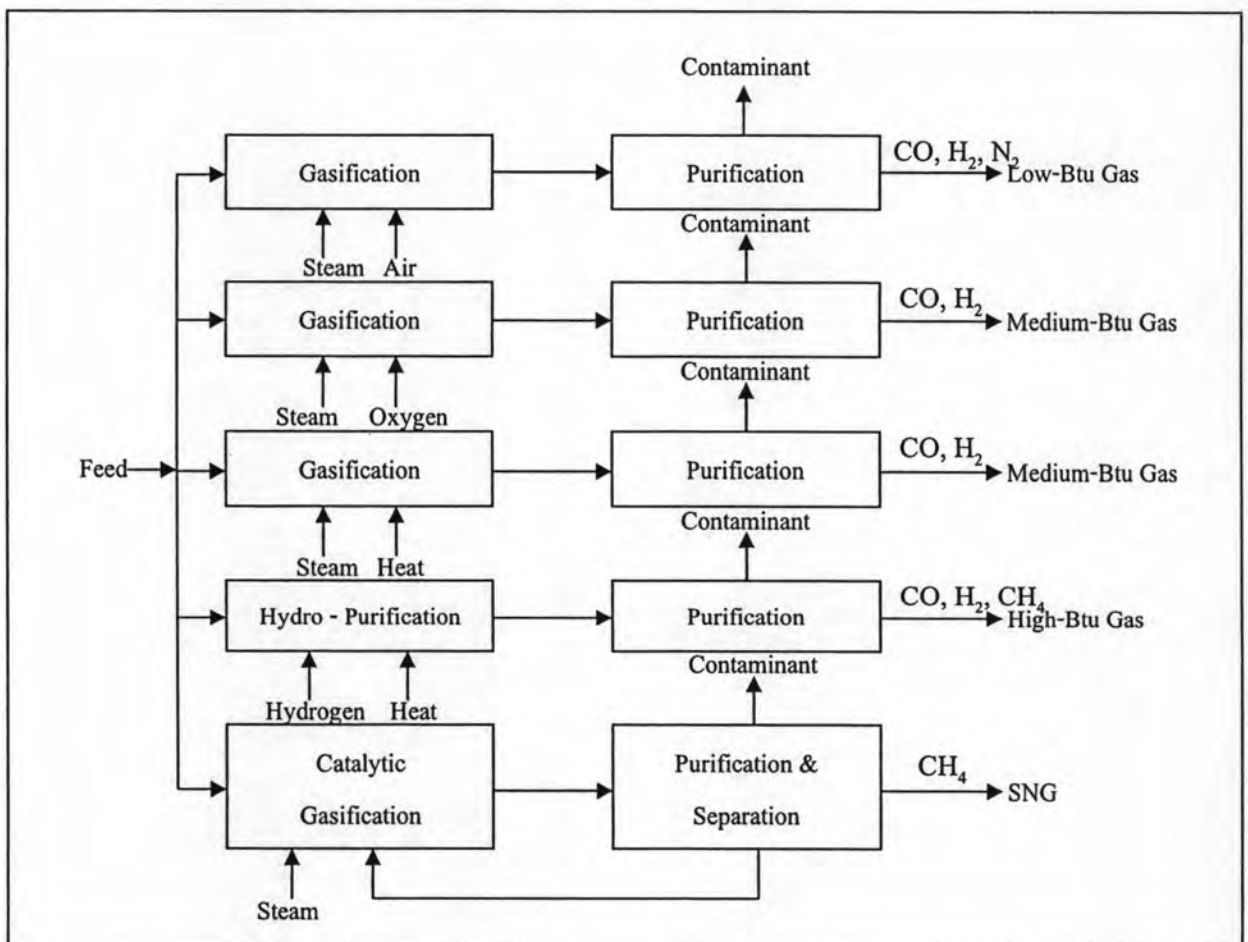
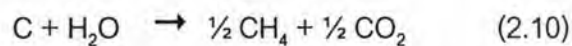
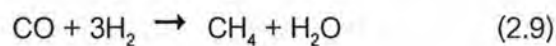
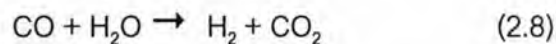
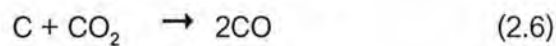
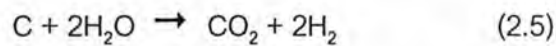
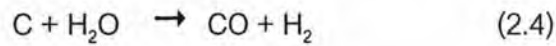
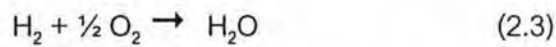


Figure 2.1 Gasification methods (Rezaiyan and Cheremisinoff, 2005)

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

Depending on the gasification process, reactions that take place in a gasifier include:



Most of the oxygen injected into a gasifier, either as pure oxygen or air, is consumed in reactions (2.1) through (2.3) to provide the heat necessary to dry the solid fuel, break up chemical bonds, and raise the reactor temperature to drive gasification reactions (2.4) through (2.9).

Reactions (2.4) and (2.5), which are known as water-gas reactions, are the principal gasification reactions, are endothermic, and favor high temperatures and low pressures.

Reaction (2.6), the Boudourd reaction, is endothermic and is much slower than the combustion reaction (1) at the same temperature in the absence of a catalyst.

Reaction (2.7), hydro-gasification, is very slow except at high pressures.

Reaction (2.8), the water-gas shift reaction, can be important if  $\text{H}_2$  production is desired. Optimum yield is obtained at low temperatures (up to  $800^\circ\text{C}$ ) in the presence of a catalyst and pressure has no effect on increasing hydrogen yield.

Reaction (2.9), the methanation reaction, proceeds very slowly at low temperatures in the absence of catalysts.

Reaction (2.10) is relatively thermal neutral, suggesting that gasification could proceed with little heat input but methane formation is slow relative to reactions (4) and (5) unless catalyzed.

In addition to the gasification agent (air, oxygen, or steam) and the gasifier operating temperature and pressure, other factors affect the chemical composition, heating value, and the end use applications of the gasifier product gas.

The following factors affect the quality of the product gas:

- Feedstock composition
- Feedstock preparation and particle size
- Reactor heating rate
- Residence time
- Plant configuration such as:
  - Feed system :dry or slurry
  - Feedstock-reactant flow geometry
  - Mineral removal system: dry ash or slag
  - Heat generation and transfer method: direct or indirect
  - Syngas cleanup system: low or high temperature and processes used to remove sulfur, nitrogen, particulates, and other compounds that may impact the suitability of the syngas for specific applications (i.e., turbine and fuel cell for electric power generation, hydrogen production, liquid fuel production, or chemical production).

Depending on the gasifier system configuration, operating conditions, and gasification agent, four types of synthetic gas can be produced:

1. Low heating-value gas ( $3.5$  to  $10$  MJ/m<sup>3</sup> or  $100$  to  $270$  Btu/ft<sup>3</sup>) can be used as gas turbine fuel in an Gasification combined cycle, as boiler fuel for steam production, and as fuel for smelting and iron ore reduction applications. However, because of its high nitrogen content and low heating value, it is not well suited as a natural gas replacement or for chemical synthesis. Use of low heating-value gas for fuel cell applications also increases gas upgrading and processing costs, including compression costs if high pressure fuel cells are used.

2. Medium heating-value gas (10 to 20 MJ/ m<sup>3</sup> or 270 to 540 Btu/ ft<sup>3</sup>) can be used as fuel gas for gas turbines in integrated gasification combined cycle applications, for substitute natural gas (SNG) in combination with methanation process, for hydrogen production, for fuel cell feed, and for chemical and fuel synthesis.

3. High heating-value gas (20 to 35 MJ/ m<sup>3</sup> or 540 to 940 Btu/ ft<sup>3</sup>) can also be used as fuel gas for gas turbines in IGCC applications, for SNG and hydrogen production, for fuel cell feed, and for chemical and fuel synthesis. However, it does not require as much upgrading and methanation to produce SNG.

4. SNG (over 35 MJ/m<sup>3</sup> or 940 Btu/ft<sup>3</sup>) can be easily substituted for natural gas and therefore is suitable for hydrogen and chemical production as well as fuel cell feed.

## 2.2 Classification of gasification processes

There are a large number of widely varying gasification processes. The gasification processes can be classified basically in two general ways: (1) by the Btu content of the product gas, and (2) by the type of the reactor hardware configuration, as well as by whether the reactor system is operated under pressure or not.

The following processes for conversion of coal to gases are grouped according to the heating value of the product gas.

### Medium – or High – Btu Gas Gasification Processes

1. Lurgi gasifier
2. Synthane gasifier
3. Atgas molten iron coal gasifier

### Low – or Medium – Btu Gas Gasification Processes

1. Koppers – Totzek gasifier
2. Texaco gasifier
3. Shell gasifier
4. Kellogg's molten salt gasifier
5. CO<sub>2</sub>-acceptor gasification process
6. U-gas process

Based on the reactor configuration, as well as by the method of contacting gaseous and solid streams, gasification processes can also be categorized into the following four types:

1. Fixed or moving bed: In the fixed bed reactor, coal is supported by a grate and the gasifying media (steam, air, or oxygen) passes upward through the supported bed, whereby the product gases exit from the top of the reactor. Only noncaking coals can be used in the fixed bed reactor. On the other hand, in the moving bed reactor, coal and gaseous streams move counter-currently, i.e., coal moves downward by gravity while gas passes upward through the coal bed. The temperature at the bottom of the reactor is higher than that at the top. Because of the lower temperature at the top for coal devolatilization, relatively large amounts of liquid hydrocarbons are also produced in this type of gasifier. In both types of reactor, the residence time of the coal is much longer than that in a suspension reactor, thus providing ample contact time between reactants. Ash is removed from the bottom of the reactor as dry ash or slag. Lurgi and Wellman-Galusha gasifiers are examples of this type of reactor. It should be clearly understood that a moving bed reactor is classified as a kind of fixed bed reactor, because solids in the bed stay together regardless of the movement of the hardware that supports the bed.

2. Fluidized bed: It uses finely pulverized coal particles. The gas (or gasifying medium) flows upward through the bed and fluidizes the coal particles. Larger coal surface area is made available, which positively promotes the gas-solid chemical reaction, which in turn results in enhancement in carbon conversion. This type of reactor allows intimate contact between gas and solid coal fines, at the same time providing relatively longer residence times than entrained flow reactor. Dry ash is either removed continuously from the bed. Or the gasifier is operated at such a high temperature that it can be removed as agglomerates. Such beds, however, have limited ability to handle caking coals, owing to operational complications in fluidization characteristics. Winkler and Synthane processes use this type of reactor.

3. Entrained bed: This type of reactor is also referred to as entrained flow reactor, because there is no bed of solids. This reactor system uses finely pulverized, with combustion and gasification occurring inside the coal particles suspended in the gas phase. Because of the entrainment requirement, high space velocity of gas stream and fine powdery coal particles are very essentially to the operation of this type of process. Because of the very short residence time (i.e., high space velocity) in the reactor, a very high temperature is required to achieve good conversion in such a short period of reaction time. This can also be assisted by using excess oxygen. This bed configuration is typically capable of handling both caking and noncaking coals without much operational difficulty. Examples of commercial gasifiers that use this type of reactor include the Koppers-Totzek gasifier and Texaco gasifier.

4. Molten salt bath reactor: In this reactor, coal is fed along with steam or oxygen in the molten bath of salt or metal operated at 1,000-1,400°C. Ash and sulfur are removed as slag. This type of reactor is used in Kellogg and Atgas processes.

### 2.3 Types of gasifiers

Since there is an interaction of air or oxygen and biomass in the gasifier, they are classified according to the way air or oxygen is introduced in it. There are three types of gasifiers (Figure 2.2); downdraft, updraft and crossdraft. As the classification implies, updraft gasifier has air passing through the biomass from bottom and the combustible gases come out from the top of the gasifier. Similarly in the downdraft gasifier the air is passed from the tuyers in the downdraft direction.

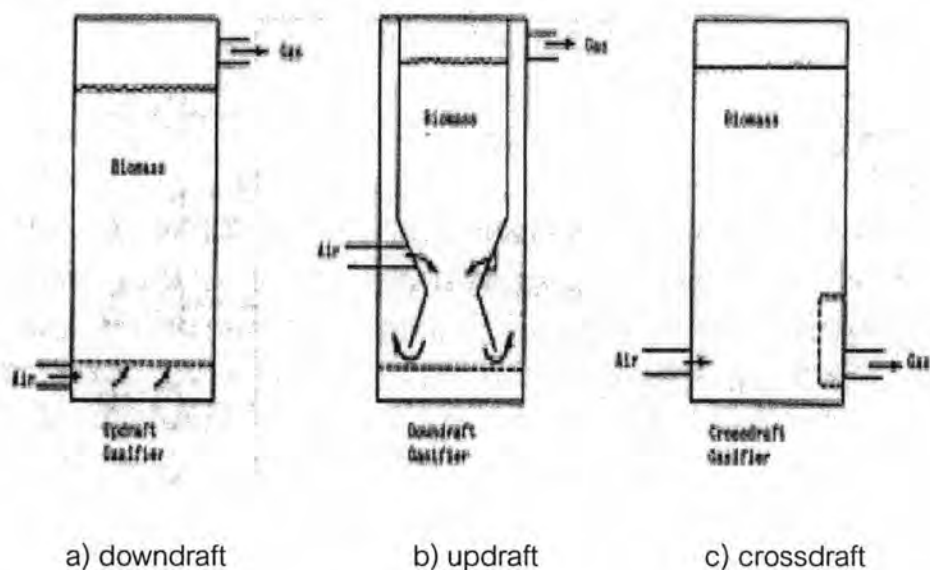


Figure 2.2 Various type of gasifiers (Rajvanshi et al. 1986)

Table 2.1 Advantages and disadvantages of various gasifiers (Rajvanshi et al. 1986)

No.	Gasifier Type	Advantages	Disadvantages
1.	Updraft	<ul style="list-style-type: none"> <li>-Small pressure drop</li> <li>-Good thermal efficiency</li> <li>-Little tendency towards slag formation</li> </ul>	<ul style="list-style-type: none"> <li>-Great sensitivity to tar and moisture and moisture content of fuel</li> <li>-Relatively long time required for start up of IC engine</li> <li>-Poor reaction capability with heavy gas load</li> </ul>
2.	Downdraft	<ul style="list-style-type: none"> <li>- Flexible adaptation of gas production to load</li> <li>-Low sensitivity to charcoal dust and tar content of fuel</li> </ul>	<ul style="list-style-type: none"> <li>-Design tends to be tall</li> <li>-Not feasible for very small particle size of fuel</li> </ul>
3.	Crossdraft	<ul style="list-style-type: none"> <li>-Short design height</li> <li>-Very fast response time to load</li> <li>-Flexible gas production</li> </ul>	<ul style="list-style-type: none"> <li>-Very high sensitivity to slag formation</li> <li>-High pressure drop</li> </ul>



There are several type of reactions occurring in the reactor. Four distinct processes take place in a gasifier as the fuel makes its way to gasification. They are :

- a) Drying of fuel
- b) Pyrolysis – a process in which tar and other volatiles are driven off
- c) Combustion
- d) Reduction

Though there is a considerable overlap of the processes, each can be assumed to occupy a separate zone where fundamentally different chemical and thermal reactions take place. Figure 2.3 shows schematically an updraft gasifier with different zones and their respective temperatures.

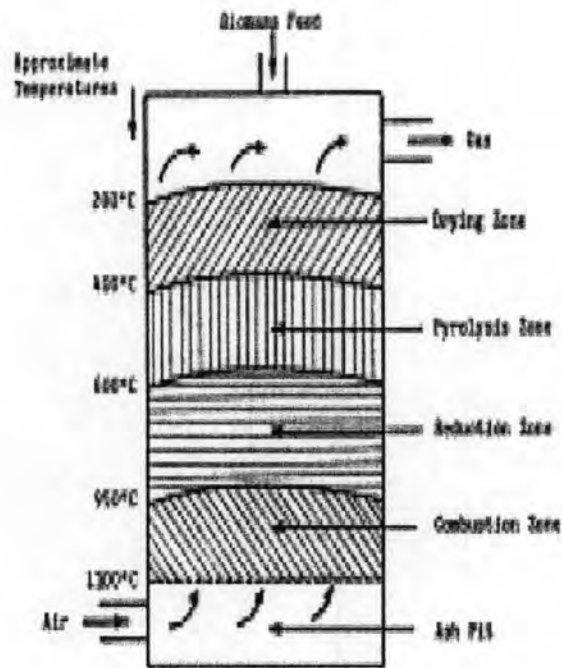
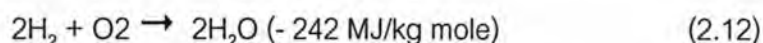
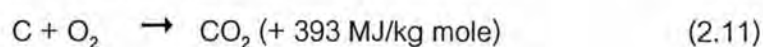


Figure 2.3 Various zones in an updraft gasifier (Rajvanshi et al. 1986)

Within different process zones, there are many chemistry reactions that take place. The following major reactions occur in combustion and reduction zone as shown in Figure 2.3.

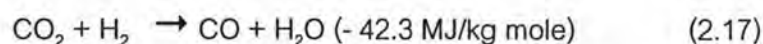
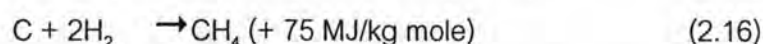
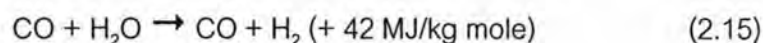
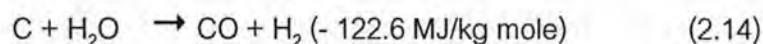
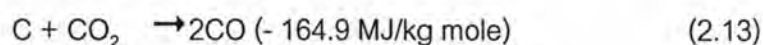
### 1. Combustion zone

The combustible substance of a solid fuel is usually composed of elements carbon, hydrogen and oxygen. In complete combustion carbon dioxide is obtained from carbon in fuel and water is obtained from the hydrogen, usually as steam. The combustion reaction is exothermic and yields a theoretical oxidation temperature of 1450°C. The main reactions, therefore, are:



### 2. Reaction zone

The products of partial combustion (water, carbon dioxide and uncombusted partially cracked pyrolysis products) now pass through a red-hot charcoal bed where the following reduction reactions take place.



Reactions (2.13) and (2.14) are main reduction reactions and being endothermic have the capability of reducing gas temperature. Consequently the temperatures in the reduction zone are normally 800-1000°C. It was suggested that the lower the reduction zone temperature (~ 700-800°C), the lower is the calorific value of gas.

### 3. Pyrolysis zone

Wood pyrolysis is an intricate process that is still not completely understood. The products depend upon temperature, pressure, residence time and heat losses. However following general remarks can be made about them. At the temperature up to 200°C only water is driven off. At the temperature between 200 to 280°C carbon dioxide, acetic acid and water are given off. The real pyrolysis, which takes place between 280 to

500 °C, produces large quantities of tar and gases containing carbon dioxide. Besides light tars, some methyl alcohol is also formed. Between 500 to 700 °C the gas production is small and contains hydrogen. Thus it is easy to see that updraft gasifier will produce much more tar than downdraft one. In downdraft gasifier the tars have to go through combustion and reduction zone and are partially broken down (Rajvanshi et al. 1986).

Renewable energy is of growing importance in satisfying environmental concerns over fossil fuel usage and its contribution to the Greenhouse Effect. Wood and other forms of biomass are some of the main renewable energy resources available and provide the only source of renewable liquid, gaseous and solid fuels. Wood and biomass can be used in a variety of ways to provide energy:

- by direct combustion to provide heat for use in heating, for steam production and hence electricity generation.
- by gasification to provide a fuel gas for combustion for heat, or in an engine or turbine for electricity generation.
- by fast pyrolysis to provide a liquid fuel that can substitute for fuel oil in any static heating or electricity generation application. The liquid can also be used to produce a range of speciality and commodity chemicals.

#### 2.4 Pyrolysis principle

Biomass is a mixture of hemicellulose, cellulose, lignin and minor amounts of other organics which each pyrolyse or degrade at different rates and by different mechanisms and pathways. Lignin decomposes over a wider temperature range compared to cellulose and hemicellulose which rapidly degrade over narrower temperature ranges, hence the apparent thermal stability of lignin during pyrolysis. The rate and extent of decomposition of each of these components depends on the process parameters of reactor (pyrolysis) temperature, biomass heating rate and pressure. The degree of secondary reaction (and hence the product yields) of the gas/vapour products depends on the time-temperature history to which they are subjected before collection, which includes the influence of the reactor configuration. Although some research has been carried out on the individual components of biomass, most applied and larger scale work has focused on whole biomass as the cost of pre-separation is

considered too high. In addition, the separation and recovery of pure forms of lignin and hemicellulose are difficult due to structural changes in their processing, although pure cellulose is relatively easy to produce. Fast pyrolysis is a high temperature process in which biomass is rapidly heated in the absence of oxygen. As a result it decomposes to generate mostly vapours and aerosols and some charcoal. Liquid production requires very low vapour residence time to minimise secondary reactions of typically 1 s, although acceptable yields can be obtained at residence times of up to 5 s if the vapour temperature is kept below 400 °C. After cooling and condensation, a dark brown mobile liquid is formed which has a heating value about half that of conventional fuel oil. While it is related to the traditional pyrolysis processes for making charcoal, fast pyrolysis is an advanced process which is carefully controlled to give high yields of liquid. Research has shown that maximum liquid yields are obtained with high heating rates, at reaction temperatures around 500 °C and with short vapour residence times to minimize secondary reactions. A compilation of published data is shown in Figure 2.4 for typical products from fast pyrolysis of wood (Toft, 1996). Fast pyrolysis processes have been developed for production of food flavours (to replace traditional slow pyrolysis processes which had much lower yields), specialty chemicals and fuels. These utilise very short vapour residence times of between 30 and 1500 ms and reactor temperatures around 500 °C. Both residence time and temperature control is important to freeze the intermediates of most chemical interest in conjunction with moderate gas vapour phase temperatures of 400-500 °C before recovery of the product to maximize organic liquid yields.

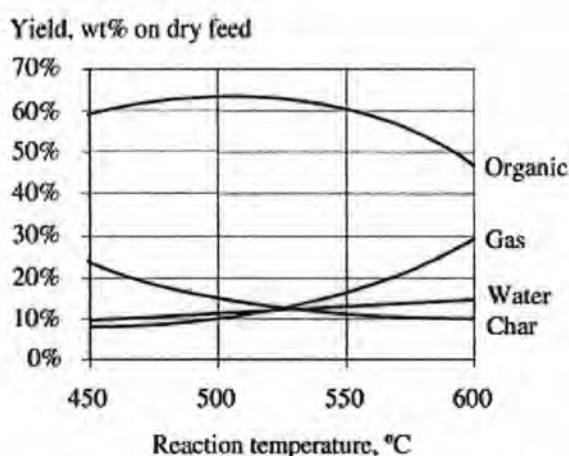


Figure 2.4 Typical yields of organic liquid, reaction water, gas and char from fast pyrolysis of wood, wt% on dry feed basis (Bridgwater et al. 1999).

The essential features of a fast pyrolysis process are:

- Very high heating and heat transfer rates, which usually requires a finely ground biomass feed.
- Carefully controlled pyrolysis reaction temperature of around 500 °C in the vapour phase, with short vapour residence times of typically less than 2 s.
- Rapid cooling of the pyrolysis vapours to give the bio-oil product.

The main product, bio-oil, is a miscible mixture of polar organics (about 75-80 wt%) and water (about 20-25 wt%). It is obtained in yields of up to 80 wt% in total (wet basis) on dry feed, together with by-product char and gas which are, or can be, used within the process so there are no waste streams. Liquids for use as fuels can be produced with longer vapour residence times (up to around 5 s) and over a wider temperature range although yields might be affected in two ways: secondary volatiles decomposition at temperatures above 500 °C and condensation reactions at gas/vapour product temperatures below 400 °C. Most woods give maximum liquid yields of up to 80wt% dry feed basis at 500-520 °C with vapour residence times not more than 1 s. Very short residence times result in incomplete depolymerisation of the lignin due to random bond cleavage and inter-reaction of the lignin macromolecule resulting in a less homogenous liquid product, while longer residence times can cause secondary cracking of the primary products, reducing yield and adversely affecting bio-oil properties. Evidence from SEC (selective exclusion chromatography) analysis of the

liquids would suggest that the reactor configuration and the dominant mode of heat transfer strongly influence the average molecular weight of the products (McKinley, 1989).

## 2.5 Biomass

Biomass is the organic substance that is the natural source of energy and can be used to produce energy e.g. agricultural residues and agro-industrial wastes as follows: rice husk and straw from rice mills and rice fields, bagasse from sugar mills, wood waste from Para wood and Eucalyptus forests and plantations, residue from palm oil extraction plants, cormcobs from corn fields, coconut shells and empty bunches from coconut oil and milk factories. Biomass composition is divided into:

### 1. Moisture

Most of the biomass contains considerably high moisture content because it comes from agricultural by-products. The biomass that is suitable for combustion should have less than 50 per cent of moisture.

### 2. Combustible substance

Combustible substance consists of volatiles matter and fixed carbon. The biomass that contains a great amount of volatiles matter is highly combustible.

### 3. Ash

Most of biomass contains 1-3 percent of ash except for rice husk that has around 10-20 percent of ash, which causes problem in combustion and dumping.

(<http://www.dedo.com/biomass>)

## 2.6 Components of biomass

Cellulose, hemicellulose and lignin and extractives are found to be the major components of biomass. Raveendran (1995) have reported the composition of biomass in terms of these components. The thermal degradation of biomass and samples of cellulose, hemicellulose and lignin has been studied extensively using TG analyzer. Most of the investigators have studied the effects of heating rates and temperature on pyrolysis using TG analyzer. Since the main objective of their studies

was to get maximum char and combustible volatiles, TGA studies were carried out in inert atmosphere with flowing nitrogen to purge out the product gases thus preventing the secondary reactions. Low heating rates with low final temperature were employed to achieve slow pyrolysis of biomass and samples of cellulose, hemicellulose and lignin. Williams and Besler (1993) have carried out TGA of wood and rice husks and samples of cellulose, hemicellulose and lignin at heating rates of 5, 20, 40 and 80 K/min with nitrogen flowing to purge out the product of gases. The following observations were made at all heating rates:

- Hemicellulose represented by xylan decomposes between 220 and 320 °C and continued heating up to 720 °C resulted in yielding char approximately 20 wt% of the original hemicellulose.
- Cellulose decomposes between 250 and 360 °C and has yielded char approximately 8 wt% of the original cellulose after heating to 720 °C. Low final temperature was employed to achieve slow pyrolysis of biomass and samples of cellulose, hemicellulose and lignin.
- Cellulose decomposes between 250 and 360 °C and has yielded char approximately 8 wt% of the original cellulose after heating to 720 °C.
- Lignin undergoes gradual decomposition between 80 and 500 °C yielding char 55 wt% of the original lignin after heating to 720 °C.
- Only one temperature for maximum weight loss has been observed for hemicellulose, cellulose and lignin.

## 2.7 Composition of biomass

Every biomass has carbon, hydrogen and oxygen in major quantities. These are represented as ultimate analysis. The chemical formula for the biomass is generally represented by  $C_xH_yO_z$ . The coefficients of x, y and z are calculated for each of the biomass (Kirubakarana et al. 2007).

Gani et al. (2007) studied on the main compositions for several types of biomass, which includes Indonesian agricultural biomass of palm oil fiber and bagasse. The pyrolysis and combustion behaviors for several types of biomass were tested by a thermo-gravimetric analyzer. The main compositions of cellulose and lignin contents for several types of biomass were analyzed chemically. The morphological changes before and after the reactions were also observed by a scanning electron microscope :

1) Pyrolysis behavior of several types of biomass, cellulose and lignin

As a representative result of the pyrolysis tests, Figure 2.5 (a) and 2.5 (b) shows profiles of fraction of the mass decrease of combustibles for several types of biomass such as hinoki sawdust, rice husk, palm oil fiber, corn stalk, rice straw, larch bark and bagasse, comparing with the cellulose and lignin chemicals. The vertical axis represents fraction of mass decrease of combustibles. The cellulose and lignin chemicals are also tested as references since the biomass mainly consists of these compounds as shown in Figure 2.6. From both the figures, the pyrolysis starts at about 200 °C for all of the samples. The combustibles in the biomass react at the two stages during pyrolysis. In the first stage, the mass rapidly decreases due to cellulose volatilization. After that, the slow mass decrease occurs at the second stage due to lignin decomposition. Focusing on pattern of the profile of mass decrease, trend of the mass decrease for bark differs from that for the others. The cellulose chemical decomposes at high decomposition rate within narrow temperature range. While, decomposition rate of the lignin chemical becomes slower than that of the cellulose chemical. Comparing these results for the actual biomass samples with those for the cellulose and lignin chemicals, the profile for bark relatively comes near to that for the lignin. This is because the bark contains the highest lignin content as shown in Figure 2.6. On the contrary, the profile for rice husks approaches to that for the cellulose. These results suggest that the volatilization behavior of biomass depends on its own component such as the cellulose and lignin content. Generally, the lignin is harder to decompose than the cellulose since part of lignin consists of benzene rings (Sharma et al., 2004).



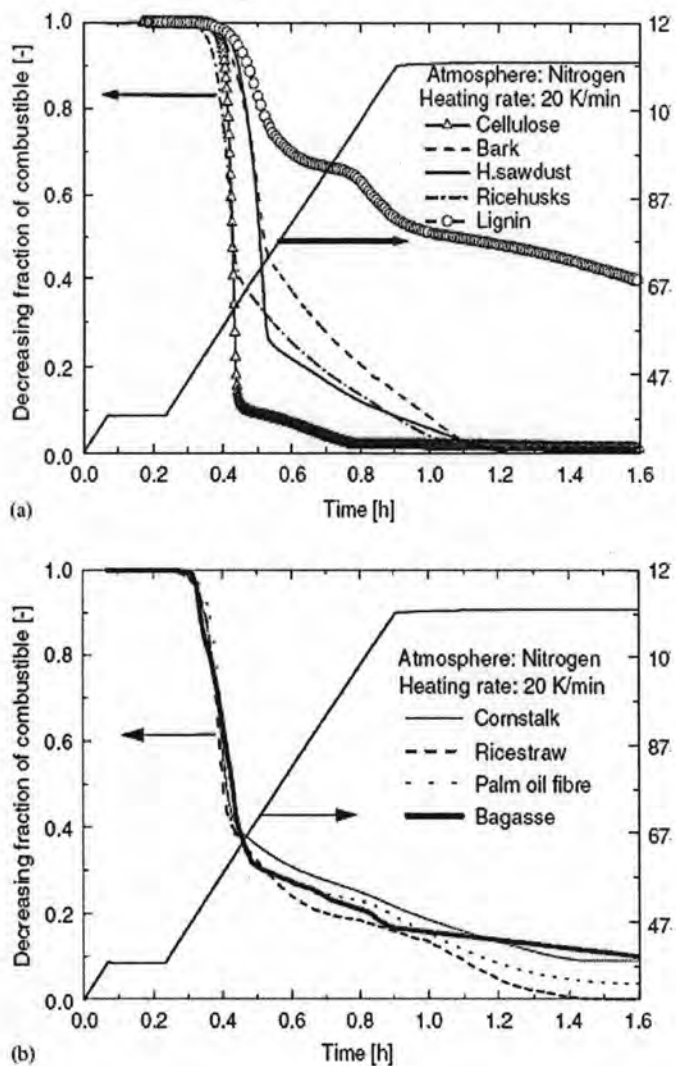


Figure 2.5 Residual fraction of combustibles for several types of biomass, cellulose and lignin during pyrolysis (Gani et al. 2007)

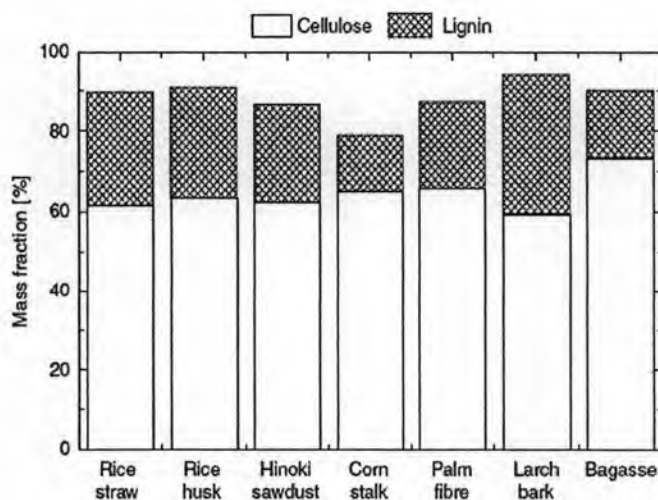


Figure 2.6 Cellulose and lignin contents in several types of biomass (Gani et al. 2007)

## 2) Combustion behavior of several types of biomass, cellulose and lignin

Changes of fraction of mass decrease of combustibles during combustion for several types of biomass, lignin and cellulose are shown in Figure 2.7 (a) and 2.7 (b). Trend of the mass decrease for combustion differs from that for pyrolysis obtained before. These results suggest that cellulose content in the biomass may enhance the ignition characteristics and decomposition of lignin since the cellulose compounds have the structure of branching chain of polysaccharides and no aromatic compounds, which are easily volatilized. Consequently, the biomass will burn at the flowing steps. First, the cellulose components in the biomass are volatilized, so that the porosity in the char particles of biomass increases and that oxygen easily diffuses into the char particles. Next, the lignin components in the biomass can also react with oxygen diffused even if the reactivity of lignin itself is low. In other words, this discussion suggests that the char morphology will be one of the important indices to evaluate the biomass reactivity during combustion.

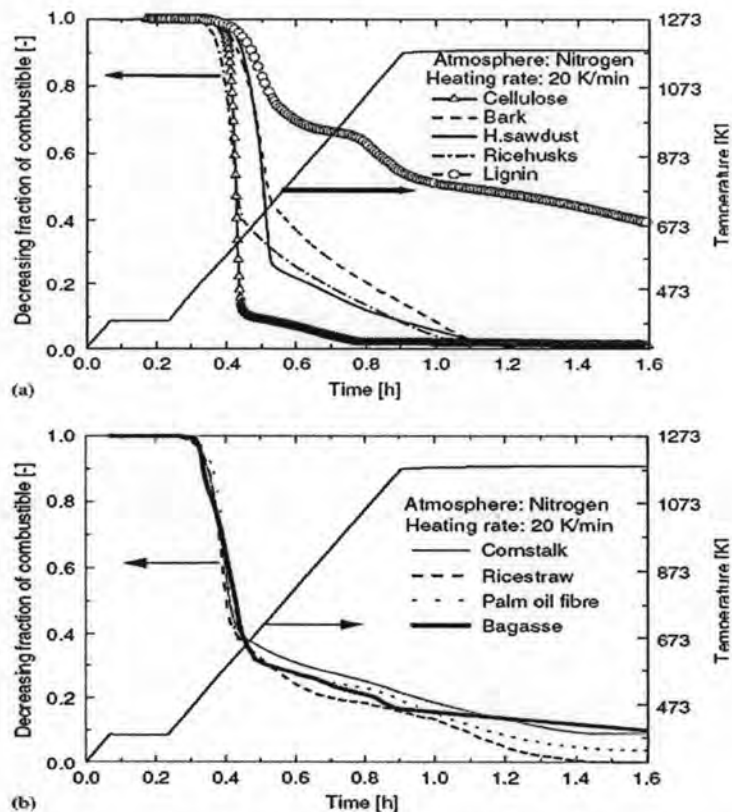


Figure 2.7 Residual fraction of combustibles for several types of biomass, cellulose and lignin during combustion (Gani et al. 2007).

### 3) Morphology of biomass on combustion characteristics

Morphological change of the simulated and actual biomass samples before and after pyrolysis and combustion are observed by a scanning electron microscope (SEM). Figure 2.8 (a)–2.8 (c) show the surface morphology of the raw material of Hinoki sawdust and the cellulose and lignin chemicals, respectively. It can be observed from this figure that Hinoki sawdust has fibrous and porous structure. The cellulose chemical also has the similar structure, as shown in Figure 2.8 (b). While, morphology of the lignin chemical is observed to be lumpy solid, as shown in Figure 2.8 (c). From these observation results, hinoki sawdust and cellulose chemical can easily decompose and burn, comparing with the lignin chemical.

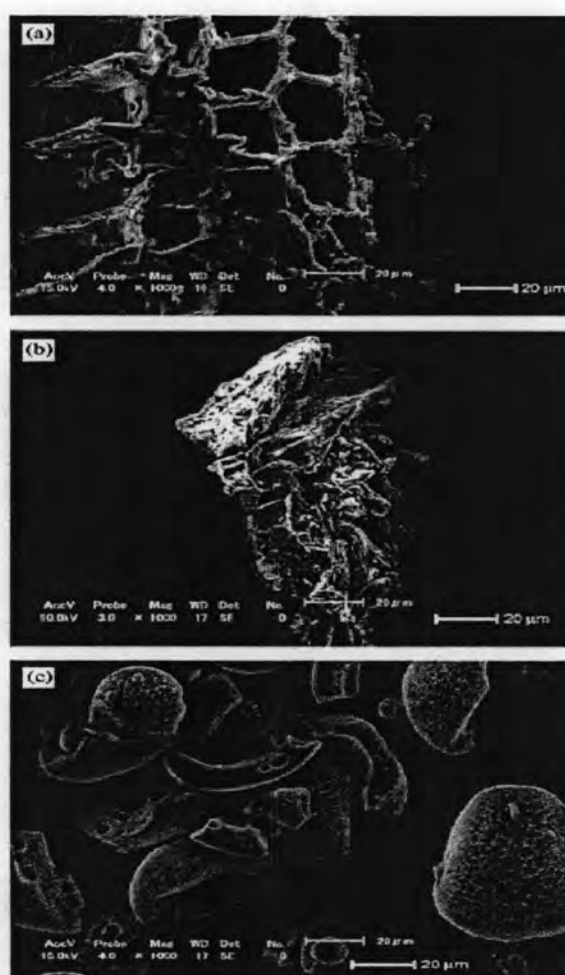


Figure 2.8 Morphology of hinoki sawdust and cellulose and lignin chemicals before reaction a) Hinoki sawdust b) cellulose c) lignin (Gani et al. 2007).

Figure 2.9 (a) and 2.9 (b), as an example, shows the morphological structure after 1 h pyrolysis for Hinoki sawdust and the simulated biomass of 60% cellulose and 40% lignin, respectively. From Figure 2.9 (a) the morphology of the actual biomass is still to be fibrous and porous, even if the pyrolysis proceeds. Under this condition, oxygen can diffuse easily inside the particle during combustion. While the simulated biomass shown in Figure 2.9 (b), while, it can be observed that the cellulose and lignin chemicals seem to react individually. In other words, the lignin chemical does not react much, so that the shape of the lignin remains lumpy solid. This is one of the reasons why the combustion reactivity for the simulated biomass differs from that for the actual biomass samples, as described in Figure 2.9 (b). The combustion reactivity of the biomass deeply relates to the char morphology formed.

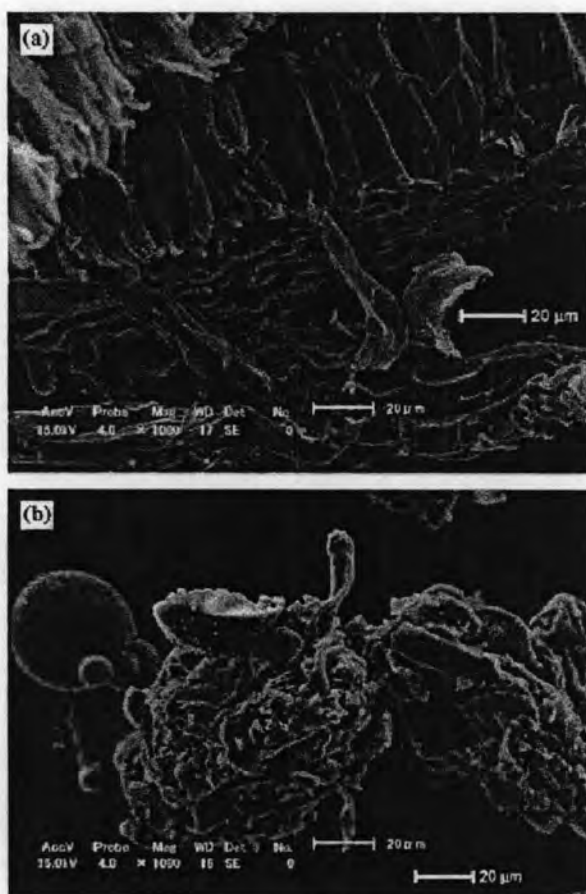


Figure 2.9 Morphology of Hinoki sawdust and the simulated biomass (60% cellulose; 40% lignin) after 1 h pyrolysis (Gani et al. 2007).

## 2.8 Tar classification (Devi et al. 2003)

Tar is a complex mixture of condensable hydrocarbons, which includes single ring to multiple ring aromatic compounds along with other oxygen containing hydrocarbons and complex polycyclic aromatic hydrocarbons. Tar is normally considered as a single lump of hydrocarbons as well as organic contaminants with a molecular weight larger than benzene. For easy understanding, the results are represented in terms of the tar classification presented in Table 2.2. This tar classification system has been developed in cooperation with Energy Research Center of The Netherlands (ECN), Toegepast Natuurwetenschappelijk Onderzoek (TNO) and University of Twente (UT). This classification is mainly based on solubility and condensability of different tar compounds, rather than reactivity of the compounds.

Table 2.2 List of tar compounds that are considered for different tar classes (Devi et al.2003)

Tar class	Class name	Property	Representative compounds	Example
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,dibenzophenlo	Benzonitril, phenol, quinoline
3	Light aromatic	Usually light hydrocarbons with single	Touene, ethylbenzene,xylenes, styrene	Styrene

		ring; do not pose a problem regarding condensability and solubility		
4	Light polyaromatic	Two and three ring compounds; condense at low temperature even at very low concentration	Indene, naphthalene, methylnaphtamlene, biphenyl, acenaphthalene, fluorene, phenanthrene, anthracene	Indene, naphthalene, 1-methylnaphthalene, 2-methyl naphthalene, biphenyl, acenaphthalene, fluorene, phenanthrene, anthracene
5	Heavy polyaromatic	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, benze(e) pyrene, benzo(j) fluoranthene, benzo(k) fluoranthene

## 2.9 Catalyst for biomass gasification (Sutton et al., 2001)

The criteria for an effective catalyst are summarized as follows:

1. The catalysts must be effective in the removal of tars.
2. If the desired product is syngas, the catalysts must be capable of reforming methane.
3. The catalysts should provide a suitable syngas ratio for the intended process.
4. The catalysts should be resistant to deactivation as a result of carbon fouling and sintering.
5. The catalysts should be easily regenerated.
6. The catalysts should be strong against attrition and compaction
7. The catalysts should be inexpensive.

Catalytic decomposition of the unwanted hydrocarbons is also known as hot gas cleaning. The catalysts employed in this process are responsible both for purification and bringing about compositional adjustment of the product gas. Hot gas conditioning is achieved by passing the raw gasifier product gas over a solid catalyst in a fluidized-bed (or a fixed-bed) under temperature and pressure conditions that essentially match those of the gasifier. As the raw gas passes over the catalyst, the hydrocarbons may be reformed on a catalyst surface with either steam (Eq. (2.18)) or carbon dioxide (Eq. (2.19)) or both to produce additional carbon monoxide and hydrogen:

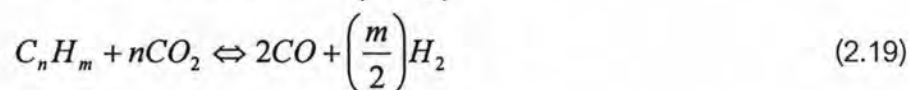
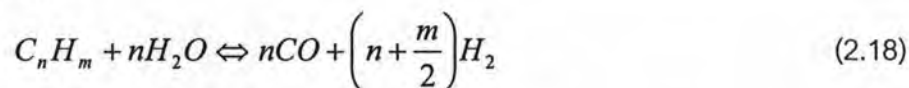


Table 2.3 Main chemical reactions of biomass gasification (Sutton et al. 2001)

Reaction no.	Reaction	$\Delta H_{298}$ KJ/mol
1	Volatile matter = $\text{CH}_4 + \text{C}$	Mildly exothermic
2	$\text{C} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2$	- 111
3	$\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2$	- 254
4	$\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$	- 242
5	$\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$	+ 131
6	$\text{C} + \text{CO}_2 \rightarrow 2\text{CO}$	+ 172
7	$\text{C} + 2\text{H}_2 \rightarrow \text{CH}_4$	- 75
8	$\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$	- 206
9	$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$	- 41
10	$\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	- 165

### Catalysis for biomass gasification

#### 1. Dolomite catalysts

Dolomite, a magnesium ore with the general formula  $\text{MgCO}_3 \cdot \text{CaCO}_3$  is used in the Pidgeon process for the manufacture of magnesium by thermal reduction. The use of dolomite as a catalyst in biomass gasification has attracted much attention since it is a cheap disposable catalyst that can significantly reduce the tar content of the product gas from a gasifier. It may be used as a primary catalyst, dry-mixed with the biomass or, more commonly, in a downstream reactor, in which case it is often referred to as a guard bed.

Orio et al. (1996) investigated four different dolomites (from Norte, Chilches, Malaga and Sevilla) for oxygen steam gasification of wood in a downstream catalytic reactor. The main chemical difference between the various samples was the  $\text{Fe}_2\text{O}_3$  content: the Malaga and Sevilla dolomites had low levels of  $\text{Fe}_2\text{O}_3$  when compared to those from Norte and Chilches. These samples were tested as catalysts at various steam carbon ratios and temperatures ranging from 805 to 875°C. Tar conversion of the order of 77% was found in the case of the Sevilla dolomite. The gas yields were



increased when using the catalyst for all of the dolomites. The order of activity of the dolomite from different source was: Norte > Chilchrs > Malaga > Sevilla. Interestingly,

Aznar et al. (1997) also investigated the use of Malaga dolomite for steam / oxygen gasification. It was reported that the H<sub>2</sub> content of the flue gas increased by 7 vol.%, while the CO content decreased by 7 vol.%. This effect was due to a greater contribution of the water-gas shift reaction as a result of a high steam content and high temperature. In another study (Aznar et al. 1996) under different gasification condition in which the CO<sub>2</sub> content varied slightly, from -2 to +6 vol. %, an overall decrease in the CO<sub>2</sub> was reported, indicating that dry reforming also occurred. The methane and steam contents also decreased by 0.8-0.2 and 3-8 vol.%, respectively, as a result of the water-gas shift. Several authors (Delgado et al., 1997) have identified naphthalene as the most abundant condensable product after reforming the tars over dolomite at 800 to 900°C. This observation highlights the limitations of the use of dolomites as catalysts for the complete elimination of tars from the product gas.

## 2. Alkali metal and other metal catalysis

Alkali metal catalysts for the elimination of tar and up-grading of the product gas have also been investigated in several works. The catalysts are often added directly to the biomass by dry mixing or wet impregnation. When added in the system using this method, the catalyst is difficult to be recovered and this is not always cost effective for the gasification process. It also gives an increase in the ash content remaining after char gasification, and the disposal of this is predicted to become a problem for the technology over the coming years.

Mudge et al. (1985) studied the catalytic steam gasification of wood using alkali carbonates and naturally occurring minerals, which were either impregnated or mixed with the biomass. They studied the effectiveness of four different primary catalysts and of different catalyst concentrations at 550 °C, 650 °C and 750 °C. The order of activity was reported as being potassium carbonate > sodium carbonate > trona (Na<sub>3</sub>H(CO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O) > borax (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O). Impregnated catalysts had little or no carbon deposition as compared to the mixed catalysts (carbon deposition resulted in deactivation).

### 3. Nickel catalysts

The most literature published on the area of hot gas cleaning for biomass gasification concerns nickel catalysts. Several groups have investigated a system of raw gas cleaning that involves a dolomite or alkali catalyst for the removal of tar (up to 95%) followed by the adjustment of the gas composition (reforming of the methane and the remaining tar) using a nickel steam reforming catalyst. Steam and dry reforming reactions are catalysed by group VIII metals, and of these, nickel is the most widely used in the industry. Consequently, the majority of published work concerns commercially available nickel catalysts designed for steam reforming of hydrocarbons and also of methane. When using these catalysts at temperatures greater than 740 °C, there is generally an increase in the hydrogen and carbon monoxide content of the exiting gas, with elimination or reduction of the hydrocarbon and methane content. At lower temperatures, the methanation reaction is favored thermodynamically and is sometimes optimized in cases when methane is desired as a predominant component of the exiting gas.

Aznar et al. (1997) investigated several commercially available catalysts for the removal of tars and the adjustment of the product gas composition. Two Haldor Topsoe catalysts (R-67-7H and RKS-1) were investigated for the steam reforming of the tar and methane. The catalyst was positioned downstream of the gasifier in a secondary reactor that was maintained at temperatures between 730 and 760 °C; space times of only 0.1 s were used. Catalyst R-67-7H is described as 12-14% Ni on a Mg/Al<sub>2</sub>O<sub>3</sub> support with a free Mg content of less than 0.5 wt.% and a SiO<sub>2</sub> content of less than 0.2 wt.%. Its specific surface area was 12-20 m<sup>2</sup> g<sup>-1</sup>. The conversions of tar, methane and C<sub>2</sub> and C<sub>3</sub> were greater for the reduced catalyst. The methane was reduced to 0.5 vol.% and the tar content to only 4 mg m<sup>-3</sup>. Deactivation of the catalysts occurred due to carbon fouling and this resulted in short catalyst lifetimes. Reduction in the tar content prior to the nickel catalysts was identified as a possible way to maintain the activity of the catalysts. Several authors have also investigated a design using a guard-bed of dolomite catalyst prior to the nickel catalyst.

## 2.10 Catalyst for tar elimination in biomass gasification process

In general, tars can be removed by physical, noncatalytic (e.g., thermal cracking), and catalytic tar elimination processes. The catalytic conversion of tars is commonly known as hot gas cleaning. A review of nine groups of catalysts has been used to reduce the tars in the producer gas obtained from the gasification process. The catalysts are divided into two classes on the basis of their production method: minerals and synthetic catalysts. Figure 2.10 shows the different reviewed catalysts that belong to these classes.

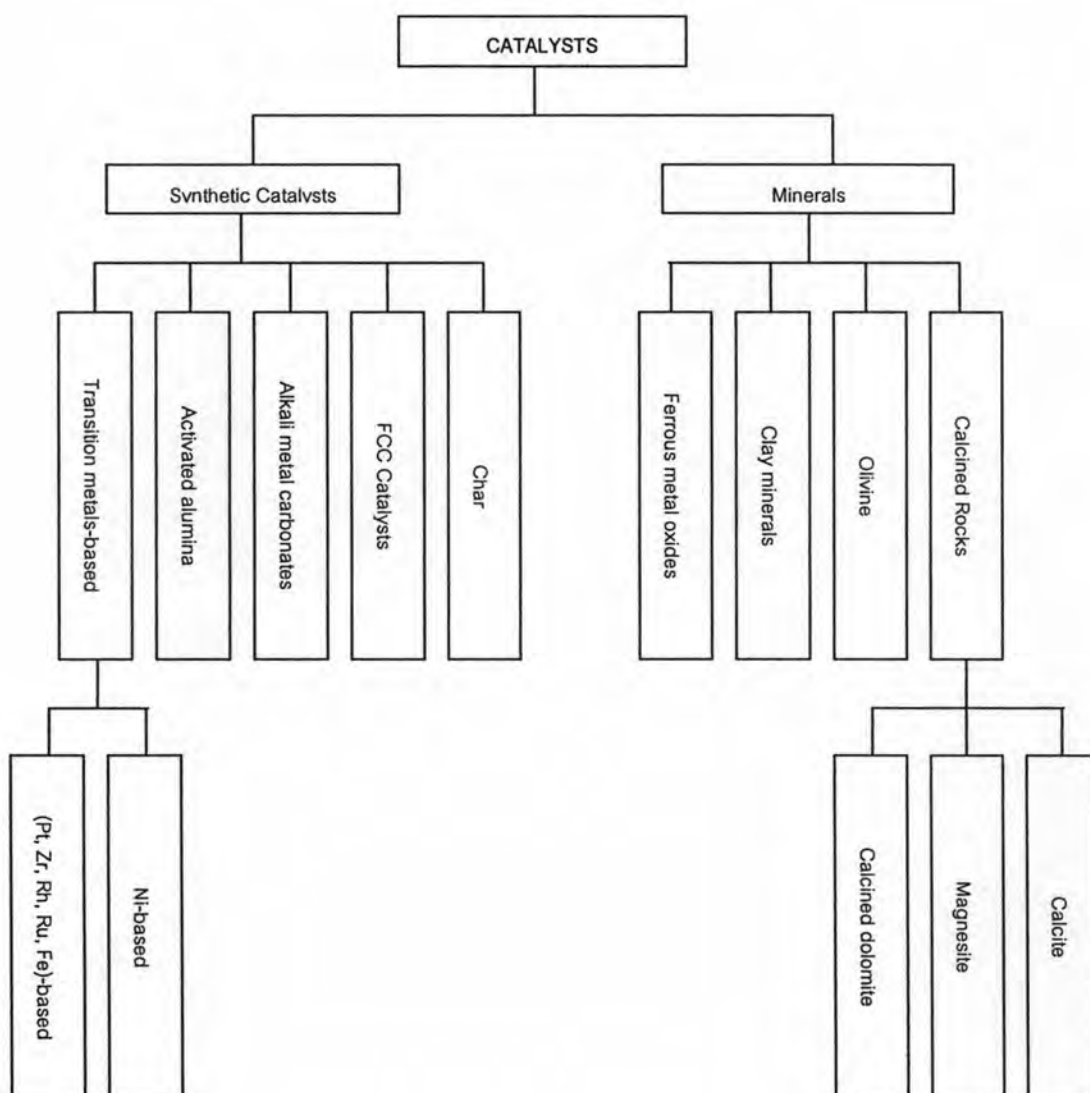


Figure 2.10 Classification and types of catalysts used for tar elimination

(Abu El-Rub et al. 2004)

## 2.11 Catalysts

Tar elimination reactions are known to be kinetically limited. Therefore, the reaction rates can be increased by increasing the temperature and/or using a catalyst. However, catalysts can only increase the rate of a reaction that is thermodynamically feasible.

2.11.1. Minerals: Minerals are naturally occurring, homogeneous solids with a definite, but generally not fixed, chemical composition and an ordered atomic arrangement. The catalysts belonging to this class are available in nature and can be used directly or with some physical treatment (such as heating) but without chemical catalysts are relatively cheap compared to synthetic catalysts.

- Calcined Rocks: These catalysts contain alkaline earth metal oxides (CaO and/or MgO). These catalysts have other names such as alkaline earth oxides, stones, minerals, and naturally occurring catalysts. The uncalcined forms of these materials are called limestone ( $\text{CaCO}_3$ ), magnesium carbonate ( $\text{MgCO}_3$ ), and dolomite ( $\text{CaCO}_3 \cdot \text{MgCO}_3$ ), respectively.

- Olivine: Olivine consists mainly of silicate mineral in which magnesium and iron cations are set in silicate tetrahedral. Natural olivine is represented by the formula  $(\text{Mg,Fe})_2 \text{SiO}_4$

- Clay Minerals: Most common clay minerals belong to the kaolinite, montmorillonite, and illite groups.

2.11.2. Synthetic Catalysts: Synthetic catalysts are chemically produced and relatively more expensive than the mineral catalysts.

- Char: Char is a nonmetallic material. It can be produced by the pyrolysis of coal or biomass. In the usual carbonization procedure, heat at 400-500°C is applied for a prolonged period of time in the absence of air.

- Fluid Catalytic Cracking (FCC) Catalysts: Zeolites represent a well-defined class of crystalline aluminosilicate minerals whose three-dimensional structures are derived from frameworks of  $[\text{SiO}_4]^{4-}$  and  $[\text{AlO}_4]^{5-}$  coordination polyhedra.

2.11.3 Alkali Metal-Based Catalysts: Alkali metals are any of the monovalent metals lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), and francium (Fr), belonging to group 1A of the periodic table.

2.11.4 Activated Alumina: Activated alumina consists of a series of non-equilibrium forms of partially hydroxylated aluminum oxide,  $\text{Al}_2\text{O}_3$ . Its chemical composition can be represented by  $\text{Al}_2\text{O}_{(3-x)}(\text{OH})_{2x}$ , where x ranges from about 0 to 0.8.

2.11.5 Transition Metal-Based Catalysts: Transition metals are considered as good catalysts for the steam and dry reforming of methane and hydrocarbons. Nickel catalyst supported on aluminum is cheaper and sufficiently active than other metals such as Pt, Ru, and Rh. Nickel metal is one of the group VIII metals. The general composition of the Ni-based catalysts can be divided into three main components: (a) Ni element (b) support, and (c) promoters.

## 2.12 Promoters

A promoter is a substance that is added in relatively small amounts into the catalyst to improve activity, selectivity or stability. The common additives are alkali metals and transition metals. In some cases, the precious metals such as Pt, Pd and Rh have been used. In this work, the effect of Platinum (Pt), Co (Cobalt) and Fe (Iron) used as promoter will be reviewed.

Nishiyama et al. (1986) studied on the behaviours of iron and nickel in the gasification of coal chars and carbons is described, giving attention to the effect of substrate, promoting action of calcium compounds, and rate changes with carbon conversion. It is indicated that an iron-calcium catalyst is highly active when hydrogen is present in the gasifier.

Ohtsuka et al. (1987) studied on brown coal gasification with  $\text{H}_2$  or  $\text{H}_2\text{O}$  in the presence of iron with a thermobalance. Iron markedly promoted the hydrogasification at as low a temperature as 873 K, and the coal conversion reached 76 wt % within 40 min. The rate enhancement by iron of the reaction with  $\text{H}_2\text{O}$  was very small at this temperature but became large at higher temperatures. The effectiveness of

the iron catalysts depended on the precursor salts. The activity sequence among these salts was the same with both gases. It was suggested from the XRD measurements that finely dispersed iron catalysts at the devolatilization stage exhibited high activity in the subsequent char gasification. The activity of iron was influenced by both the iron loading and the addition of foreign metals. The gasification proceeded in a single stage with  $H_2O$  but in two stages with  $H_2$ . The main chemical form of iron during the reaction with  $H_2O$  was magnetite and with  $H_2$  was metallic iron. The presence of fine metallic particles seems to be necessary for the occurrence of the two-stage gasification.

Chen et al. (1997) studied on reforming of  $CH_4$  with  $CO_2$  to produce synthesis gas by using  $Ni_{0.03}Mg_{0.97}O$  solid solution catalyst and its bimetallic derivative catalysts which contained small amounts of Pt, Pd and Rh, respectively (the atomic ratio of  $M/(Ni+Mg)$  was varied from 0.007 to 0.032%,  $M=Pt, Pd$  or  $Rh$ ). It was found that there was a significant promotion in both activity and stability due to the addition of noble metals. The optimum loadings of these noble metals were observed at the atomic ratio of  $M/(Ni+Mg) \sim 0.021\%$ . Temperature programmed hydrogenation (TPH) of carbonaceous species formed during the catalytic reaction indicated that the good resistance of  $Ni_{0.03}Mg_{0.97}O$  solid solution to carbon deposition was retained on the bimetallic catalysts. Furthermore, a clear evidence showing the formation of Pt-Ni alloy particles by means of TEM and EDS observation. The kinetic study and temperature programmed reaction (TPR) of  $CH_4$  suggested that  $CH_4$  decomposition as the rate-determining step on the  $Ni_{0.03}Mg_{0.97}O$  is accelerated by the alloy formation. The improved stability was attributed to the promotion in catalyst reducibility.

Takanabe et al. (2005) studied on the catalytic behavior of bi-metallic Co-Ni/ $TiO_2$  catalysts for  $CO_2$  reforming of  $CH_4$  to synthesis gas was investigated under atmospheric pressure with a particular attention to carbon deposition. The catalysts with optimized Co/Ni ratios showed high catalytic stability towards the reaction with very little amount of deposited carbon at a wide range of reaction temperature (500–850 °C). The results suggested that adjusting of composition of the active metals (Co and Ni) could kinetically control the elementary steps (formation of carbon species and its removal oxygen species) of  $CH_4/CO_2$  reaction.

Haryanto et al. (2007) studied on noble metal (Rh, Pt, Pd, Ir, Ru, and Ag) and Ni catalysts supported on  $\text{CeO}_2\text{-Al}_2\text{O}_3$  for water gas shift reaction at ultrahigh temperatures.  $\text{Pt/CeO}_2\text{-Al}_2\text{O}_3$  and  $\text{Ru/CeO}_2\text{-Al}_2\text{O}_3$  demonstrated as the best catalysts in terms of activity, hydrogen yield and hydrogen selectivity. At  $700^\circ\text{C}$  and steam to CO ratio of 5.2:1,  $\text{Pt/CeO}_2\text{-Al}_2\text{O}_3$  converted 76.3% of CO with 94.7% of hydrogen selectivity. At the same conditions, the activity and hydrogen selectivity for  $\text{Ru/CeO}_2\text{-Al}_2\text{O}_3$  were 63.9% and 85.6%, respectively. Both catalysts showed a good stability over 9 h of continuous operation. However, both catalysts showed slight deactivation during the test period. The study revealed that  $\text{Pt/CeO}_2\text{-Al}_2\text{O}_3$  and  $\text{Ru/CeO}_2\text{-Al}_2\text{O}_3$  were excellent ultrahigh temperature water gas shift catalysts, which can be coupled with biomass gasification in a downstream reactor.

Profeti et al. (2008) investigated the catalytic performance of  $\text{Co/Al}_2\text{O}_3$  catalysts promoted with small amounts noble metals (Pt, Pd, Ru, Ir) for steam reforming of ethanol (SRE) has been investigated. The catalysts were characterized by the energy dispersive X-ray, X-ray diffraction, BET surface area, X-ray absorption fine structure and temperature reduction programmed techniques. The results showed that the promoting effect of noble metals included a marked decrease of the reduction temperatures of both  $\text{Co}_3\text{O}_4$  and cobalt surface species interacting with the support due to the hydrogen spillover effect, leading to a significant increase of the reducibilities of the promoted catalysts. The better catalytic performance for the ethanol steam reforming at  $400^\circ\text{C}$  was obtained for the  $\text{CoRu/Al}_2\text{O}_3$  catalyst, which presented an effluent gaseous mixture with the highest  $\text{H}_2$  selectivity and the reasonable low CO formation.

Nishikawa et al. (2008) studied on the modification of  $\text{Ni/CeO}_2/\text{Al}_2\text{O}_3$  with Pt can make the activation by  $\text{H}_2$  reduction unnecessary, and this indicates that the  $\text{Pt/Ni/CeO}_2/\text{Al}_2\text{O}_3$  catalyst can be activated automatically by the compounds contained in tar. This can be explained by the enhancement of the Ni reducibility by the addition of Pt. The results of the temperature programmed reduction with  $\text{H}_2$  also support this enhancement. Furthermore, the addition of 0.1% Pt to  $\text{Ni/CeO}_2/\text{Al}_2\text{O}_3$  (4 wt% Ni, 30 wt%  $\text{CeO}_2$ ) enhanced the performance in the steam gasification of biomass, compared to  $\text{Ni/Al}_2\text{O}_3$  and  $\text{Ni/CeO}_2/\text{Al}_2\text{O}_3$  in terms of low tar yield and high gas yield. This can be

related to the Pt–Ni alloy formation indicated by the extended X-ray absorption fine structure analysis.

### 2.13 Steps in a heterogeneous catalytic reaction

To maximize reaction rates on porous catalyst, it is essential to maximize accessibility of all reactants to the active catalytic sites, which are dispersed throughout the internal pore structure of the catalyst. Imagine gas A flowing through a bed of a heterogeneous catalyst and reacting on the catalyst surface to form a gaseous species B. In order for A to convert at any appreciable rate to product B, the following physical and chemical steps (shown schematically in Figure 2.11) must occur:

1. Film mass transfer of the reactant A, i.e. bulk diffusion of A through the stagnant gas film or boundary layer surrounding the catalyst particle to the external catalyst surface.
2. Diffusion of species A (by either bulk or molecular (Knudsen) diffusion) through the porous network of the catalyst to the catalytic surface.
3. Adsorption of A onto the catalyst surface.
4. Reaction of A to B on catalytic sites on the catalyst surface.
5. Desorption of the product B molecules from the surface.
6. Diffusion of species B through the porous network to the pore mouth.
7. Film mass transfer of product B, i.e. bulk diffusion of B from the external catalyst surface through the stagnant gas film to the bulk gas stream.



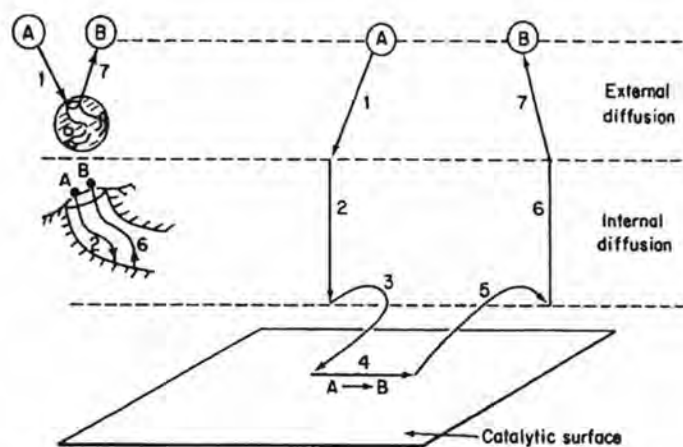


Figure 2.11 Steps in a heterogeneous catalytic reaction  $A \rightarrow B$  in a porous, supported catalyst (adapted from Fogler, 1999; courtesy of Prentice Hall).

## 2.14 Catalyst preparation

Making of the finished catalyst generally involves one of general approaches: 1) deposition of the active component onto a carrier by impregnation, adsorption, ion exchange or precipitation followed by washing, drying, calcinations and activation. 2) precipitation of a complex high surface oxide or carbonate containing active component followed by drying, calcinations and activation; and 3) preparation of a dense, nonporous compound or alloy containing the active component, followed by extraction of inactive material leaving a porous, high surface area and active phase. Some examples are provided for the most common preparation methods (Bartholomew and Farrauto, 2005).

### 2.14.1 Impregnation

The simplest and probably the most common procedure for dispersing a catalytic species on a carrier involves impregnating the predried support to incipient wetness with an aqueous or non aqueous solution containing a salt (precursor) of the catalytic element or elements. The precursor salt is dissolved in a volume of solvent equal to the catalyst pore volume, and this solution is added slowly to the support in which capillary forces of up to several hundred atmospheres draw the liquid into the

pores. Addition of solution continues until the pores of the support are saturated, as evident by the beading of the excess solution. Then drying in air, inert gas or vacuum (typically at 80-150 °C) crystallites of the precursor are deposited in the pores.

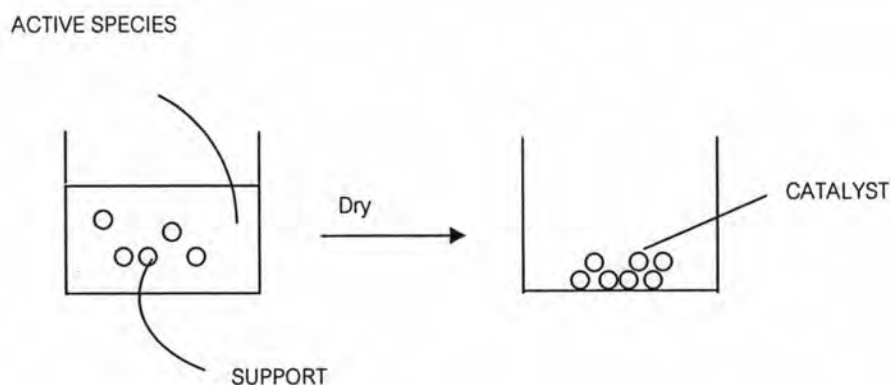


Figure 2.12 Wet impregnation method (Mongkolsri, 2003)

#### 2.14.2 Precipitation

The objective of this method is to precipitate the catalyst precursor in the form of a hydroxide or carbonate in the pores and on the surface of the carrier by adjusting the pH of the metal salt solution-support slurry through addition of a base such as NaOH and  $\text{NH}_4\text{OH}$ . Alternatively, support and catalyst precursor are coprecipitated together. Generally, support in the form of pellets or powder is added to the salt solution, after which the alkali solution is usually added dropwise, accompanied by rapid stirring of the slurry. Upon addition of sufficient alkali solution, catalyst precursor sols precipitate in the pore and catalyst precursors are formed by reaction on the interior surfaces of the support.

## 2.15 Mechanisms of deactivation

Prevention of catalyst degradation poses substantial challenges in the design and operation of a large-scale, catalytic process. There are many paths for catalyst decay. For example, a catalyst may be poisoned by any one of a dozen contaminants present in the feed; its surface, pores and voids may be fouled by carbon or coke produced by cracking/condensation reactions of hydrocarbon reactants, intermediates and/or products. In the treatment of a power plant flue gas, the catalyst can be dusted or eroded and/or plugged with fly ash. Catalytic converters used to reduce emissions from gasoline or diesel engines may be poisoned or fouled by fuel or lubricant additives and/or engine anticorrosion products. If the catalytic reaction is conducted at high temperatures, thermal degradation may occur in the form of active phase crystallite growth, collapse of the carrier (support) pore structure and/or solid-state reactions of the active phase with the carrier or promoters. In addition, the presence of oxygen or chlorine in the feed gas can lead to formation of volatile oxides or chlorides of the active phase followed by gas phase transport from the reactor. Similarly, changes in the oxidation state of the active catalytic phase can be induced by the presence of reactive gases in the feed. Thus, the mechanisms of catalyst deactivation are many; nevertheless, they can be grouped into six intrinsic mechanisms of catalyst decay: (i) poisoning, (ii) fouling, (iii) thermal degradation, (iv) vapor compound formation accompanied by transport, (v) vapor–solid and/or solid–solid reactions, and (vi) attrition/crushing. As (i), (iv), and (v) are chemical in nature while (ii) and (vi) are mechanical, the causes of deactivation are basically three-fold: chemical, mechanical and thermal. Each of the six basic mechanisms is defined briefly in Table 2.4 and treated in some detail in the subsections which follow an emphasis on the first three. Mechanisms (iv) and (v) are treated together, since (iv) is a subset of (v).

Table 2.4 Mechanisms of catalyst deactivation (Bartholomew, 2001)

Mechanism	Type	Brief definition/description
1.Poisoning	Chemical	Strong chemisorption of species on catalytic sites, thereby blocking sites for catalytic reaction
2.Fouling	Mechanical	Physical deposition of species from fluid phase onto the catalytic surface and in catalyst pores
3.Thermal degradation	Thermal	Thermally induced loss of catalytic surface area, support area, and active phase–support reactions
4.Vapor formation	Chemical	Reaction of gas with catalyst phase to produce volatile compound
5.Vapor–solid and solid–solid reactions	Chemical	Reaction of fluid, support, or promoter with catalytic phase to produce inactive phase
6.Atrition/crushing	Mechanical	Loss of catalytic material due to abrasion Loss of internal surface area due to mechanical-induced crushing of the catalyst particle.

### 2.15.1 Poisoning

Poisoning is the strong chemisorption of reactants, products or impurities on sites otherwise available for catalysis. Thus, poisoning has operational meaning; that is, whether a species acts as a poison depends upon its adsorption strength relative to the other species competing for catalytic sites. Mechanisms by which a poison may affect catalytic activity are multifold as illustrated by a conceptual two-dimensional model of sulfur poisoning of ethylene hydrogenation on a metal surface. To begin with, a strongly adsorbed atom of sulfur physically blocks at least one three- or four-fold adsorption/reaction site (projecting into three dimensions) and three or four topside sites

on the metal surface. Second, by virtue of its strong chemical bond, it electronically modifies its nearest neighbor metal atoms and possibly its next nearest neighbor atoms, thereby modifying their abilities to adsorb and/or dissociate reactant molecules.

### 2.15.2 Fouling, coking and carbon deposition

Fouling is the physical (mechanical) deposition of species from the fluid phase onto the catalyst surface, which results in activity loss due to blockage of sites and/or pores. In advanced stages it may result in disintegration of catalyst particles and plugging of the reactor voids. Important examples include mechanical deposits of carbon and coke in porous catalysts, although carbon- and coke-forming processes also involve chemisorption of different kinds of carbons or condensed hydrocarbons which may act as catalyst poisons. The definitions of carbon and coke are somewhat arbitrary and by convention related to their origin. Carbon is typically a product of CO disproportionation while coke is produced by decomposition or condensation of hydrocarbons on catalyst surfaces and typically consists of polymerized heavy hydrocarbons. Nevertheless, coke forms may vary from high molecular weight hydrocarbons to primarily carbons such as graphite, depending upon the conditions under which the coke was formed and aged as shown in Figure 2.13.

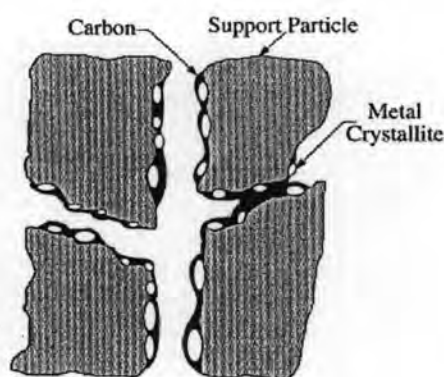


Figure 2.13 Conceptual model of fouling, crystallite encapsulation and pore plugging of a supported metal catalyst due to carbon deposition (Bartholomew et al. 2001).

### 2.15.3 Thermal degradation and sintering

Thermally induced deactivation of catalysts results from (i) loss of catalytic surface area due to crystallite growth of the catalytic phase, (ii) loss of support area due to support collapse and of catalytic surface area due to pore collapse on crystallites of the active phase, and/or (iii) chemical transformations of catalytic phases to non-catalytic phases. The first two processes are typically referred to as sintering. Sintering processes generally take place at high reaction temperatures (e.g.  $>500^{\circ}\text{C}$ ) and are generally accelerated by the presence of water vapor as shown in Figure 2.14.

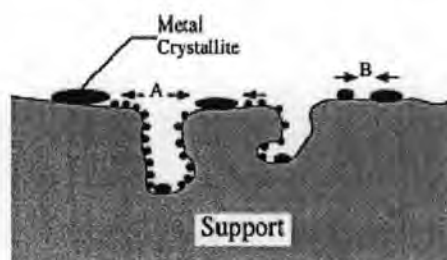


Figure 2.14 Two conceptual models for crystallite growth due to sintering by (A) atomic migration or (B) crystallite migration (Bartholomew et al. 2001).

### 2.15.4 Gas/vapor–solid and solid-state reactions

In addition to poisoning, there are a number of chemical routes leading to catalyst deactivation: (1) reactions of the vapor phase with the catalyst surface to produce (a) inactive bulk and surface phases (rather than strongly adsorbed species) or (b) volatile compounds which exit the catalyst and reactor in the vapor phase, (2) catalytic solid–support or catalytic solid–promoter reactions, and (3) solid-state transformations of the catalytic phases during reaction.

### 2.15.5 Mechanical failure of catalysts

Mechanical failure of catalysts is observed in several different forms, including (1) crushing of granular, pellet or monolithic catalyst forms due to a load, (2) attrition, the size reduction and/or breakup of catalyst granules or pellets to produce fines, especially in fluid or slurry beds, and (3) erosion of catalyst particles or monolith coatings at high fluid velocities. Attrition is evident by a reduction in the particle size

easily observed under an optical or electron microscope. A Large increases in pressure drop in a catalytic process are often indicative of fouling, masking or the fracturing and accumulation of attrited catalyst in the reactor bed.

## 2.16 Literature reviews

Baker et al. (1987) studied Nickel catalyst (Ni/Mo) on silica alumina support with a United catalyst and ICI catalyst. Three different configurations were investigated for each catalyst in fluid bed reactor, in a secondary fixed bed reactor and in the secondary fluid bed reactor. The activities of the catalysts in all cases were initially high, the exit gases consisting primarily of H<sub>2</sub>, Co, CO<sub>2</sub> and trace of CH<sub>4</sub>.

Bectancur et al. (1995) studied the catalytic steam gasification of naphthalene, a model compound of tars produced in coal gasification processes. A thermally activated magnesium oxide was used as a catalyst. They investigated the influence of reaction temperature, residence time, feed ration, and catalyst pretreatment, on the gaseous products yields. It was found that as the temperature increased from 1003 K to 1033 K, a substantial rise in the H<sub>2</sub> and CO yields was observed. Furthermore, the gaseous products yields were a function of residence time at different gasification temperatures. Comparison of the activity between this oxide and natural raw materials used as precursors, like limestone and dolomite, was also performed. The result indicated that the catalytic activity depends on the catalyst precursor. The activity decreased in the order: limestone (CaO) > dolomite (CaO.MgO) > MgO. These differences were attributed mainly to the surface acidity of these materials, which decreased in the same order.

Baker et al. (1996) studied G-90C, C-13-3 and a trimetallic nickel alloy catalyst (Ni-Co-Mo on silica alumina) developed in their own organization. All of these catalysts gave high activity for removal of hydrocarbons and methane at temperature above 740°C. Deactivation was most severe for the Harshaw catalyst, which could not be regenerated with only a slight loss of activity due to sintering.

Narvaez et al. (1997) studied the upgrading of the raw gas from a biomass gasifier with the commercial steam-reforming BASF G1-25 S nickel-based catalyst. It was located downstream of the gasifier, a bubbling fluidized bed type in which air was used as gasifying agent. In order to increase the catalyst lifetime, a guard bed of a dolomite calcined at 800-850°C was used. This decreased the throughput amount of tar entering the catalytic bed to below 2 g tar/m<sup>3</sup>(NC). This work was focused only on the catalytic bed which easily decreased the tar content in the gas to only 1-2 mg/m<sup>3</sup>(NC). Both tar and gas compositions in the reactor depend on the equivalence and H/C ratios existing in the gasifier and on the operating conditions of the guard bed of dolomite. A simple kinetic model was used to describe the overall tar elimination network. Its overall kinetic constant was used as index of the catalyst activity for tar elimination. Values of this overall kinetic constant were given for very different operation conditions.

Hepola et al. (1999) studied the effect of different process parameters on sulfur poisoning on nickel catalyst in tar (toluene), ammonia and methane decomposition. Tests were carried out in a fixed-bed tube reactor at 800-1000°C at 5 and under 20 bar total pressure using a synthetic gasification gas mixture. Under the same conditions, sulfur affected less the toluene and methane decomposition than the ammonia decomposing activity. The ammonia conversion was affected by the catalyst type but not by the nickel content of catalyst. The effect of sulfur poisoning was decreased when the temperature was increased. The poisoning effect of sulfur at 5 bar was less than at 20 bar. Moreover, they also found that the process should be operated at temperatures more than 900°C in order to prevent sulfur poisoning.

Hepola et al. (1997) investigated the effect of different components of gasification gas on sulfur poisoning of nickel catalyst. In addition, the sulfur distribution and content in nickel catalyst beds were analyzed to account the poisoning effect of sulfur on the activity of catalysts in the decomposition of tar, ammonia and methane. The desorption behavior of chemisorbed sulfur from the bed materials was monitored by temperature programmed hydrogenation (TPH). It was observed that the bulk nickel sulfide was activated in decomposing ammonia in high-temperature gasification gas-



cleaning conditions. The decomposition of methane was not affected by bulk nickel sulphide formation, but that of toluene was decreased. The activity of the catalyst recovered rapidly when  $\text{H}_2\text{S}$  was removed from the gas. However, the conversion of ammonia was not regained the level as high as that before sulfur addition, probably due to irreversible sulfur adsorption on the catalyst. The increasing in temperature could also be used to regenerate the catalyst performance, especially in respect to methane and toluene. Sulfur adsorbed on nickel catalysts in different chemical states depending on the process conditions applied. At over  $900^\circ\text{C}$  the sulfur adsorbed on the catalyst formed an irreversible monolayer, while at under  $900^\circ\text{C}$  the adsorbed sulfur, probably composed of polysulphides (multilayer sulfur), was desorbed from the catalyst in sulfur-free hydrogen containing atmosphere. However, as monolayer of sulfur still remained on the catalyst after the desorption. The enhancement effect of high total pressure on sulfur-poisoning of nickel catalysts could be accounted for the increased amount of sulfur, probably as mode of polysulphides, adsorbed on the catalyst.

Simell et al. (1997) compared the activity in tar and ammonia decomposition over dolomite, nickel catalyst, alumina and SiC in different gas atmosphere. Tests were carried out in a fixed-bed tube reactor at  $900^\circ\text{C}$  under 2.0 and 5 MPa pressure. Toluene was used as a tar model compound. The gas atmospheres studied were a mixture of nitrogen carrier, toluene and ammonia with any of  $\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CO}_2+\text{H}_2\text{O}$ ,  $\text{H}_2+\text{H}_2\text{O}$ , and  $\text{CO}+\text{CO}_2$ . A gasification gas mixture containing all the components was also used. The predominant reaction of toluene in the empty tube and over SiC and alumina was hydrocracking. With dolomite and nickel catalyst, steam and  $\text{CO}_2$  reforming types of reaction took place at high rate,  $\text{CO}_2$  reforming being the faster. However, in gasification gas the rates of steam and  $\text{CO}_2$  reforming reactions were lowered due to the inhibiting effect of  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{H}_2$ . Ammonia reacted rapidly with  $\text{CO}_2$  even with the inert reference materials and very rapidly over the nickel catalyst. The presence of toluene increased the ammonia reaction rate on the nickel catalyst.

Tomishige et al. (1998) studied the methane reforming by carbon dioxide over ultra-stable Ni catalysts. The nickel-magnesia solid solution catalyst containing low nickel has shown excellent stability over 3000 hours and no carbon deposition. It was

also found that small nickel metal particle interaction with support surface is effective for an inhibition of carbon formation. Simell et al. (1999) developed the model of tar decomposition over a dolomite catalyst in gasification using benzene as a tar model compound. The reactions of the main gas components were included in the models studied. The kinetic studies were carried out in plug flow reactor using a mixture of simulated gasification gas at 750-925°C and under ambient pressure. The operating conditions without external or internal mass-transfer limitations were applied. The mechanistic models of Langmuir-Hinshewood type describing benzene decomposition were developed and tested. Experimental results could be best described by the kinetic rate-determining step and that adsorption of hydrogen inhibited benzene decomposition.

Garcia et al. (1999) investigated the catalytic gasification of three tars from different sources (oil refinery, Petrox; coking, Huachipato; coal gasification, Gasco). The experiment was carried out in a laboratory scale fixed bed reactor using CaO as catalyst, obtained by limestone calcinations. Gasification runs were performed with constant tar feed flow rate, as well as the steam concentration. The residence time was regulated through the carrier gas (argon) flow. The results indicated that for steam to tar ratios equal to or larger than 3.5 and temperatures over 750°C, the complete conversion to gaseous products was obtained. In addition, solid carbon deposition was observed at lower values of steam to carbon ratios, and the gas yields varied accordingly. It was also reported that under high temperature gasification conditions ( $T > 950^\circ\text{C}$ ), the reactivity of tar decreases in the order; Petrox > Gasco > Huachipoto. However  $\text{H}_2$  and CO yields were higher for the less reactive tars showing that the gasification of deposited carbon is the predominant factor.

Coll et al. (2001) investigated the purification of biomass-derived syngas via tar abatement by catalytic steam reforming using benzene, toluene, naphthalene, anthracene and pyrene as surrogated molecules. The effect of temperature and steam-to-carbon ratio on the conversion, and the tendency toward coke formation were explored for each model compound. Two commercial nickel-based catalysts, the UCI G90-C and the ICI 46-1, were evaluated. The five tar model compounds had very

different reaction rates. Naphthalene was the most difficult compound to steam reform; the conversion was between  $0.008 \text{ g}_{\text{org conv}} / \text{g cat min}$  ( $790^\circ\text{C}$ ) and  $0.022 \text{ g}_{\text{org conv}} / \text{g cat min}$  ( $890^\circ\text{C}$ ) at a steam/C ratio of 4.2. In contrast, the most reactive compound was benzene, with conversion of  $1.1 \text{ g}_{\text{org conv}} / \text{g cat}$  at  $780^\circ\text{C}$  at the steam/C ratio of 4.3. The tendency towards coke formation grew as the molecular weight of aromatic compounds increased. The minimum S/C ratio for toluene and pyrene was 2.5 at  $725^\circ\text{C}$ , 8.4 at  $790^\circ\text{C}$ , respectively. In general, reaction temperatures and S/C ratios need to be higher than naphthalene in order to prevent the formation of coke on the catalyst.

Franco et al. (2003) studied reactions influencing the biomass steam gasification process. The gasifier was operated over a temperature range of  $700\text{--}900^\circ\text{C}$  by varying a steam/biomass ratio from 0.4 to 0.85 w/w. Three types of forestry biomass were studied: *Pinus pinaster* (softwood), *Eucalyptus globulus* and holm-oak (hardwood). The operating conditions were optimized for a gasification temperature around  $830^\circ\text{C}$  and a steam/biomass ratio of 0.6–0.7 w/w, because a gas richer in hydrogen and poorer in hydrocarbons and tars were produced. These conditions also favoured greater energy and carbon conversions, as well the gas yields. The main objectives of this work were to determine what reactions were dominant within the operation limits of experimental parameters studied and what was the effect of biomass type on the gasification process.

Wang et al. (2004) studied the activity, sulfur tolerance and coking resistance of ZSM-5-zeolite-supported nickel catalysts and novel bimetallic catalysts of Ni-Co, Ni-Mo and Ni-Re in the steam reforming of liquid hydrocarbons. Results were compared with those for traditional Ni/ $\text{Al}_2\text{O}_3$  catalyst. The activity and sulfur tolerance of the Ni-based catalyst supported on ZSM-5 zeolites, especially on CeZSM-5, was much better than those of alumina-supported Ni catalyst. A novel highly active bimetallic Ni-Re/ $\text{Al}_2\text{O}_3$  catalyst system was developed. This catalyst exhibited unique high activity and promising sulfur tolerance for steam reforming of the liquid fuel, even at a comparatively lower reaction temperature of 853 K, while the activity of the traditional Ni/ $\text{Al}_2\text{O}_3$  catalyst was relatively much lower and was sharply suppressed by the presence of 20 ppm sulfur in the feed. The order of activity and sulfur tolerance of catalyst was Ni-

Re/Al<sub>2</sub>O<sub>3</sub>>Ni/CeZSM-5>Ni/HZSM-5>Ni/Al<sub>2</sub>O<sub>3</sub>. The activity of the novel bimetallic Ni-Re catalyst was quite stable with time on stream, and the high activity was maintained well even after about 300 hours of time on stream.

Ketcong et al. (2004) studied the influence of operating parameters on the catalytic gasification of a eucalyptus biomass into CO and H<sub>2</sub> in presence of steam. Steam gasification studies were carried out in an atmospheric fixed bed. The gasifier was operated over a temperature range of 500 - 800 °C, varying a catalyst composition from 0 to 10% of nickel loading on dolomite in steam flow rate of 0.01-0.07 g/min/g of biomass and 0 to 1.5 g. of °C, percentage of nickel loading on dolomite 9.32% and a steam flow rate of 0.01 g/min/g of biomass. At this condition, the composition of product gas was 56.45% of carbon monoxide and 45.26% of hydrogen.

Wang et al. (2005) studied steam reforming of naphthalene as a model compound, catalytic cracking experiments on biomass tar were made on Ni-dolomite catalysts. The performance of catalyst preparation, activity, coke formation and regeneration were analyzed. The results showed that the ratio of the one-step conversion of naphthalene was 95% at space velocity 0.81 h<sup>-1</sup> and 700 °C; with saturated wet air as regeneration gas, the regeneration time was within 0.5 h. compared with thermal cracking at the same reaction temperature, the catalytic cracking was propitious to deep cracking of naphthalene.

Srinakruang et al. (2005) developed Ni on dolomite catalyst (Ni/dolomite) exerted high activity and stability under a short contact time of W/F:0.55 g h/mol for the gasification of tar by steam, which was investigated by using toluene as the model compound. Moreover, the performance of the Ni/dolomite catalysts gave negligible carbon deposition, while the conventional supported Ni catalysts gave fairly large carbon deposition. It was found that the calcination temperature significantly influenced the property and the activity of the Ni/dolomite catalyst.

Srinakruang et al. (2006) developed Ni/dolomite catalysts for coking resistance and promising sulfur tolerance for steam reforming of tar. Experiments were carried out in a fixed bed reactor at 730–850 °C with a short contact time (W/F: 0.55 g h/mol) and under atmospheric pressure. Toluene and naphthalene were selected as the model component of tar. The process variables such as calcination temperature, reaction temperature and the content of nickel had substantial influenced on promising sulfur tolerance in catalytic tar removal by Ni/Dolomite catalysts. Results were compared with the Ni/Al<sub>2</sub>O<sub>3</sub>, Ni/SiO<sub>2</sub> as a representative of commercial catalysts. The novel 15%Ni/Dolomite almost gasified tar component even at 770 °C and the presence of 100 ppm H<sub>2</sub>S in the feed. The poisoning effect of H<sub>2</sub>S was discovered to be reversible. The suppression of the catalytic activity by adding H<sub>2</sub>S was much lower for Ni/Dolomite than Ni/Al<sub>2</sub>O<sub>3</sub>. The TGA–DTA analysis of used catalysts revealed that Ni/Dolomite exhibited high resistance to coke deposition over those of the Ni/Al<sub>2</sub>O<sub>3</sub>, Ni/SiO<sub>2</sub>.